Estimates of residence times of sulfate aerosols in ambient air

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ABSTRACT

The aerodynamic size distribution of sulfates in ambient aerosol particles were measured using a high-resolution, submicron region low-pressure cascade impactor. In continental areas the mass (volume) distribution of sulfates determined by ion chromatography, was largely associated with submicron aerosols in the accumulation mode (0.1–2 μm) peaking in the 0.2–0.5 μm size range. The mass median aerodynamic diameter (MMAD) varied from 0.25 to 0.31 μm (mean 0.28 μm). The mean value of the geometric standard deviation σ_g was 2.06. In estimating lifetimes of sulfate aerosols, the residence times of 12 days applies to aerosols of ~ 0.3 μm MMAD size.

Key words: residence time; sulfate aerosols; ambient aerosols

INTRODUCTION

Gas-phase transformations in the atmosphere produce low-vapor pressure species, with the oxidation of SO_2 and other reduced sulfur species dominating aerosol formation and growth. Oxidation of SO_2 in the gas phase produces H_2SO_4, a readily condensable species that either combines with other molecules (new particle formation) or condenses on existing aerosols.

The size distribution of sulfates on aerosol particles in the atmosphere is the result of a combination of various independent processes including coagulation and growth on the small Aitken particles, large particle sedimentation, precipitation scavenging, etc. (Moore et al., 1980). As an aerosol popu-

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*We regretfully inform readers of the tragic early death of Dr E.A. Bondietti who considerably contributed to science.

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lation ages, coagulation depletes the mass in the smallest size ranges, while the wet and dry removal processes preferentially deplete the mass in the largest sizes. Both trends are offset by new aerosol production (Milford and Davidson 1987), hence size characteristics might affect atmospheric residence time. Moore et al. (1980) reported that calculated mean residence times increase with increasing particle size interval in the troposphere.

This paper summarizes part of the results of an investigation designed to characterize the aerodynamic size distributions and the aging of atmospheric aerosols in the context of sulfate distibutions as well as the naturally-occurring radioactive aerosols (particularly 22-year ^{210}Pb, a long-lived daughter in the ^{222}Rn decay chain). These results indicate an appreciably shorter residence time for atmospheric aerosols than values estimated by several different methods in numerous, but very old published reports which indicate about one month for tropospheric aerosols (Stewart et al., 1956; Goel et al., 1959; Pierson et al., 1966) and ~ 15–16 days in surface air (Aegerter et al., 1966; Gedeonov and Rys'yev, 1969).

INSTRUMENTATION

The measurements were carried out with an Andersen high-resolution, submicron region low-pressure ambient particle sizing cascade impactor (LPI) (Model 20-725, Andersen Samplers Inc, Atlanta, GA) for aerosol collection. This low-pressure impactor involves a regulated flow rate of 3 1 min^{-1}, five low-pressure (114 mmHg) stages for the submicron region and eight atmospheric pressure stages for collecting aerosols > 1.4 μm. The effective cut-off diameters (ECDs) of the low-pressure stages were as follows: 0.08, 0.11, 0.23, 0.52 and 0.90 μm, whereas for the upper stages they were 1.4, 2.0, 3.3, 6.6. 10.5, 15.7, 21.7 and 35.0 μm. The stainless steel plates supplied by the manufacturer were used for aerosol collection. A back-up polycarbonate filter (pore size 0.4 μm Nuclepore, type 111807, Nuclepore Corporation, Pleasanton, CA) was used to collect particles below the 0.08-μm collecting plate. These polycarbonate membranes were usually used for SO$_4^{2-}$ measurements to avoid artifacts that might result from SO$_2$ adsorption by glass fiber filters when used as backup filters (Bondietti and Papastefanou 1989). The length of each collection period was varied from 2 to 4 days.

The stainless steel collecting plates of the impactors were leached with a 2-ml solution of 0.001 M HCl. Sulfates were measured with a Dionex anion-exchange chromatograph after deionized water-leaching of the impactor plates. Procedure blanks were used to test for anion contamination from sources other than the sampled air.

The samples were collected by two LPI impactors 13 m above the ground on the roof of the Environmental Sciences Division building, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

RESULTS AND ANALYSIS

Sulfate size distribution data

The observed sulfate size distribution versus aerodynamic diameter (D_p) is represented in Fig. 1. This distribution was selected from 12 measurements made over an almost 6-month period (14 March–6 September 1985).

