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Atmospheric Environment 38 (2004) 3305–3318

**ATMOSPHERIC  
ENVIRONMENT**

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## Mass balance closure and the Federal Reference Method for PM<sub>2.5</sub> in Pittsburgh, Pennsylvania

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### Abstract

Daily ambient aerosol samples were taken in Pittsburgh, Pennsylvania from the summer 2001 to the winter 2002 as part of the Pittsburgh Air Quality Study (PAQS). The study measured PM<sub>2.5</sub> mass by the Federal Reference Method (FRM) and the PM<sub>2.5</sub> chemical composition by a variety of filter-based and continuous instruments. This paper examines the mass balance between the FRM-measured mass and the sum of the aerosol chemical components. For the 7-month study period, the average FRM-measured mass is 11% greater than the sum of the mass of the aerosol chemical components. This mass balance discrepancy varies seasonally, with the average FRM-measured mass 17% greater than the sum of the chemical components for the summer months, with discrepancies as large as 30% during certain periods. Meanwhile, the FRM-measured mass was at or slightly below the sum of the chemical components for the winter months.

The mass balance discrepancy and its seasonal shift cannot be explained by measurement uncertainty; instead the discrepancy is due to combination of retained aerosol water on the conditioned FRM filters and volatilization losses. The relative importance of these different effects varies with aerosol composition and causes the observed seasonal variation in the mass balance. The contribution of the aerosol water to the FRM-measured mass is estimated using continuous measurements of aerosol water at the site; volatilization losses are estimated from other filter-based instruments. Water contributes 16% of the FRM mass in the summer, and 8% of the FRM mass in the winter; it also appears responsible for episodes where the FRM-measured mass is significantly greater than the sum of components. Retention of water is greatest during acidic conditions, which commonly occur during the summer months. Volatilization losses are estimated at 5% of the FRM mass during the summer, and 9% for the winter. Volatilization losses appear to be most significant on days dominated by organic aerosol, or winter days with relatively high nitrate concentration. Accounting for the effects of water and volatilization losses closes the mass balance between the FRM and the sum of the chemical components, providing insight into the FRM measurements.

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*Keywords:* Federal Reference Method; Mass balance; Aerosol water; Aerosol sampling; Aerosol composition; Aerosol volatilization

### 1. Introduction

Fine particulate matter is a cause for concern because of its impact on human health and the environment. The US Environmental Protection Agency (EPA) promulgated standards regulating particulate matter with an aerodynamic diameter of 2.5 μm or less in July 1997

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(PM<sub>2.5</sub>), setting the 24 h standard at 65 µg m<sup>-3</sup>, and the annual average standard at 15 µg m<sup>-3</sup>. The new standards define PM<sub>2.5</sub> as the mass measured by the Federal Reference Method (FRM). These instruments use gravimetric analysis of filters sampled over a 23–25 h period to determine PM<sub>2.5</sub> mass concentration. EPA also specified operating and handling conditions for the FRM to minimize effects that could impact measurement accuracy, and to provide a consistent measure for regulatory standards. These effects include volatilization of species from sample filters, errors in filter tare and sample weights, and the presence of water on filters.

As a filter-based measurement, the FRM measures accumulated mass on a filter for a 24-h period, and therefore may not be truly reflective of atmospheric PM<sub>2.5</sub> mass. The effects of emission reductions are estimated using chemical transport models and other analytical tools that are based on a scientific definition of PM<sub>2.5</sub> behavior in the atmosphere, not FRM measurements. It is therefore important to understand the relationship between what the FRM measures and different definitions of PM<sub>2.5</sub> mass in the atmosphere to ensure alignment in regulatory development.

One frequently used method of quality assurance of PM measurements is comparison of the gravimetrically measured mass to the sum of the aerosol chemical components as measured by collocated samplers. Many previous studies have used this method to evaluate aerosol measurements often finding gaps in mass closure (e.g., Chow et al., 1993; Malm et al., 1994a, b; Turpin et al., 1997; Andrews et al., 2000; Tanner and Parkhurst, 2000; Tolocka et al., 2001; Jansen et al., 2002). Mass closure gaps have exceeded 40% (Jansen et al., 2002) and include both instances where gravimetric-measured mass exceeds the sum of the chemical components (“positive discrepancy”) and where it is less than the sum of the chemical components (“negative discrepancy”). Sometimes the mass discrepancy observed in these studies can be explained by uncertainties stemming from analytic measurements (Tolocka et al., 2001). In other studies measurement uncertainty accounts for only a portion of mass discrepancy, the remainder believed attributable to the presence of aerosol water (positive artifact) (Meng et al., 1995), volatilization of organics and nitrates (negative artifact) (Anderson et al., 2002), and uncertainty in the assumptions used to estimate chemical species not directly measured, or a combination thereof (Andrews et al., 2000).

This paper presents FRM data from the Pittsburgh Air Quality Study (PAQS), and uses these data and other measurements from PAQS to investigate FRM mass balance closure. First, the FRM-measured mass is compared to mass measured by a Tapered Element Oscillating MicroBalance (TEOM) and a dichotomous sampler to provide a measure of validation of the mass results. A daily mass balance is constructed for a

7-month period beginning in July 2001, capturing both summer and winter periods. The mass balance compares the sum of major chemical components (sulfate, nitrate, ammonium, elemental carbon (EC), organic carbon (OC), and crustal) measured by a variety of filter-based and continuous instruments at PAQS to FRM-measured mass. We then discuss several hypotheses explaining the mass balance discrepancy observed, including the impact of measurement uncertainty, the presence of water, and volatilization effects.

## 2. Experimental

The main PAQS ambient monitoring station was located in Schenley Park within the city of Pittsburgh (Wittig et al., 2004b). This location was not significantly impacted by local sources. Aerosol samples were taken with both filter-based and continuous instruments; sampling times for filter-based instruments were coordinated to run concurrently, with filter changes scheduled between 22:00 and 00:00 daily.

