

RELATIONSHIPS AMONG SURFACE OBSERVATIONS OF PARTICLE MASS, NUMBER, COMPOSITION, AND GASEOUS PRECURSORS DURING THE SUMMER 1999 PHILADELPHIA NE-OPS STUDY

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Introduction.

The overall objective of the North East Oxidant and Particle Study (NE-OPS) is to investigate factors determining the occurrence of ozone and fine particles in a northeastern U.S. urban environment using a variety of surface, remote sensing, balloon, and airplane platform pollution measurements. The first of two summer intensive studies of particles and ozone was performed between 28 June and 20 August 1999 in Philadelphia PA. Data for hourly surface level measurements of PM_{2.5}, total sulfate, black carbon soot (BC), and particle count (number) concentrations and 10-hour [day/night] measurements of nitrate and nitric acid made by the Harvard School of Public Health (HSPH) are reported here, as is a limited preliminary data set for hourly elemental and organic carbon mass from the 2001 summer NE-OPS intensive. Temporal relationships between these pollutants are explored, focusing on associations of various pollutants with PM_{2.5}. Further details on the various aspects of this study can be found in these proceedings¹ and on the NE-OPS web site.²

Methods.

The NE-OPS monitoring site is on the grounds of the City of Philadelphia's Baxter water treatment plant, off of State Rd., in northeast Philadelphia near the Delaware River, 18 km ENE of downtown Philadelphia, and 0.4 km SE of I-95. Continuous measurements (hourly means) of the following pollutants were made at this location:

PM_{2.5}: R&P 1400A TEOM® at 50°C using a Harvard Impactor 4-lpm inlet; data corrected for average SVOC loss by collocation with integrated PM samples

Total Sulfate: HSPH Continuous Sulfate/Thermal Speciation System (CSTS) using flame-photometry detection with SF₆ for enhanced sensitivity³

Particle Count: TSI 3934L Scanning Mobility Particle Sizer (15 to 500 nm)

Black Carbon: Andersen Instruments Aethalometer™ (optical density), with TOR EC cal factor of 1.4 applied
Elemental and Organic Carbon (2001 only): Sunset Laboratory's Semi-Continuous OCEC Carbon Aerosol Analyzer (NIOSH Method)

Integrated measurements of PM and composition were also made; 10-hour nitrate and nitric acid (10AM and 10PM EDT start times) from the Harvard-EPA Annular Denuder Filter-Pack System (HEADS) are reported. Hourly data for ozone and sulfur dioxide from the City of Philadelphia Air Management Services Laboratory site (9 km WSW of the Baxter site and 9 km from the center of Philadelphia) are reported. Pearson correlations

were calculated for hourly data sets, daily maximum 1-hour values, and daily means.

Results.

The summer of 1999 in the Philadelphia area had several intervals of elevated PM_{2.5} and/or ozone. A detailed summary of the meteorological conditions for seven of these events for ozone during the study period is on the web.⁴ The strongest association for data from all hours was between PM_{2.5} and sulfate ($r=0.94$). Figure 1 shows a scatter plot of these data. On average, sulfate-related mass (assuming ammonium sulfate) accounted for 55% of the PM_{2.5}; this proportion increases with higher PM_{2.5} as indicated by the somewhat non-linear relationship. Correlations between hourly PM_{2.5} and particle number concentration ($r=0.43$) or BC ($r=0.31$) were much lower. On a daily (24-hour average) basis, the number vs. PM_{2.5} correlation was somewhat higher ($r=0.63$). For sulfate and SO₂, $r=0.42$ (for daily 1-hour maximum values, $r=0.55$). Because of the strong urban diurnal pattern of ozone, 1-hour daily maximum ozone values were used to assess the relationship between PM_{2.5} and ozone (Figure 2); $r=0.58$. Ozone data collected for a portion of the study period at the Baxter site are approximately 30% higher than the LAB site, which is consistent with the Baxter site being further down-wind from downtown Philadelphia. Strong day/night patterns of nitric acid are clear from a time-series plot over the study period (Figure 3). Note that almost all of the nitric acid is removed (presumably by deposition to surfaces) during the overnight period. The hourly EC and OC time-series from the summer 2001 intensive measurement period (Figure 4) shows a clear pattern for both EC and OC. EC tends to peak during morning rush hour (local, primary sources), while OC peaks during the mid-day, implying a more regional source involving photochemical processes.

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References.

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3. Appel, BR, RL Tanner, DF Adams, PK Dasgupta, KT Knapp, GL Kok, WR Pierson, KD Reiszner (1989). Method 713: "Semi-Continuous Determination of Atmospheric Particulate Sulfur, Sulfuric Acid, and Ammonium Sulfates." Methods of Air Sampling and Analysis, 3rd edition, JP Lodge, Jr, editor. Lewis Publishers, Inc., Chelsea MI
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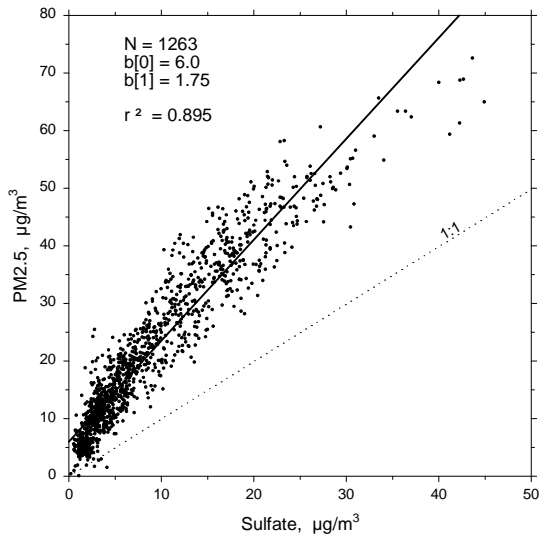


