

CHARACTERIZATION OF A RURAL AEROSOL FROM EASTERN ARIZONA

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Abstract—The aerosol in a rural area in eastern Arizona was sampled in the spring and fall of 1980 and subsequently studied by scanning electron microscopy. The most abundant microparticles were ammonium sulfate, soil components and other salts (sulfates and chlorides). In May the geometric volume mean diameter (DGV) of the ammonium sulfates was $0.43\mu\text{m}$ and the sulfate concentration $5.8\mu\text{g m}^{-3}$. In October the DGV was $0.28\mu\text{m}$ and the sulfate concentration $4.5\mu\text{g m}^{-3}$. The salts (except ammonium sulfates) were probably derived from salt flats.

INTRODUCTION

Recently many environmental studies have evaluated the impact of anthropogenic activities on air quality. We have been especially interested in the aerosols in arid, urban areas and have studied the Phoenix urban area and its surroundings, primarily by the analyses of individual particles (Armstrong and Buseck, 1978; Bradley *et al.*, 1981; Buseck and Bradley, 1982; Post and Buseck, 1983). In this paper we describe the aerosol at a rural location close to the Salt River Canyon, 200 km NE of Phoenix. The site is remote from smelter plumes and other major anthropogenic sources and so enables an estimation of the contribution of the background aerosol to Phoenix. Except for ammonium sulfates, the most abundant constituents of the aerosol were soil particles and sulfate and chloride salts (here called 'sulfochloride salts' to distinguish them from the ammonium sulfates).

There was no conspicuous external source area for air in the Arizona airshed during our first sampling period. However, there was transport of air from the north into the Arizona airshed for several days before and during the second sampling period.

METHODS OF INVESTIGATION

Samples were collected on stacked Nuclepore filters (diameter 47 mm) with pore sizes of 8 and $0.2\mu\text{m}$. Air was pumped through the filters at flow rates of about $1.2\text{ m}^3\text{ h}^{-1}$ for 3 h per sample. Two sets of samples were collected, on 17 May and 19 October, 1980 between 11 a.m. and 6 p.m. The samples were studied with a JEOL JSM 35 scanning electron microscope (SEM) with a PGT energy dispersive X-ray spectrometer (EDS). The analytical procedures permit quantitative analysis of individual particles from ~ 0.1 to $20\mu\text{m}$ in maximum dimension (Aden and Buseck, 1979; Aden, 1981). Several $5\times 5\text{ mm}$ pieces of filter were carbon-coated for

analysis; others were Au/Pd-coated for imaging. Micrographs were taken at an accelerating voltage of 25 kV and a sample current of about 1.5×10^{-11} amps. Analyses were made at an accelerating voltage of 15 kV and a sample current of about 4×10^{-10} amps.

Particles were sized and counted on micrographs (magnification $\sim 14,000\times$) in squares of about $160\mu\text{m}^2$. Particles with diameters greater than $\sim 0.05\mu\text{m}$ could be distinguished.

The volumes were calculated of the roughly spherical particles that we think are ammonium sulfate (see below). Geometric number mean diameters (DGN) and geometric volume mean diameters (DGV) were obtained from log-probability plots. The total mass was calculated assuming the density to be that of ammonium sulfate. To facilitate comparison with data in the literature, the aerodynamic geometric number mean diameter (EDGN) and aerodynamic geometric volume mean diameter (EDGV) were also calculated by substitution of the values for DGN and DGV in the Stokes–Cunningham equation for settling velocity. No shape correction is necessary since the particles are approximately spherical.

RESULTS

Table 1 summarizes the types of particles observed in this study. Most of the particles were collected on the $0.2\text{-}\mu\text{m}$ filter, and the loading on all filters was sufficiently low to minimize particle interactions. The total suspended particulate matter on the combined filters varied little (from 35 to $55\mu\text{g m}^{-3}$).

The particles on the $8\text{-}\mu\text{m}$ filters were mainly silicates between 5 and $15\mu\text{m}$ in diameter. The $0.2\text{-}\mu\text{m}$ filters had a considerable loading of spheroidal particles with diameters between 0.05 and $1.0\mu\text{m}$. Most showed only an S peak in their EDS spectra and suffered rapid beam damage. No extraneous cores larger than about $0.01\mu\text{m}$ (the lower detection limit of our SEM) were observed. We concluded that these particles are ammonium sulfate, as this compound has a similar appearance and shows similar behaviour in the electron beam. A few of the particles displayed minor peaks of Fe, Cu, Zn or Cd.