### 2.1. PM<sub>2.5</sub> mass measurements

PM<sub>2.5</sub> mass was measured using three different instruments collocated at the PAQS station; a Partisol<sup>®</sup>-FRM Model 2000 PM<sub>2.5</sub> Air Sampler (Rupprecht & Pataschnick Co., Inc.), a Series 241 Dichotomous Sampler for PM<sub>10</sub>/PM<sub>2.5</sub> (Thermo Andersen) (“Dichot”) and a Model 1400a “TEOM<sup>®</sup>” (Rupprecht & Pataschnick Co., Inc.). All three instruments were operated continuously for the duration of the study; the FRM and Dichot were operated daily to collect 24-h samples. Both the FRM and Dichot were operated according to the specifications provided by the manufacturer, and the EPA guidelines (40 C.F.R. Part 51 and the EPA Quality Assurance Manual). The TEOM operated at 30°C with a Nafion dryer on the inlet. Validated data from all three mass instruments are available for 92% of sampling time.

The FRM used 47 mm Teflon filters (Whatman No. 7592-104), while the Dichot used 37 mm Teflon filters (Pall Gelman No. R2PJ037). Prior to sampling, the filters for both of the instruments were conditioned for 24 h and then weighed in a controlled-environment chamber maintained at a relative humidity of 35 ± 2% and a temperature of 22 ± 2°C. Filters were weighed on a UTM50 microbalance (Toledo Instruments). Strips of Polonium (Staticmaster) were used to minimize weighing errors induced by electrostatic charge. Filters were loaded into the filter cartridges for both the FRM and Dichot in the laboratory under a HEPA-filtered laminar flow hood to minimize contamination, and brought to the PAQS station at the time of the scheduled filter change. After the filter change, the exposed filters from

both instruments were returned to the laboratory, and stored in a freezer to minimize loss of semi-volatile species. Exposed filters were typically weighed within a day or two of collection, which involved returning the filters to the controlled-environment chamber, conditioning the filters for 24 h, and then weighing the filters to determine sample weight.

## 2.2. Intercomparison of $PM_{2.5}$ mass measurements

$PM_{2.5}$  mass measurements of all three instruments compare well to each other, with linear regression  $r^2$  values of 0.95, and the regression lines within 10% of the 1:1 line for each comparison (Figs. 1 and 2). The time-averaged TEOM is on average 1.5% higher than the FRM, and the FRM about 3% higher than the Dichot

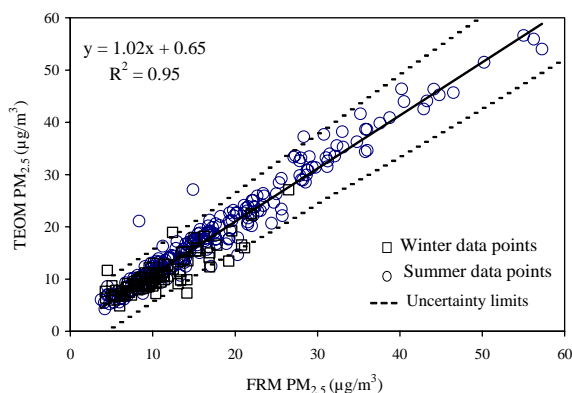


Fig. 1. FRM versus TEOM  $PM_{2.5}$  mass for the period of July 2001–March 2002. “Summer data points” are from 1 July to 31 October 2001; “winter data points” are from 1 November 2001 to 31 March 2002. TEOM data averaged to 24-h periods to correspond to FRM measurements.

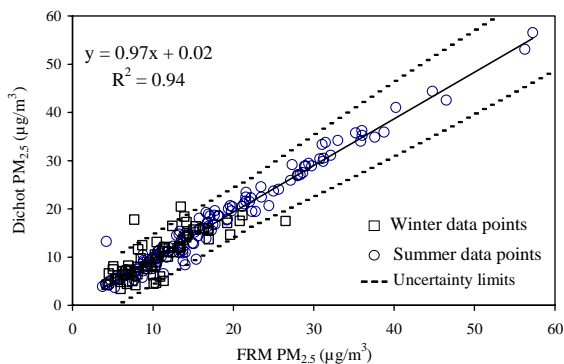


Fig. 2. FRM versus Dichot for the period of July 2001–March 2002. “Summer data points” are from July to November 2001; “winter data points” are from November 2001 to March 2002.

for the study period. However, the scatter shown in Fig. 1 indicates that there are some periods of greater discrepancy, mostly occurring when  $PM_{2.5}$  concentrations are  $< 20 \mu\text{g m}^{-3}$  and during the winter months.

The TEOM has been reported to under-measure mass due to volatilization, particularly during the winter months (Allen et al., 1997). In December 2001 and January 2002, there are about 10 days where the TEOM measurements are significantly lower than those measured by the FRM and Dichot—up to 50% lower. This behavior is not unexpected, given the elevated temperature of the TEOM compared to the other instruments. The TEOM used in PAQS is a  $30^\circ\text{C}$  TEOM, not the  $50^\circ\text{C}$  TEOM that has typically been used in previous studies. Because we only observed the effect on a handful of exceptionally cold (ambient temperatures  $< -6^\circ\text{C}$ ) days when the  $PM_{2.5}$  mass was relatively low, volatilization did not significantly impact TEOM performance during days where  $PM_{2.5}$  mass exceeded  $20\text{--}30 \mu\text{g m}^{-3}$ . However, the winter of 2002 was relatively mild compared to those typically experienced in Pittsburgh, so TEOM volatilization may be more significant in colder regions or during a more typical Pittsburgh winter.

## 2.3. Sulfate, nitrate, and ammonium

$PM_{2.5}$  sulfate, nitrate, and ammonium were measured using both continuous instruments and filter-based samplers. To evaluate the mass balance, we used data from the CMU inorganic sampler, a denuder/filter-based speciation sampler (Takahama et al., 2004). The CMU inorganic sampler yielded daily inorganic  $PM_{2.5}$  composition on a 24-h basis for the entire sampling period, except for July 2001, when it provided five measurements per day.

