

MASTER

CONF-790115--1

Prepared for presentation at the New York Academy of Sciences Conference on Aerosols: Anthropogenic and Natural-Sources and Transport, New York, N.Y., January 9-12, 1979.

## SULFUR AND NITROGEN COMPOUNDS IN URBAN AEROSOLS

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The need for additional knowledge concerning the spatial and temporal distribution of sulfur- and nitrogen-containing compounds, principally secondary aerosols, which result from the primary emission of sulfur dioxide, nitrogen oxides and particulate matter has stimulated several major field studies in the northeastern U.S.A. The keys to the utility of such studies appear to be at least three in number: (a) the development of improved analytical techniques for ground and airborne sampling and analysis (using both filter-based and real time methods) of trace aerosol and gaseous constituents; (b) the inclusion of emission, transport, transformation and removal phenomena for S- and N-compounds within the scope of the studies; and (c) the application of sophisticated, potentially predictive models to this new, detailed data base.

We report in this paper some of the results gleaned from a detailed chemical and meteorological data base that has been accumulated for the New York City subregion. Improved analytical methodologies for sulfur- and nitrogen-containing constituents were used as well as more conventional gaseous chemical, meteorological and particle size-classifying instrumentation as shown in Table 1.

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Aerosol sampling during August, 1976 and February, 1977 sampling periods was done only in an urban New York site and a background site at High Point, N.J. The sampling program was expanded to Brookhaven (Long Island) and New Haven, Connecticut sites during summer, 1977 and winter, 1978 sampling. Time resolution for aerosol filter samples was 6 hr, with some 3 hr sampling for the latter three periods. Parameters measured included chemical constituents: strong acid (quartz filters only), ammonium, sulfate and nitrate, sulfuric acid (limited data); physical parameters: aerosol size distributions by cascade impactor, cyclone sampler, EAA, an optical counter and a special diffusion battery-CNC apparatus; light scattering nephelometer and other instrumentation; chemically-specified size classification by diffusion sampler; trace metals by atomic absorption; halogen compounds by NAA; meteorological measurements of RH, temperature, wind speed and direction; gaseous measurements of  $\text{SO}_2$ , ozone,  $\text{NO}_x$  and hydrocarbons at some locations for some sampling periods. Data analysis is nearing completion only for the summer, 1976 sampling period, but the following trends and conclusions relative to S- and N-compounds are substantiated by the data.

The existence of aerosol sulfate in the ambient environment predominantly in the chemical form of sulfuric acid mostly neutralized by ammonia is now well documented. The average composition of fine particle ( $<3.5\mu\text{m}$ ) sulfate in summer, 1976 aerosols was approximately that of letovicite  $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$ . Based on the impactor data, about 85% of the aerosol sulfate mass was in the fine particle fraction. About 50% of this aerosol sulfate was deduced to be in the suboptical size regime ( $<0.25\mu\text{m}$ ) from diffusion processor data. The  $\text{H}^+/\text{SO}_4^{2-}$  ratio in suboptical aerosols did not significantly differ from that in fine fraction aerosol. The coarse particle sulfate was not associated with  $\text{H}^+$  or  $\text{NH}_4^+$  and comprised about 15% of the sulfate mass.

Thus it was found that aerosol sulfate concentrations in summer were remarkably similar to those in an upwind rural location. In addition, the size classification data from the diffusion sampler was in close agreement with that found in rural Illinois during July, 1975. These data indicate that a major portion of the urban sulfate aerosol may be transported through New York City in summer rather than being formed there.

The data from the winter, 1977 sampling period were substantively different than observed in summer. Sulfate concentrations were lower, fine fraction sulfate was more nearly neutralized by  $\text{NH}_4^+$  ( $\text{H}^+/\text{SO}_4 \leq 0.10$ ), and, based on diffusion sampler data, aerosol sulfate may have been in somewhat smaller particles on the average than in the summer. Analysis of diurnal trends from 6 hr-Hi Vol sampling indicates maximum sulfate concentrations during the 06-12 hr period, but closest association of sulfate with ammonium was during the 00-06 hr period ( $r = 0.9$ ).

Investigation of the spatial variability of sulfate concentrations in the New York subregion with inclusion of summer, 1977 and winter, 1978 data is still in progress. It does appear that sulfate concentrations in New York were elevated in New York relative to an upwind rural site by from  $3\text{--}6 \mu\text{g}/\text{m}^3$  during the winter, 1977 sampling period, in contrast to summer, 1976 when elevated urban values were not observed.

