

COMPOSITION OF THE ATMOSPHERIC AEROSOL AT THE POINT OF OBSERVATION

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INTRODUCTION

It is difficult to avoid altering particulate matter suspended in the atmosphere with most particulate matter measurement techniques. We address the extent to which methods based on the separation of the particulate and gas phases adulterate the particulate phase in suspension at the point of sampling with respect to particles up to and including 2.5 μm in aerodynamic diameter (PM_{2.5}). Specifically, we consider mass alteration during sampling and subsequent sample processing due to the volatility of ammonium nitrate and organic matter, and due to the adsorption of organic compounds on quartz fiber filters.

Here we present results from sampling the ambient aerosol during July 1999 at Fort Meade, MD (39.083°N, 76.750°W), a non-urban site in the Baltimore-Washington corridor. Additional sampling will take place during the (ideally) seasonally representative months of January 2000, April 2000, July 2000, and January 2001 as part of the Maryland Aerosol Research and Characterization (MARCH-Atlantic) study, a multi-year project designed to facilitate improved understanding of atmospheric fine particulate matter. Specific objectives of the study are (1) to characterize the changes in composition of PM_{2.5} as a function of time, (2) to identify the most likely sources of PM_{2.5} to the region, (3) to investigate potential biases in various PM_{2.5} measurement techniques, and (4) to provide useful information to the State of Maryland and EPA concerning PM measurements and regulations.

We add to the growing body of studies that have investigated potential sampling biases in filter based methods for particulate phase nitrates (e.g. Zhang and McMurry, 1992; Hering and Cass, 1999) and organics (e.g. Tang et al., 1994; Turpin et al., 1994; Gundel et al., 1995; Eatough et al., 1996). We compare the 24-hour TEOM PM_{2.5} mass concentration with those measured by a collocated filter sampler, and examine how the PM_{2.5} composition varied as a function of PM_{2.5} mass concentration during July 1999. We also compare inorganic aerosol composition measurements to expectations based on aerosol thermodynamic equilibrium calculations.

EXPERIMENTAL

In July 1999, 24-hour filter samples for PM_{2.5} concentration and composition along with gas phase HNO₃, NH₃ and hourly measurements of SO₂, CO and PM_{2.5} were added to an existing state air quality monitoring site at Fort Meade, MD. The existing measurements consisted of 24-hour Federal Reference Method (FRM) for PM_{2.5}, 1-hour O₃, NO, NO_x, and surface and aloft meteorology

This study employed two Sequential Filter Samplers (SFSs) and two Sequential Gas Samplers (SGSs) programmed to sample for 24 hours through filter packs that are replaced manually every third day. Detailed descriptions of these samplers can be found in Chow et al. (1996) and references therein. In brief, each sampler has two channels, each containing a filter pack containing one or two sampling filters through which a pump draws air at a rate of 20 L/min.

SFS-1 is used to determine PM_{2.5} mass and chemical composition. The sampling stream to both channels of SFS-1 is preceded by a PM_{2.5} size-selective inlet and nitric acid denuder. A Teflon filter is used on one channel to determine mass and elemental concentrations via gravimetry and x-ray fluorescence, respectively, after equilibration at 21.5 \pm 1.5 °C and 35 \pm 5% relative humidity. The second channel contains a quartz filter followed by a sodium chloride impregnated cellulose filter. A section of the quartz filter is extracted and used to determine the concentration of water-soluble ions: sodium and potassium by atomic absorption spectroscopy; chloride, sulfate, and non-volatilized nitrate by ion chromatography; and ammonium by automated colorimetry. The sodium chloride impregnated cellulose filter is used to determine the

amount of particulate nitrate that evaporates off the front quartz filter. SFS-2 is used to determine the amount of organic (OC) and elemental (EC) carbon in $PM_{2.5}$. SFS-2 is equipped with sampling cartridges containing two quartz filters in series on one channel, and a Teflon filter followed by a quartz back-up filter on the second channel. A section of each quartz filter is analyzed by thermal optical reflectance (TOR) for organic and elemental carbon.