R&P sulfate (Model 8400S) and nitrate (Model 8400N) analyzers were run concurrently with the CMU inorganic sampler to provide high time resolution data. We used the data from the R&P instruments in conjunction with TEOM data to evaluate the  $PM_{2.5}$  mass balance on an hourly basis. Wittig et al. (2004a) discuss in detail the comparison between the R&P instruments and the traditional samplers, as well as the approach used for the calibration of the continuous instruments. The calibrated final values of Wittig et al. (2004a) are used for the analysis here.

A steam sampler (Khlystov et al., 1995) was used to provide high time resolution data for ammonium and data for intercomparison. To construct the mass balance, we used  $PM_{2.5}$  ammonium measurements from the CMU inorganic sampler for the summer months. Because data indicate that atmospheric conditions are neutral in the winter (December 2001–March 2002), we estimated winter  $PM_{2.5}$  ammonium concentrations by

assuming ammonium was present in sufficient concentrations to result in neutral particles.

#### 2.4. Organic carbon/elemental carbon

PM<sub>2.5</sub> OC and EC were measured by the CMU-designed Teflon–Quartz, Quartz–Quartz sampler (TQQQ). The TQQQ is a two-port sampler with a double quartz filter pack in one line and a Teflon filter followed by a quartz filter in the second. The OC is estimated as a value between OC from the upstream quartz filter ('bare quartz') of the double quartz filter pack, and that obtained by subtracting the OC of the quartz behind the quartz from the bare quartz OC. Comparison with a denuder-based sampler showed that this configuration provides robust estimate of particulate OC (Subramanian et al., 2004). EC is estimated from the bare quartz alone. Each quartz filter is analyzed for OC/EC using a Sunset Labs Thermal-Optical Transmittance analyzer with the NIOSH 5040 protocol (NIOSH, 1998) as implemented by Subramanian et al. (2004). A Sunset Laboratories semi-continuous OC/EC analyzer using the same analysis protocol (Cabada et al., 2004) was used to provide higher time resolution OC/EC data.

Most mass balance studies use a value of 1.4 for the OC multiplier. Recent work by Turpin and Lim (2001) examines this factor, recommending values ranging from 1.1 for fresh emissions to 1.6–2.1 for an aged aerosol. Comparison of PAQS main site data with satellite sites indicates that the air quality in Pittsburgh is dominated by regional transport (Tang et al., 2004). We therefore used a multiplication factor of 1.8 which is representative of an aged, regional aerosol to estimate total organic mass from OC measurements. The sensitivity of the results to this factor will be discussed in a subsequent section.

#### 2.5. Crustal

We estimated the crustal component of PM<sub>2.5</sub> using metals data from XRF analysis of filter-based samples taken daily from the PAQS sites during July 2001 and January 2002. Elemental composition was also measured using ICP-MS analysis of high volume filter samples taken at the main PAQS site. The trace metal composition data do not vary substantially from site to site, indicating that Pittsburgh aerosol is of a regional nature and that none of the sampling sites were heavily impacted by local sources.

We used the sum of oxides algorithm (Malm et al., 1994a, b) to estimate the daily crustal PM<sub>2.5</sub> for July 2001 and January 2002 using the XRF data. The average crustal contribution was  $1 \mu\text{g m}^{-3}$  (approximately 3–6% of total PM<sub>2.5</sub> mass) with a standard deviation of  $0.4 \mu\text{g m}^{-3}$ . This estimate compares well with crustal

estimates from similar studies in the Eastern US (Andrews et al., 2000; Tolocka et al., 2001). The ICP-MS data suggest that the crustal contribution remains fairly constant throughout the year; however, these data were not used to estimate the crustal contribution because the ICP-MS data quality for Si, an important crustal species, are poor due to analytical interferences. Therefore, for the remaining months, we assume that crustal material contributes  $1 \mu\text{g m}^{-3}$ , or 4% of the average PM<sub>2.5</sub> mass. The potential effects of this assumption on the mass balance are discussed below.

#### 2.6. Water

Aerosol water content at ambient relative humidity (RH) was measured by the Dry and Ambient Aerosol Size Spectrometer (DAASS), an automatic in situ system, built to measure ambient aerosol size and distributions at both ambient and low RH conditions (Khlystov et al., 2004). The system consists of two Scanning Mobility Particle Sizers (SMPS, TSI, Inc.) and an Aerodynamic Particle Sizer (APS, TSI, Inc.). The instruments measure the aerosol size distribution between 5 nm and 10  $\mu\text{m}$  in diameter. By measuring alternatively "wet" and "dry" size distributions and the corresponding integrated volume concentrations, the aerosol water content of ambient aerosol can be estimated. The water content at 35% RH, the RH at which FRM filters were conditioned, was then estimated according to the method described later in this paper.

Aerosol water content at 35% RH was also calculated directly using the GFEMN aerosol thermodynamic model (Ansari and Pandis, 1999). GFEMN predicts inorganic aerosol composition, including aerosol water, based on chemical thermodynamic principles. Using PAQS chemical speciation data (sulfate, nitrate, ammonium, etc.), temperature and RH, the model estimates the PM water concentration at the RH of the FRM measurements.

### 3. Results and discussion

Fig. 3 shows the PM<sub>2.5</sub> FRM daily time series for July 2001–March 2002. The average PM<sub>2.5</sub> mass measured with the FRM was  $16.1 \mu\text{g m}^{-3}$ . There is significant seasonal variation in the PM<sub>2.5</sub> mass levels, with an average mass concentration of  $24.1 \mu\text{g m}^{-3}$  for the summer of 2001 and  $12.2 \mu\text{g m}^{-3}$  for the winter of 2002. Fig. 3 also illustrates the episodic nature of PM<sub>2.5</sub> concentrations in the Pittsburgh area, with high peaks and low valleys of PM<sub>2.5</sub> levels occurring over periods of several days due to the effect of meteorological conditions on ambient air quality. This behavior occurs throughout the sampling period, but is more pronounced in the summer than in the winter months.