Sulfate values in the subregion were remarkably constant during July-August, 1977 at the four sites except where attenuated by local meteorological variations such as wind direction and precipitation. Nitrate concentrations were elevated at New Haven with nighttime maxima and ammonium/sulfate ratios were higher (and  $\text{H}^+/\text{SO}_4^{2-}$  lower) at both New Haven and BNL sites as compared to the High Point, N.J. site. The relevance of the interposition of the urban area between these sites during prevailing wind direction is not yet clear. However, because of

the regional nature of, and high temporal correlation between elevated sulfate values, lowered visibility and high oxidant concentrations, it would appear that the assessment of urban air quality in the northeast U.S. requires a knowledge of the history of air masses reaching the urban area in order to deduce quantitative roles of local emissions and regional transport to local air quality with respect to sulfur and nitrogen compounds. Statistical and tracer techniques are actively being investigated for this purpose.

Acknowledgment:

I acknowledge the support and extensive assistance of several of my colleagues in the Atmospheric Sciences Division, Brookhaven National Laboratory as well as the collaborators in the New York Aerosol Study, in particular Dr. Brian Leaderer, Pierce Foundation, Yale University. I also acknowledge support of this work by the Division of Biomedical and Environmental Research, U.S. Department of Energy.

Table 1. New York Aerosol Study Measurements

| Measured Parameter             | Sampling Method    | Analysis Method         | Time Resolution, hr | Sampling Period |
|--------------------------------|--------------------|-------------------------|---------------------|-----------------|
| Aerosol Sulfate                | HiVol              | Turbidimetry            | 24 hr               | S76,W77         |
|                                | HiVol              | Turbidimetry            | 6 hr                | W77,S77         |
|                                | HiVol              | MTB                     | 6 hr                | W77-S78         |
|                                | HiVol              | IC                      | 6 hr                | W77             |
|                                | HiVol              | MTB                     | 3 hr                | S77,S78*        |
|                                | Diffusion Sampler  | MTB or Turb.            | 12 hr               | S76,W77         |
| H <sub>2</sub> SO <sub>4</sub> | HiVol              | Benzaldehyde Extraction | 6 hr, 3 hr          | S77-S78         |
| Aerosol Nitrate                | HiVol              | Reduction-Colorimetry   | 24 hr               | S76,W77         |
|                                | HiVol              | Reduction-Colorimetry   | 6 hr                | W77-S78         |
|                                | Diffusion Sampler  | Reduction-Colorimetry   | 12 hr               | S76,W77         |
| Strong Acid                    | HiVol <sup>+</sup> | Gran Titration          | 6 hr                | S77-S78         |
|                                | Diffusion Sampler  | Gran Titration          | 12 hr               | S76,W77         |
| Ammonium                       | HiVol              | Indophenol Colorimetry  | 24 hr               | S76,            |
|                                | HiVol              | Indophenol Colorimetry  | 6 hr                | W77-S78         |
|                                | Diffusion Sampler  | Indophenol Colorimetry  | 12 hr               | S76,W77         |
| Aerosol Mass                   | Real-Time          | Nephelometer            | 1 hr                | S76-S78         |
|                                | HiVol              | Gravimetry              | 24 hr               | S76,W77         |
|                                | HiVol              | Gravimetry              | 6 hr                | W77-S78         |
| Size Distribution              | 1-6 min Ave/hr     | EAA                     | 1 hr                | S76,W77         |
|                                | 1-6 min Ave/hr     | Diffusion Battery-CNC   | 1 hr                | S76,W77         |
|                                | 1-6 min Ave/hr     | Optical Counter         | 1 hr                | S76-S78         |
| Trace Metals                   | HiVol              | Atomic Absorption       | 24 hr, 1 wk         | S76,W77         |
|                                | Cyclone Sampler    | Atomic Absorption       | 24 hr, -1 wk        | S76-S77         |
|                                | HiVol              | Atomic Absorption       | 6 hr                | W77-S78         |
| Halogen Compounds              | HiVol              | NAA                     | 1 wk                |                 |
| Light Scattering               | Real Time          | Laser Backscatter       | 1 hr                | S76,W77         |
|                                | Real Time          | Nephelometer**          | 1 hr                | S76-S78         |
| Meteorological Parameters      | Real Time          | RH                      | 1 hr                | S76-S78         |
|                                | Real Time          | Dew Point               | 1 hr                | S76-S78         |
|                                | Real Time          | Temperature             | 1 hr                | S76-S78         |
|                                | Real Time          | Wind Speed              | 1 hr                | S76-S78         |
|                                | Real Time          | Wind Direction          | 1 hr                | S76-S78         |

\* BNL, NYU site only.

+ Quartz filters only; no valid data for NYU site.

\*\* See also Aerosol Mass/Nephelometer.