Gas phase nitric acid is sampled using SGS-1. Channel one contains a quartz filter followed by a sodium chloride impregnated cellulose filter. Channel two contains a nitric acid denuder upstream of the two filters. A section of every filter is extracted and analyzed for nitrate by ion chromatography. The ambient gas phase nitric acid concentration is determined from the difference between the total nitrate collected on the channel 1 filters minus the total nitrate collected on the channel 2 filters. A second SGS, SGS-2, is used to measure gas phase ammonia concentrations. One channel contains a quartz filter followed by a citric acid impregnated cellulose filter. The second channel contains an ammonia denuder upstream of the two filters. A section of each filter is extracted and analyzed for ammonium using automated colorimetry. The ambient gas phase ammonia concentration is determined from the difference between the total ammonium collected on the channel 1 filters minus the total ammonium collected on the channel 2 filters. The SFSs and SGSs were operated at ambient temperature.

The SFS and SGS filter packs are shipped cooled and sealed between a central laboratory and the sampling site approximately once each week. Filters are sealed and kept cold immediately after removal from the sampler. Each sampler contains a filter pack open to the atmosphere that is changed out every 3rd day. It serves as a dynamic blank, the variance of which determines the lower quantifiable limit for the respective observables.

Continuous measurements of $PM_{2.5}$ mass using a TEOM[®] Series 1400a (Patashnick and Rupprecht, 1991) equipped with a $PM_{2.5}$ inlet have been obtained at the site for all months after July 1999. The TEOM's sample stream of 3 L/min is preheated to 50°C prior to entering the sampling chamber.

RESULTS

The average 24-hour $PM_{2.5}$ concentration measured during July 1999 from SFS-1 was $20.6 \mu\text{g}/\text{m}^3$, with a range of 5.5 to $37.1 \mu\text{g}/\text{m}^3$. The 24-hour TEOM mass concentration averaged $3.5 \pm 1.2 \mu\text{g}/\text{m}^3$ higher (95% confidence interval, paired t-test) than the collocated SFS sampler. Measurements from the two samplers were tightly correlated with $R = 0.98$. On average, sulfate, ammonium, nitrate, organic carbon, elemental carbon, and crustal material composed 38%, 13%, 2%, 36%, 7%, 4% of $PM_{2.5}$ in July 1999 at Fort Meade, respectively. Substantial differences in the composition of $PM_{2.5}$ were observed between days with high and low $PM_{2.5}$ concentrations. On the days with the highest $PM_{2.5}$ concentrations ($>30 \mu\text{g}/\text{m}^3$, 8 days) in July 1999, the fraction in sulfate + ammonium averaged 59% ($19.6 \mu\text{g}/\text{m}^3$) of the total mass, while the fraction in carbonaceous material ($1.4 \cdot \text{OC} + \text{EC}$) averaged 27% ($8.9 \mu\text{g}/\text{m}^3$). The averages changed to 37% ($2.8 \mu\text{g}/\text{m}^3$) and 67% ($4.9 \mu\text{g}/\text{m}^3$), respectively, on the days with the lowest $PM_{2.5}$ concentrations ($<11 \mu\text{g}/\text{m}^3$, 7 days). Figure 1 displays how the composition of $PM_{2.5}$ varied with $PM_{2.5}$ concentration. It is apparent from Figures 1d and 1e that changes in the $PM_{2.5}$ concentration is driven largely by sulfate and ammonium rather than carbonaceous material.

The amount of nitrate collected on the backup NaCl impregnated cellulose filter in SFS-1 was approximately 9 times larger than the amount collected on the front quartz filter (Figure 2). Thus, evaporative losses of particle phase nitrate from quartz filters can result in a large underestimation of particulate nitrate in the eastern US in the summer. We assume that the nitrate collected on the backup filter represents the amount of ammonium nitrate that evaporated off the front quartz filter, which ranged from -1% to 9% (0.1 to $1.1 \mu\text{g}/\text{m}^3$) and averaged ~2% ($0.36 \mu\text{g}/\text{m}^3$) of the total $PM_{2.5}$ mass measured on the Teflon filter of SFS-1. If the Teflon filter is subject to the same evaporative losses of ammonium nitrate as the quartz filter, the $PM_{2.5}$ mass measurement may be underestimating the true ambient $PM_{2.5}$ concentration by 1 to 9% on any given day.