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Table 1. Components of the aerosol in the Salt River Canyon area, Arizona (1980)

Type of particle	Estimated relative abundance	Estimated relative weight	Elements in X-ray EDS spectra	Size range (μm)
Ammonium sulfate H_2SO_4 droplets	> 95%	May: 20% Oct.: 15%	usually only S; rarely minor Fe, Cu, Zn, Cd	0.05–1
Silicate and carbonate mineral fragments	< 5%	May: 79% Oct.: 85%	Na, Mg, Al, Si, K, Ca, Ti, Fe; in some cases minor S, Cl	0.3–15
Mixed salts, sulfates and chlorides	< 0.07%	May: 1% Oct.: 4%	Na, S, and Cl, with minor Mg, K and Ca	0.4–6
Flyash	rare	< 1%	Al and Si, with Na, Mg, K, Ca, Ti, Ba, Fe and sometimes minor S and Cl	0.5–4.5
Metal sulfides, sulfates and oxides	rare	< 1%	Cu, Zn, Fe, Cd, sometimes with S	0.4–3
Pollen and spores	rare	< 1%	none	> 5

Although ammonium sulfate can form after collection (e.g. Dingle and Joshi, 1974; Klockow *et al.*, 1979), the particle shapes in our samples do not support such an origin (Gras and Ayers, 1979). Our observations suggest that most of the submicron particles from the study area existed as ammonium sulfate while still in the aerosol, in agreement with the observations of Moyers *et al.* (1977).

The absence of extraneous cores suggests that heterogeneous SO_2 -oxidation reactions were not important in forming our samples. This result is consistent with the model of Gillani *et al.* (1981) and the study by McMurphy *et al.* (1981). This is not surprising since heterogeneous reactions occur in liquid films around solid particles (e.g. Graedel and Weschler, 1981), and such films are absent or rare in desert aerosols (Ho *et al.*, 1974).

The size distributions of the ammonium sulfates are log-normal, and the sizes are in the accumulation mode (Whitby, 1978). Data are given in Table 2, which also contains estimates of total soluble sulfate. The latter values agree well with data collected by Neuroth (1980) during the same period in the same area. Hering *et al.* (1981) found smaller sulfates in northern Arizona (EDGV about $0.17 \mu\text{m}$). However, they measured an EDGV of about $0.5 \mu\text{m}$ in the Phoenix area; they suggest that their size difference is a result of a difference in relative humidity. Our data are consistent with this idea; relative humidities during our sampling events were 50% in May and 37% in October, i.e.

higher than the < 20% during the periods that Hering *et al.* sampled their 'desert type' aerosol. However, experimental data on hygroscopic properties of ammonium sulfates predict no size increase with increasing relative humidity if the relative humidity is below 80% (Charlson *et al.*, 1978). Possibly some of the size differences result from sampling aerosols at different stages of aging.

Particles between 0.01 and $0.05 \mu\text{m}$ in maximum diameter were rare and only present in the October sample; they consisted of droplets, probably of sulfuric acid. They do not contribute significantly to the total sulfate mass.

Mineral particles, primarily silicates (clay minerals, feldspars, quartz) and calcite, are the second most numerous group of submicron particles. Most have diameters greater than $0.4 \mu\text{m}$. Even though we sampled at a distance of only a few meters from an old dump, chrysotile fibers were extremely rare in the samples, below the average concentration in city air (Holt and Young, 1973).

The main constituents of the sulfochloride salts are Na, Cl and S. Mg and Ca predominate in some particles. The DGN of the sulfochloride salts was $1.2 \mu\text{m}$ in October and $0.8 \mu\text{m}$ in May. Charge balance considerations suggest the presence in some particles of carbonates, nitrates or borates (not detectable with our EDS). Salt grains from dried desert lake beds (playas) in SE Arizona (e.g. the Wilcox playa) have a similar composition and, we believe, are the probable

Table 2. Sulfate size distributions and concentrations

	N_{as} ($1 \times 10^3 \text{ cm}^{-3}$)	V_{as} ($\mu\text{m}^3 \text{ cm}^{-3}$)	DGN (μm)	σ_g	EDGN (μm)	DGV (μm)	σ_g	EDGV (μm)	M_s ($\mu\text{g m}^{-3}$)	M_{ss} ($\mu\text{g m}^{-3}$)
May	0.303	4.5	0.22	1.62	0.31	0.43	1.49	0.58	5.7	5.8
October	0.512	3.2	0.17	1.47	0.24	0.28	1.64	0.52	4.1	4.5

N_{as} : concentrations by number of ammonium sulfate particles; V_{as} : concentration by volume of ammonium sulfate particles; M_s : mass of sulfate in ammonium sulfate; M_{ss} : mass of soluble sulfate; σ_g : geometric standard deviation.

sources of the sulfochloride salts. A contribution of chlorides from playas might also be the explanation of the presence of Cl in excess of normal crustal values, as observed in Arizona by Moyers *et al.* (1977) and Macias *et al.* (1980). Other particles are rare; they include flyash and metal-rich particles (Table 1).

CONCLUSIONS

(1) Based on our limited samples, the submicron aerosol in rural eastern Arizona consists mainly of ammonium sulfates. Other aerosol constituents are soil particles (but with negligible amounts of asbestos), sulfochloride salts that are probably derived from playas, and minor Cu-Fe-Zn-Cd sulfides, sulfates and oxides.

(2) Analysis of individual ammonium sulfate particles suggests that homogeneous SO₂ oxidation was the most common process of sulfate formation for our samples.

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