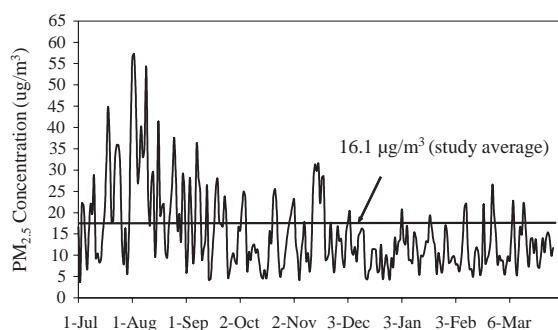


Fig. 3. Daily  $PM_{2.5}$  mass measured with an FRM sampler from July 2001 to March 2002. Horizontal line is the average  $PM_{2.5}$  for this period.

### 3.1. Comparison of FRM mass to sum of chemical components

Fig. 4 presents the monthly average  $PM_{2.5}$  mass and composition. The height of each bar represents the FRM mass. The component labeled “missing” is the difference between the FRM-measured mass and the sum of chemical components; it is positive when the FRM-measured mass exceeds the sum of chemical components, and negative when it is less than the sum of chemical components. During the summer, sulfate comprises over 45% of the FRM-measured  $PM_{2.5}$  mass, while nitrate comprises <3%. In the winter months, the sulfate contribution drops to 35%, while the nitrate contribution approaches 15% of FRM-measured  $PM_{2.5}$  mass. The organic mass varies slightly through the year, contributing approximately 20% of total mass in the summer, 30% in the fall, and 20% in the winter, for a study average contribution of 23% of the FRM-measured  $PM_{2.5}$  mass. For the period of July 2001–March 2002, the average FRM-measured mass is 11% greater than the average mass of the sum of the components (Fig. 5).

Examination of the mass balance on a monthly average basis (Fig. 4) indicates that there is a significant seasonal dependence of the mass balance discrepancy. From July to November 2001, the FRM mass exceeded the sum of the chemical components with an average missing mass from the sum of the chemical components of  $2.9 \mu\text{g m}^{-3}$ , or 15% of the FRM-measured mass. For the period of December 2001–March 2002, the sum of the chemical components slightly exceeds the FRM-measured mass, with an average excess mass of  $0.2 \mu\text{g m}^{-3}$  or 2% of the FRM-measured mass. As discussed below, the average discrepancy for the summer is greater than the measurement uncertainty, while the average discrepancy for the winter is within the range of measurement uncertainty.

Fig. 6 shows the daily mass balance for August 2001 and February 2002, months with the largest positive and

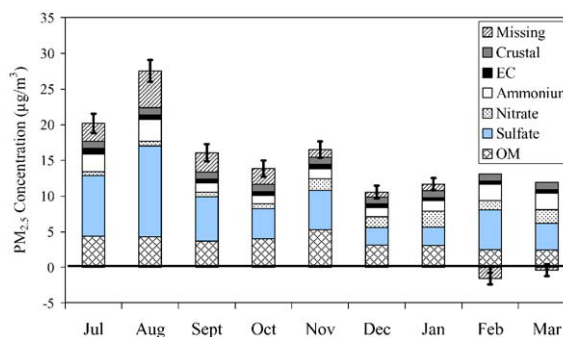


Fig. 4. Monthly average  $PM_{2.5}$  mass and composition calculated from daily 24-h measurements. The “missing” component is the difference between the FRM measurement and the sum of the chemical components. The FRM mass is greater than the sum of the chemical components for July–December, and less than the sum of the chemical components in February and March. The error bars represent uncertainty in the mass balance on a monthly average basis. OM is defined as  $1.8 \times \text{OC}$ .

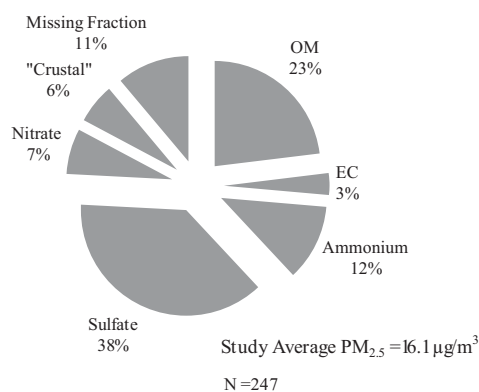


Fig. 5. Average  $PM_{2.5}$  composition July 2001–March 2002 calculated from 247, 24-h measurements.

negative discrepancies, respectively. Overall for August 2001, 19% ( $5.2 \mu\text{g m}^{-3}$ ) of the FRM-measured mass was unaccounted for by the sum of the chemical components indicating a positive discrepancy. The positive discrepancies in August are episodic, occurring periodically and lasting for several days at a time, interspersed with short episodes of mass closure. Similar behavior was observed for the other months when the FRM mass was greater than the sum of the chemical components. In February, the FRM-measured mass was 12% ( $1.4 \mu\text{g m}^{-3}$ ) less than the sum of the chemical components indicating a negative discrepancy. For the other winter months, there are periods of both slight positive and negative discrepancy, but the periods of positive discrepancy observed are far fewer than those observed in the summer. The overall effect in the winter is that the periods of positive discrepancy approximately equal the