Potential biases associated with the organic particulate material may be larger. Each channel on SFS-2 employed the use of a quartz fiber back-up filter. One backup filter was preceded by a Teflon filter, while the other was preceded by a quartz filter. Figure 3 shows the amount of organic carbonaceous material that was detected on the backup filters, relative to what was measured on the front quartz filter of SFS-1. The amount of organic carbon measured on the backup filter behind the Teflon averaged over 50% of what was measured on the front quartz filter, while the backup filter behind quartz averaged ~30% of the OC measured on the front quartz filter. These amounts are on the order of 10% of the total $PM_{2.5}$ mass, indicating sampling biases associated with organic particulate material can be substantial in the eastern US in the summer. The material detected on the backup filters likely comes from two sources: 1) OC that evaporates off the front filters, which results in a negative sampling bias for OC and $PM_{2.5}$, and 2) gas phase organic compounds that adsorb on quartz filters, which contributes to a positive sampling bias for OC and the reconstructed mass. However, the relative contributions from each of these possibilities are highly uncertain. An additional source of uncertainty in the

determination of the concentration of organic particulate material resides in the multiplier of 1.4 used to estimate the average molecular weight of organic particulate matter (what actually resides on the filter) per carbon weight (what the TOR technique measures). The concentrations of organic particulate material reported here (as in Figure 1) were calculated by TOR analysis of the front quartz filters of SFS-2, without corrections from a backup filter.

We use the SCAPE2 (Kim et al., 1993) inorganic aerosol equilibrium model to compare the observed gas-particle partitioning of ammonia-ammonium and nitric acid-nitrate to calculations based on thermodynamic equilibrium. The SCAPE2 model requires inputs of observed temperature, relative humidity, total nitrate (gas + particulate phases), total ammonium, sulfate, sodium, chloride, potassium, and magnesium. The last four species are not significant in the data presented here. The model then calculates the gas phase concentrations of ammonia and nitric acid as well as the particulate phase concentrations of ammonium and nitrate at thermodynamic equilibrium. Figure 4 compares the SCAPE2 calculated and observed concentrations of the four species. The agreement between the equilibrium calculations and observations is excellent for the dominant phase species ($R \geq 0.99$ for gas phase nitric acid and particulate ammonium). The correlations for the minor phase species are not as strong. However, the differences between the SCAPE2 calculated and observed concentrations are not statistically significant at the 95% confidence level, except in the case of ammonia where the observed concentration is $0.11 \pm 0.07 \mu\text{g}/\text{m}^3$ larger (95% confidence interval) than the calculated concentration.

CONCLUSIONS

Based on measurements and theoretical evaluation of aerosol observations made in July 1999 at a non-urban site in the Baltimore-Washington Corridor, 24-hour $\text{PM}_{2.5}$ mass concentration measurements appear to underestimate the highest 20th percentile concentration of "dry" suspended particles by approximately 10%. This bias appears to be a function of losses of particulate ammonium nitrate and organics from the filters during sampling. Additional research is required to determine the sign and magnitude of the potential error in sampling organics.

Evaporative loss of particulate nitrate from filters during sampling can represent a large fraction of the total particulate nitrate. However, particulate nitrate appears to be only a small fraction of the total $\text{PM}_{2.5}$ in the Mid-Atlantic US in the summer. The observed partitioning of nitrate and ammonium between the particulate and gas phases is well reproduced by thermodynamic equilibrium theory.

Although the carbonaceous material accounts for approximately 20 to 70% of the $\text{PM}_{2.5}$ mass from the highest to the lowest mass concentration days, ammonium sulfate is the dominant constituent of the $\text{PM}_{2.5}$ on the higher mass concentration days.

Comparison of diurnal mass measurements of $\text{PM}_{2.5}$ using a TEOM instrument with a collocated 24-hour $\text{PM}_{2.5}$ filter sampler correlate with a small positive bias in the TEOM average over the filter sampler measurements.