All the measurements showed a dominant (submicron) peak in the 0.23–0.52-μm region (Table 1). On the average, about 68.7% of the mass of sulfates were found to be associated with aerosols in the 0.08–1.4-μm size range of low-pressure stages (accumulation mode) (NRC, 1979). These particles originate and grow by condensation and droplet-phase process (John et al., 1990) and dominate the surface area and usually the volume (mass) of the atmospheric aerosol. The mass of sulfates associated with aerosols < 0.08 μm (Aitken nuclei) was 12.6%, while > 1.4-μm (coarse mode) it was 18.7%. Evidence of both Aitken nuclei and the coarse mode aerosols is also shown in Fig. 1.
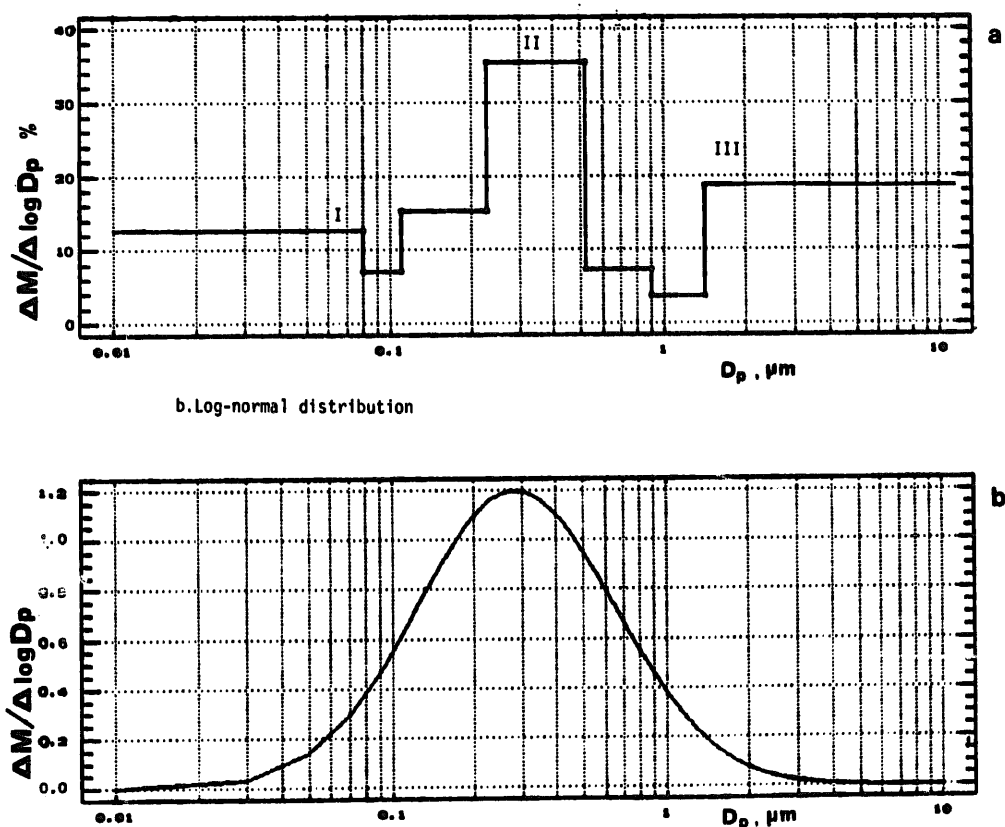

Fig. 1. Aerodynamic size distribution of sulfate aerosols from 12 low-pressure impactot measurements made between March and September 1985. Lower D_p limits are arbitrary. (a) Frequency distribution. (b) Log-normal distribution. I. Aitken nuclei, II. Accumulation mode, III. Coarse mode.

TABLE 1

Experimental data for sulfate aerosols. The size range is expressed in μm

Date	Days[a]	$\mu g/m^3$	% in size range							MMAD (μg)	σ_g
			<0.08	0.08–0.11	0.11–0.23	0.23–0.52	0.52–0.9	0.9–1.4	>1.4		
14 March	4	3.23	9.1	6.6	22.45	36.5	8.85	3.3	13.2	0.28	1.98
28 March	3	3.4	13.5	5.1	14.7	37.9	12.2	3.2	13.4	0.31	1.94
12 April	4	6.5	2.3	3.3	15.1	45.8	8.0	3.3	22.4	0.30	1.78
6 May	2	12.7	15.3	3.7	8.8	23.65	7.0	0.8	40.75	0.31	1.66
20 May	2	10.28	20.16	3.92	11.19	39.75	8.40	2.01	14.56	0.28	1.83
4 June	3	13.4	21.15	5.43	12.85	28.59	6.87	3.86	21.25	0.28	2.10
21 June	3	11.78	8.19	3.81	11.92	31.95	3.24	2.37	38.51	0.29	1.93
1 July	2	13.95	12.99	5.87	10.27	54.48	4.19	1.30	10.89	0.26	1.80
19 July	3	22.0	16.67	8.24	16.28	43.14	6.47	3.14	6.08	0.27	2.01
2 August	3	12.3	12.27	12.89	20.55	28.54	6.75	5.20	13.50	0.25	2.42
26 August	2	13.4	8.23	12.12	17.75	28.14	7.79	7.79	18.18	0.28	2.56
6 September	3	12.4	11.73	13.45	21.38	26.20	7.93	7.59	11.72	0.26	2.61
Average (N = 12)		11.28	12.63	7.04	15.27	35.40	7.30	3.66	18.70	0.28	2.06

[a]Length of collection period.