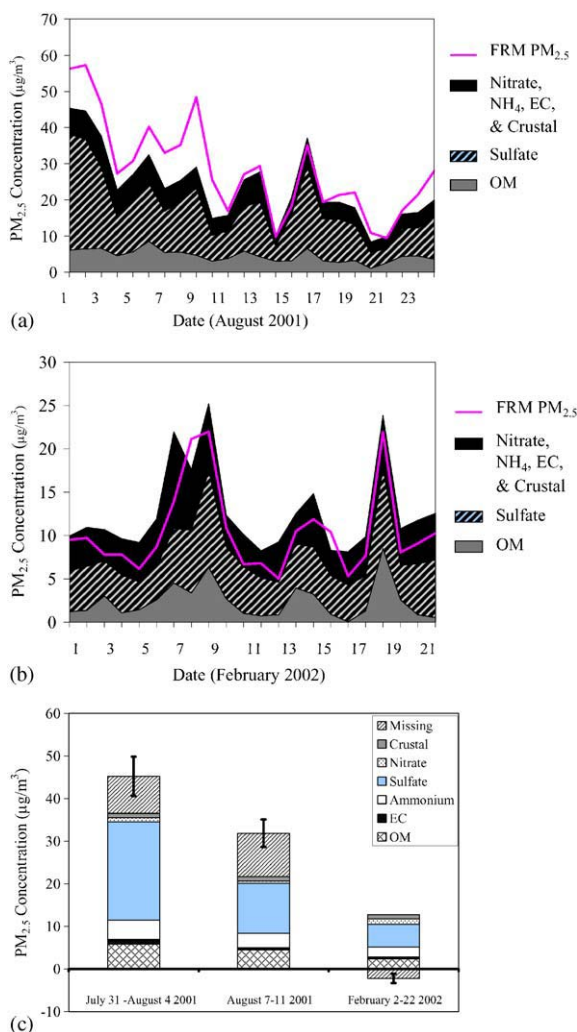


Fig. 6. (a) Time series mass balance for August 2001 ( $\mu\text{g m}^{-3}$ ). (b) Time series mass balance for February 2002 ( $\mu\text{g m}^{-3}$ ). Data in (c) are averages of daily 24-h data over the indicated period. The error bars in (c) represent average mass balance uncertainty for the period. OM is defined as  $1.8 \times \text{OC}$ .

negative discrepancy, resulting in mass balance closure on the average.

The positive mass discrepancy can be further explored by evaluating the average mass balance for select episodes in August 2001 shown in Fig. 6c. The average FRM-measured mass exceeded the sum of chemical components by 19% or  $8.7 \mu\text{g m}^{-3}$  for the period between 31 July and 4 August 2001, and by 32% or  $10.2 \mu\text{g m}^{-3}$  for the period between 7 and 11 August 2001. Both of these periods occurred during episodes of hot, humid weather with relatively high  $\text{PM}_{2.5}$  concentrations. Fig. 6c also shows data for a winter period with significant negative discrepancy; the average

FRM-measured mass for 1–22 February 2002 was 21% or  $2.2 \mu\text{g m}^{-3}$  below the sum of the chemical components.

Fig. 7 presents the ratio of the FRM-measured mass to the sum of chemical components as a function of FRM mass. For this analysis the data have been averaged into periods with similar  $\text{PM}_{2.5}$  mass concentrations. If the mass balance is closed, the data points will fall close to 1 within measurement uncertainty. The results indicate that the mass discrepancy varies with mass concentration. When the FRM-measured mass is less than about  $10 \mu\text{g m}^{-3}$ , there is a consistent negative discrepancy. This observation reflects the negative mass balance discrepancy observed during the winter months, when the  $\text{PM}_{2.5}$  concentration averages around  $10\text{--}12 \mu\text{g m}^{-3}$  with large fractions of nitrates and organics. Positive discrepancy occurs at  $\text{PM}_{2.5}$  levels  $> 10 \mu\text{g m}^{-3}$ , which primarily occur during the warmer months of the summer and fall.

### 3.2. Hypotheses explaining the mass balance

Several hypotheses may explain the periods of mass balance discrepancy observed:

- (1) the discrepancy could be due to uncertainty in the measurements of chemical composition and  $\text{PM}_{2.5}$  mass;
- (2) periods of significant positive mass discrepancy could be explained by the presence of bound water on the FRM filter post-conditioning;
- (3) periods of negative mass discrepancy could be due to volatilization of organic compounds and nitrates;
- (4) the discrepancy could result from the use of an incorrect OC multiplication factor; and
- (5) inaccuracies in estimates for the crustal component of  $\text{PM}_{2.5}$  mass could impact mass balance closure.

We discuss each of these hypotheses below.

#### 3.2.1. Impact of measurement uncertainty

In order to evaluate whether the mass balance discrepancy is significant, it is important to quantify the uncertainty in the individual measurements used to evaluate the mass balance. The uncertainties for the individual measurements are listed in Table 1. These conservative estimates were derived from intercomparisons of data from different samplers and instruments used during PAQS (Wittig et al., 2004b), and therefore account for both stochastic and systematic uncertainties. To minimize potential biases due to systematic uncertainties, we eliminated the small number of data points for which large unexplained discrepancies exist between the different measurements of the same parameter. For the remaining data we are confident that the systematic uncertainties are reasonably small because it

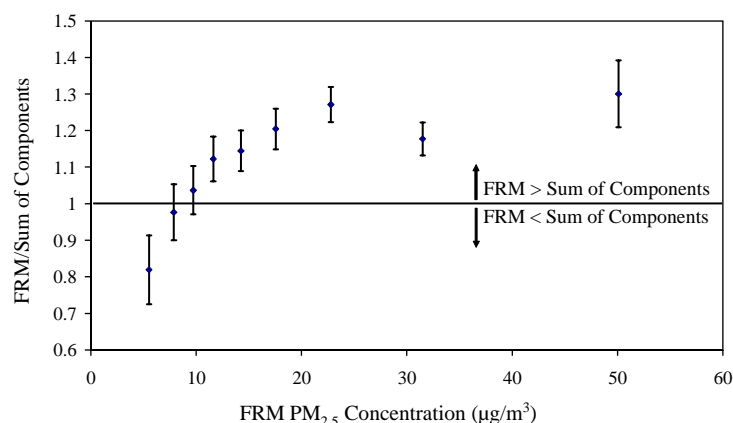


Fig. 7. Mass discrepancy ratio as a function of FRM  $PM_{2.5}$ . The mass balance discrepancy ratio is the FRM mass divided by the sum of the chemical components. The FRM measurement exceeds the sum of the chemical components when the ratio  $> 1$ , indicating a positive mass discrepancy. When the ratio  $< 1$ , the FRM measurement is less than the sum of the chemical components, indicating a negative mass discrepancy. The data in this figure are averages computed by sorting the FRM data into bins as a function of  $PM_{2.5}$  mass concentrations and then calculating the average mass discrepancy ratio and average mass balance uncertainty (Eq. (2)) for each bin. Approximately 30 days of data are in each bin.