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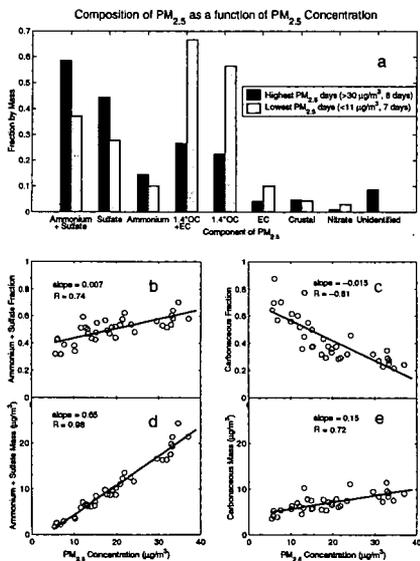


Figure 1. (a) Composition of PM_{2.5} on the days with the highest (>30 µg/m³, 8 days) and lowest (<11 µg/m³, 7 days) PM_{2.5} mass concentrations in July 1999 at Fort Meade, MD. The unidentified fraction represents the difference between PM_{2.5} measured on the Teflon filter of SFS-1 and the sum of sulfate + ammonium + 1.4*OC + EC + crustal + nitrate + volatilized ammonium nitrate. The crustal component is taken as 2.14*Si + 1.89*Al + 1.43*Fe + 1.67*Ti + 1.4*Ca + 1.2*K from x-ray fluorescence analysis. (b) The relationship between the fraction of PM_{2.5} in sulfate + ammonium and PM_{2.5} concentration. (c) The relationship between the fraction in carbonaceous material and PM_{2.5} concentration. (d) The relationship between the ammonium + sulfate mass and PM_{2.5} concentration. (e) The relationship between the carbonaceous mass and PM_{2.5} concentration. The carbonaceous material is determined from the front quartz filter of SFS-2, without corrections from a backup filter and is taken as 1.4*OC + EC.

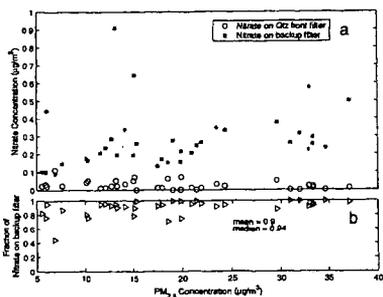


Figure 2. (a) The amount of nitrate collected on the front quartz filter and the backup sodium chloride impregnated cellulose backup filter in SFS-1 as a function of $PM_{2.5}$ concentration. (b) The fraction of nitrate collected on the backup filter ([nitrate on backup filter]/[nitrate on front filter + nitrate on backup filter]) versus $PM_{2.5}$ concentration.

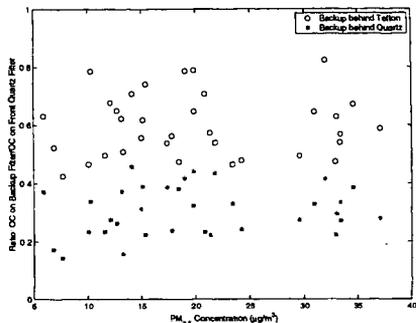


Figure 3. The amount of OC collected on each quartz backup filter in SFS-2 divided by the amount of OC measured on the front quartz filter of SFS-2 as a function of $PM_{2.5}$ concentration.

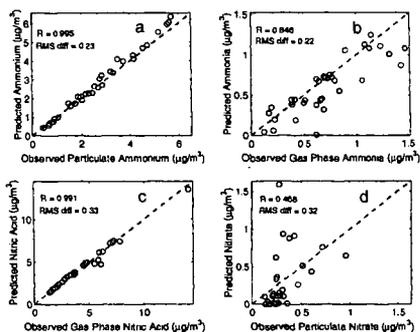


Figure 4. Comparison of the concentrations of inorganic $PM_{2.5}$ components calculated by the SCAPE2 aerosol equilibrium model to those observed for (a) particulate ammonium, (b) gas phase ammonia, (c) gas phase nitric acid, and (d) particulate nitrate. The dashed line is the 1:1 line. Observed particulate nitrate is taken as the sum of nitrate measured on the front quartz and backup sodium chloride impregnated cellulose filters of SFS-1. Observed particulate ammonium includes the ammonium that is assumed to have evaporated off the front quartz filter of SFS-1 in the form of ammonium nitrate, which is determined from the amount of nitrate collected on the backup sodium chloride impregnated cellulose filter.