TABLE 2

Percentage of sulfate dominance in each size range of atmospheric aerosols (12 measurements)

Size range (μm)	average (%)	min (%)	max (%)
<0.08	12.63	2.3	21.15
0.08–0.11	7.04	3.3	13.45
0.11–0.23	15.27	8.8	22.45
0.23–0.52	35.40	23.65	54.48
0.52–0.9	7.30	3.24	12.2
0.9–1.4	3.66	0.8	7.79
>1.4	18.70	6.08	40.75
	100.00		

The mass median aerodynamic diameter (MMAD) for the accumulation mode aerosols varied from 0.25 to 0.31 μm (average 0.28 μm). The mean value of the geometric standard deviation (σ_g) was 2.06. The sulfate loadings varied from 3.2 to 22 μg m^{-3} (average 11.3 μg m^{-3}). Table 2 presents the percentage in which sulfates appeared in size range on the average of twelve measurements.

Mean residence times of sulfate aerosols

Atmospheric aerosol size distributions consist basically of three separate modes: nuclei (≤ 0.1 μm diam.), accumulation (<2.0 μm but >0.1 μm diam) and coarse particle (>2.0 μm diam.). Depending on their source there may be from one to three distinct maximums in the surface or volume (mass) distributions (National Research Council, 1979). Assuming that the fraction of the aerosol with particle diameter ranged from 0.08 μm up to 1.4 μm, low-pressure stages (accumulation mode) is F_1 and the fraction below 0.08 μm, back-up filter (Aitken nuclei) is F_2, then, according to the aerosol formation mechanism, the mean residence time τ_R of the aerosol is controlled by the ratio F_1/F_2, which was affected by homogeneous nucleation, source injection of very small particles, variabilities in the dominance of gas and liquid phase reactions, aerosol removal, etc. i.e.,
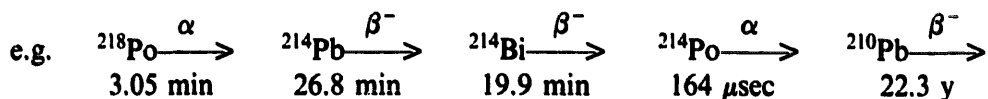
$$\frac{\dfrac{F_1}{F_2}}{\tau_R} = \text{constant}$$

Therefore, if we consider the sulfate aerosols in respect of the naturally-
radioactive aerosols (e.g. ^{210}Pb-aerosols), the following equation applies:

$$\frac{\dfrac{F_1}{F_2, SO_4^{2-}}}{\tau R, SO_2^{4-}} = \frac{\dfrac{F_1}{F_2, \,^{210}Pb}}{\tau_R, \,^{210}Pb} \qquad (2)$$

Using the data of radon daughter aerosols Papastefanou and Bondietti
(1991) reported that a mean residence time, τR of 8 days for aerosols of 0.3
μm activity median aerodynamic diameter (AMAD) size as determined from
^{210}Bi/^{210}Pb activity ratios. From the decay scheme of ^{218}Po, because of rela-
tive short radioactive half-lives this produces ^{210}Pb-aerosols.

e.g. $^{218}Po\xrightarrow{\;\alpha\;}$ $^{214}Pb\xrightarrow{\;\beta^-\;}$ $^{214}Bi\xrightarrow{\;\beta^-\;}$ $^{214}Po\xrightarrow{\;\alpha\;}$ $^{210}Pb\xrightarrow{\;\beta^-\;}$
       3.05 min   26.8 min   19.9 min   164 μsec   22.3 y

From 32 experiments for radon daughter aerosols (Papastefanou and Bon-
dietti 1987) we calculated average values of fractions F_1 and F_2 of about
76.11 and 21.32, respectively. The estimated fractions F_1 and F_2 for sulfate
aerosols calculated in the same manner from 12 experiments (Table 2) are
about 68.67 and 12.63, respectively. According to equation 2 and the above
data a mean residence time, τR, SO_4^{2-} of about 12 days would apply to sul-
fate aerosols of 0.3 μm mass median aerodynamic diameter (MMAD) size.

If we assume the resulting particle diameter growth rate during the spring
and summer seasons for a continental area $\sim$ 0.001 μm h^{-1}, according to
the theory of aerosol growth by condensation and coagulation (McMurry
and Wilson 1982, 1983), then the value of mean residence time, τ_R can be
calculated by dividing the difference between the mean value of the mass me-
dian aerodynamic diameter (MMAD) $\sim$ 0.3 μm for sulfate aerosols as a
result of the mean size distribution; Table 1 and the size of Aitken nuclei
peaking at 0.01–0.015 μm size range (National Research Council, 1979) by
the growth rate of 0.001 μm h^{-1}. From this calculation a mean residence
time of about 11 days may result for sulfate aerosols.

CONCLUSIONS

In a previous paper (Papastefanou and Bondietti, 1991) it was reported
that the residence times of 8 days would apply to radon daughter aerosols
with 0.3 μm activity median aerodynamic diameter (AMAD) size. In the pre-
sent paper a mean residence time of about 12 days is applicable to sulfate

aerosols with 0.3 μm mass median aerodynamic diameter (MMAD) size. This result is in good agreement with the result of Moore et al., (1980) for the mean troposphere aerosol residence time for tropospheric aerosol particles of about 1 week.

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