Table 1  
Average estimated uncertainty of individual instrument measurements (relative and absolute)

Parameter	Relative uncertainty (%)	Absolute uncertainty ( $\mu\text{g m}^{-3}$ )
FRM $PM_{2.5}$ mass	$\pm 15$	$\pm 2$
$SO_4$	$\pm 25$	$\pm 1.5$
$NO_3$	$\pm 40$	$\pm 0.5$
$NH_4$	$\pm 30$	$\pm 0.5$
OM	$\pm 25$	$\pm 0.9$
EC	$\pm 50$	$\pm 0.25$
Crustal <sup>a</sup>	$\pm 50$	

Note: The higher of the relative or absolute value was used to calculate daily uncertainty for each parameter. As described in the text, these values were determined based on intercomparison of different samplers and instruments at the site.

<sup>a</sup>Crustal uncertainty is assumed at 50% based on estimates from previous work (Andrews et al., 2000).

is extremely unlikely that different samplers and instruments operating on different physical principles and by different groups would produce consistent results if significant systematic errors were present.

The approach used to determine the measurement uncertainty is illustrated in Figs. 1 and 2 using the intercomparisons of the  $PM_{2.5}$  mass measurements. During PAQS, the  $PM_{2.5}$  mass was measured using two filter samplers (FRM and DICHOT) and a TEOM. The high degree of correlation between the  $PM_{2.5}$  measurements provides confidence in the precision of the measurements and indicates that any systematic

biases are small. The estimated uncertainty of the  $PM_{2.5}$  mass measurements is shown by the dashed lines in Figs. 1 and 2, and accounts for the variation among the different measurements of  $PM_{2.5}$  mass at the site. These uncertainty limits were defined to include  $> 95\%$  of the data lie within these limits and therefore they can be viewed as 95% confidence limits. Uncertainty estimates for the aerosol chemical components were derived using similar intercomparisons: Subramanian et al. (2004) provide a detailed intercomparison of carbon measurements, and Wittig et al. (2004a) provide a detailed intercomparison of the inorganic measurements.

The uncertainty in the mass balance was estimated by combining the uncertainties of the individual measurements using standard analysis procedures assuming that the uncertainties of the individual measurements are uncorrelated:

$$\sigma_T = \sqrt{\sigma_{SO_4}^2 + \sigma_{NO_3}^2 + \sigma_{NH_4}^2 + \sigma_{OM}^2 + \sigma_{EC}^2 + \sigma_{Crustal}^2}, \quad (1)$$

where  $\sigma_T$  is the overall uncertainty, and  $\sigma_{SO_4}$ ,  $\sigma_{NO_3}$ ,  $\sigma_{NH_4}$ ,  $\sigma_{OM}$ ,  $\sigma_{EC}$ , and  $\sigma_{Crustal}$  are the uncertainties of each individual measurement (sulfate, nitrate, ammonium, organic matter (OM), EC, and crustal, respectively). The uncertainty of averaged data (e.g., monthly average) is estimated using

$$\sigma_{Ave} = \frac{\text{Average } \sigma_n}{\sqrt{n}}, \quad (2)$$

where Average  $\sigma_n$  is the average uncertainty in the mass balance (Eq. (1)) for the given set of data, and  $n$  is the number of data points. Eq. (2) is strictly valid for averaged data when only stochastic errors are present.

The measurement intercomparisons (e.g., Figs. 1 and 2) indicate that the variations in the data between the different samplers are largely stochastic (there are no significant systematic biases in the data). Therefore, Eq. (2) should provide a reasonable estimate of uncertainty for averaged data.

A statistically significant discrepancy in the daily mass balance was observed on 82 study days. A statistically significant discrepancy is larger than the uncertainty defined by Eq. (1). The data support the conclusion that the mass balance discrepancy varies seasonally in Pittsburgh. In the summer months, the FRM mass is consistently greater than the sum of the chemical components with 17 days exhibiting a significant positive discrepancy, and only 1 day with a significant negative discrepancy. In the winter months, there are a large number of days with either a positive or a negative discrepancy: 16 winter days had a significant negative discrepancy, while 10 had a significant positive discrepancy. The remaining 38 days of significant mass discrepancy were spread from September to November 2001, with 27 days of positive discrepancy, and 11 days of negative discrepancy. It is clear from these observations that positive and negative mass discrepancies occur during both seasons, but that the positive discrepancy is dominant in the summer, and that the negative discrepancy is more prevalent in the winter.

Evaluating select periods with significant mass balance discrepancy further supports the conclusion that the observed discrepancy cannot be explained by measurement uncertainty. Measurement uncertainty was approximately  $\pm 8\%$  for the periods of 31 July–4 August and 7–11 August (Fig. 6c), much smaller than the observed mass discrepancy of 19% and 32%, respectively. For the period 1–22 February 2002, the FRM mass was 21% greater than the sum of the chemical components; a significantly larger difference than the average measurement uncertainty for that period,  $\pm 14\%$ . On a monthly average basis the mass balance discrepancy was statistically significant for the months of July, August, September, October, and November 2001 and February 2002 (Fig. 4).