Figure 1. Hourly PM2.5 vs. Sulfate

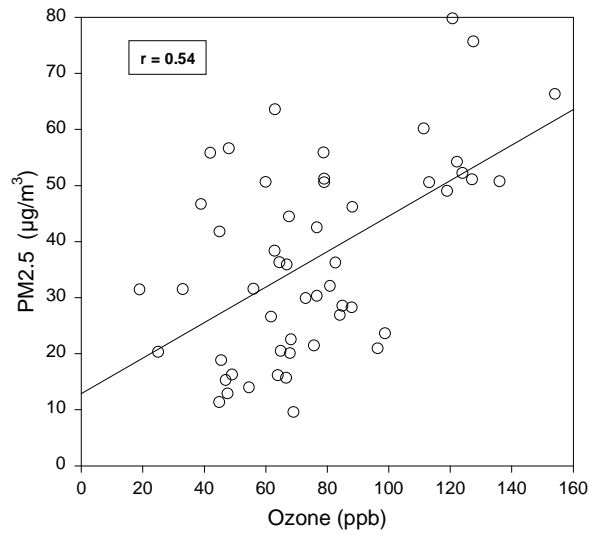


Figure 2. PM2.5 vs. Ozone for Max. Daily Ozone Hour

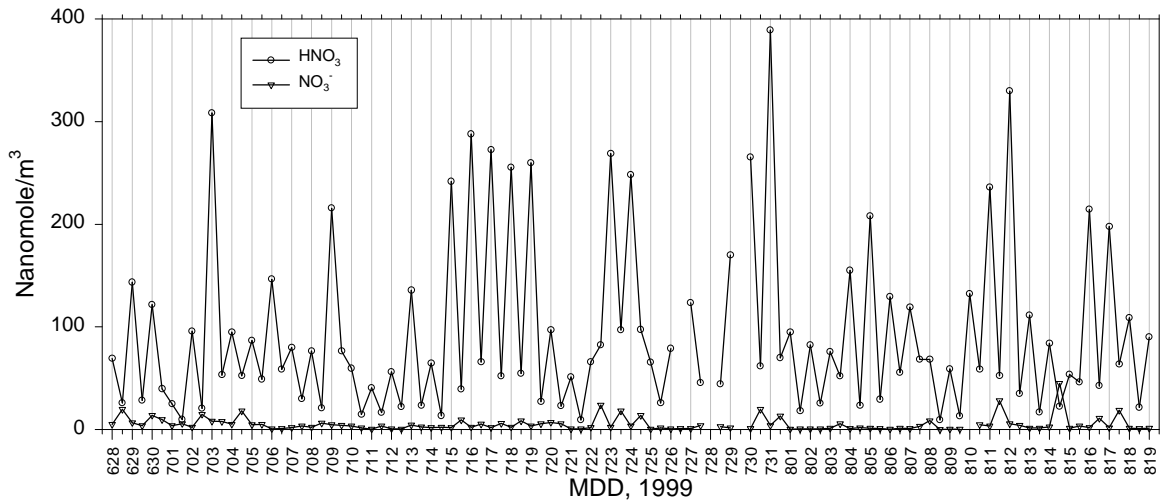


Figure 3. HNO₃ and NO₃⁻, Day and Night Samples

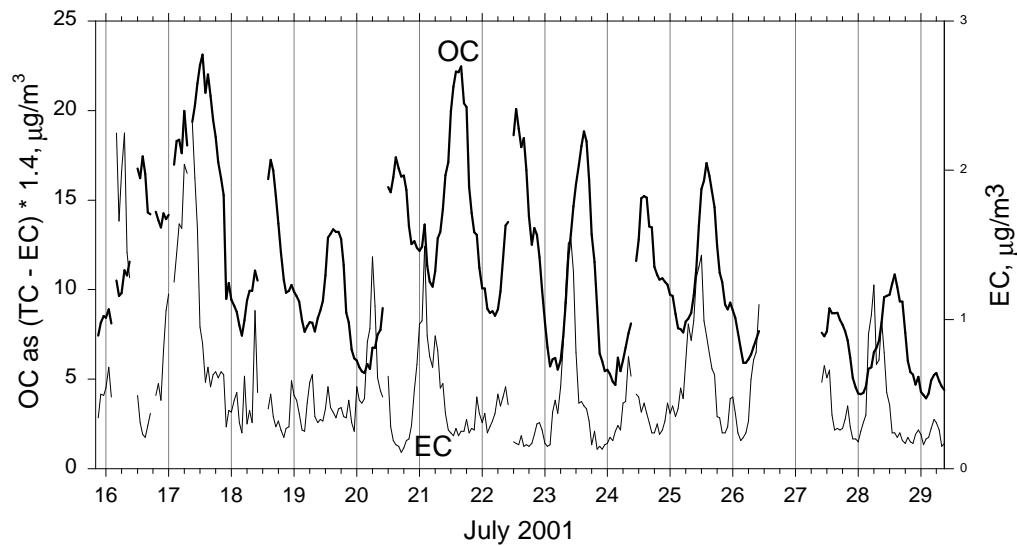


Figure 4. Hourly EC and OC, Sunset Labs NIOSH method