### 3.2.2. Retention of water on conditioned FRM filters

Retention of water on the conditioned FRM filters is a concern in Pittsburgh and other areas of the Eastern US because particles are often acidic in the summer, containing substantial amounts of ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ).  $\text{NH}_4\text{HSO}_4$  retains significant water at 35% RH, the RH at which FRM filters are conditioned (Speer et al., 1997; Hand et al., 2000). The presence of  $\text{NH}_4\text{HSO}_4$  could therefore cause aerosol on FRM filters to retain water post-conditioning, potentially explaining the observed mass balance discrepancy.

Two types of evidence are available to examine the potential contribution of particle bound water to the

FRM mass measurements. First, data are presented to identify periods when  $\text{NH}_4\text{HSO}_4$  is likely present. Second, direct measurements of ambient aerosol water content are used to estimate the contribution of water to the conditioned FRM filters. We examine each of these types of evidence below.

In Pittsburgh, a significant fraction of the  $\text{PM}_{2.5}$  mass is sulfate. During the summer, the aerosol is periodically acidic because insufficient ammonium is available to neutralize the sulfate aerosol present. Under these conditions, some of the sulfate will be present in the form of bisulfate ( $\text{NH}_4\text{HSO}_4$ ); the more acidic the aerosol, the larger the fraction of bisulfate present. Since bisulfate retains water at a low RH, we expect that the positive mass balance discrepancy will be present on acidic days. To examine this hypothesis, estimates of aerosol acidity are compared to mass balance discrepancy. Aerosol acidity can be estimated using the ratio of anions to cations (acidity ratio). In the summer in Pittsburgh this ratio is largely determined by ammonium and sulfate levels because nitrates and crustal material are minor  $\text{PM}_{2.5}$  components. For the summer periods we calculate the acidity ratio as

$$\text{acidity ratio} = \frac{2[\text{SO}_4]}{[\text{NH}_4]}, \quad (3)$$

where  $[\text{SO}_4]$  is the measured molar concentration of aerosol sulfate, and  $[\text{NH}_4]$  is the measured molar concentration of ammonium. A ratio of approximately 1 indicates neutral conditions; ratios  $> 1$  indicates acidic conditions when some bisulfate is likely present; and ratios of 2 or greater indicate that all of the sulfate present is likely in the form of bisulfate.

Time series of the acidity ratio (Eq. (3)) indicates that the aerosol is periodically acidic, and that specific episodes of positive discrepancy are correlated with acidity. For example, during the August mass discrepancy episodes shown in Fig. 6c, the atmospheric acidity ratio averaged 2.0 for the 31 July–4 August period, and 1.33 for the 7–11 August period, indicating acidic conditions. Meanwhile, the average acidity ratio for periods in August with no mass discrepancy was 1.08, indicating conditions close to neutral.

High time resolution data provide further evidence of the relationship between periods of positive mass discrepancy and aerosol acidity. For this analysis, the TEOM is used to measure mass, the R&P continuous instruments are used for sulfate and nitrate, the steam sampler is used for ammonium, and the semi-continuous OC/EC analyzer is used for OC and EC measurements. Fig. 8 shows an interesting 5-day period during July 2001, which includes episodes of both positive and negative mass balance discrepancies. There are large variations in atmospheric acidity, and periods of high atmospheric acidity correlate well with periods of positive discrepancy.



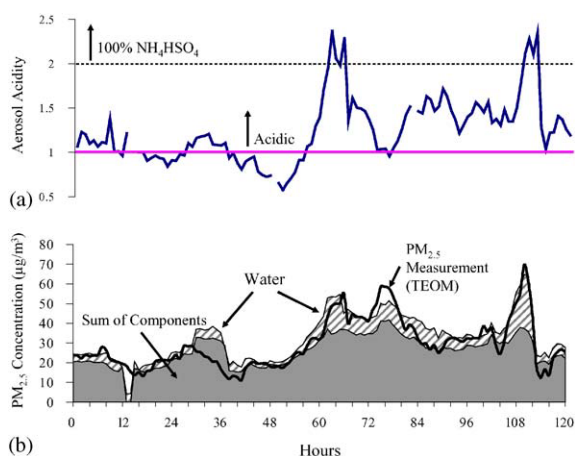


Fig. 8. Hourly atmospheric (a) acidity (Eq. (3)) and (b)  $PM_{2.5}$  mass balance for 20–25 July 2001. Data are from continuous instruments. Aerosol acidity  $> 1$  indicates acidic conditions, aerosol acidity  $> 2$  indicates 100%  $NH_4HSO_4$ . Water estimates are from DAASS measurements. The data illustrate that mass balance discrepancy is accounted for by measured aerosol water and generally corresponds to acidic conditions.

These data support the conclusion that the periods when the FRM mass exceeds the sum of the chemical components correspond to acidic conditions. This relationship appears most strongly during episodes of significant positive discrepancy, when the acidity ratio indicates the presence of  $NH_4HSO_4$ . It is also observed on a monthly basis; months with positive mass discrepancy tend to be acidic. However, acidity and the positive mass discrepancy are not always correlated, indicating that other factors besides acidity influence the mass balance. For example, a significant positive mass discrepancy was observed on the morning of 23 July ( $\sim 76$  h in Fig. 8) even though the atmosphere was not especially acidic. Most of these events appeared to be “triggered” by a preceding high acidity event, and are probably related to the history of the air mass and the hysteresis behavior of inorganic PM.

The second piece of evidence of the role of aerosol water in the mass balance uses measurements of ambient aerosol water content. The amount of water at 35% RH was estimated from the DAASS growth factor data ( $V_{wet}/V_{dry}$ ) by assuming that the aerosol water content is proportional to its water-soluble mass as follows from Raoult's law:

$$M_w(RH) = aM_s \frac{RH}{1 - RH} = A \frac{RH}{1 - RH}, \quad (4)$$

where  $M_w$  is the amount of water in the aerosol,  $M_s$  is the mass of water-soluble aerosol components,  $a$  and  $A$  are proportionality coefficients, and RH is the relative humidity expressed as a fraction of 1. The aerosol water content measured with the DAASS at both wet and dry

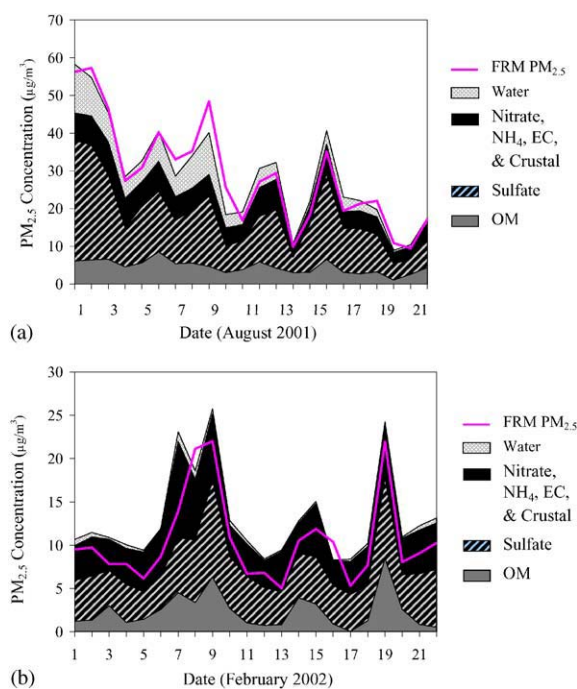


Fig. 9. Time series daily mass balances with estimated water content for (a) August 2001, and (b) February 2002. Water estimated from DAASS measurements extrapolated to a 35% RH to reflect FRM filter conditioning. OM is defined as  $1.8 \times OC$ .

RH points was fitted using Eq. (4) by plotting all DAASS growth factor data to find coefficient  $A$ . The amount of water at 35% RH was then estimated using Eq. (4) on an hourly basis.

It should be noted that the water content estimated by Eq. (4) is an upper limit estimate for the amount of water that could be retained on the filter after conditioning. The DAASS measures the water content of particles that are suspended in air. At low RH, such as that during filter weighing, any amount of water associated with the aerosol is in a state of a supersaturated salt solution. Contact with the filter surface or with an insoluble particle collected on the filter may initiate crystallization which would lead to a partial or a complete loss of water from the filter.

Water estimates from the DAASS measurements are included in daily and high time resolved mass balances shown in Figs. 8 and 9. The estimated aerosol water content fits well with periods of positive mass balance discrepancy on an hourly basis (Fig. 8). The fit is not perfect, for example the morning of 21 July ( $\sim 30$  h in Fig. 8) when there is a significant negative mass balance discrepancy; however, these periods correspond to times with relatively high OC concentrations, during which volatilization losses may be more significant than

aerosol water. Fig. 9a shows that there is a significant amount of estimated water present in August, which fills in the periods of mass discrepancy. This estimate of water, at an average of  $3.9 \mu\text{g m}^{-3}$  (16%), closes the mass balance within measurement uncertainty during the summer months. Fig. 9b shows that there is almost no water present in February, corresponding to the overall negative mass discrepancy observed during that month.

The data indicate a seasonal variation in the contribution of water to the mass balance discrepancy. The positive discrepancy due to water is the largest during acidic conditions in the summer, and relatively small during the neutral conditions found in the winter. The lower water content of the winter aerosol is thermodynamically expected because atmospheric conditions tend to be more neutral in Pittsburgh during the winter months.

### 3.2.3. Sampling losses of semi-volatile species

Loss of semi-volatile aerosol species due to evaporation from FRM filters during sampling and post-sampling filter handling can cause a negative mass discrepancy. The two primary species of issue are nitrate and organics. Volatilization of organic material is a concern throughout the year, whereas volatilization of nitrate tends to be more significant in the winter months, when nitrate constitutes a greater proportion of  $\text{PM}_{2.5}$  mass.

The volatilization loss of nitrates was estimated using data from the CMU inorganic sampler. The sampler consists of a denuder followed by a filter pack containing a Teflon filter followed by a nylon filter. The nylon filter captures the nitrate that volatilizes off the Teflon filter during sampling. Since the filter pack is downstream of a denuder, the nitrate volatilization estimate represents an upper bound for losses during sampling. However, this estimate for nitrate volatilization does not account for nitrate losses that occur after sampling, such as losses during filter handling and conditioning, which are likely to be significant.

During the summer months, 80–90% of the particulate nitrate present evaporated from the Teflon filter used in the CMU inorganic sampler. This loss represents approximately  $0.5 \mu\text{g m}^{-3}$  or 2% of FRM mass and therefore does not significantly impact the mass balance discrepancy. During the winter months, 20–30% of particulate nitrate volatilized from the Teflon filter used in the CMU inorganic sampler. Because nitrates contribute significantly to  $\text{PM}_{2.5}$  mass in the winter months in Pittsburgh, this loss, approximately  $1.8 \mu\text{g m}^{-3}$  or 15% of FRM mass, is a significant contributor to the negative discrepancy observed in the winter.

Evaporation of organic material tended to occur consistently throughout the year. Subramanian et al.

(2004) estimated that on average 19% of the OC volatilized from Teflon filters during sampling at the PAQS site. Again, this volatilization estimate represents only that which occurs during sampling, not accounting for additional losses expected during filter handling and conditioning. Over the 7-month period evaluated, this volatilization artifact amounts to  $0.7 \mu\text{g m}^{-3}$ , or 4% of FRM  $\text{PM}_{2.5}$  mass, and remained relatively constant throughout the year. The largest OC volatilization artifact was observed in Fall 2001, where the artifact was approximately  $1 \mu\text{g m}^{-3}$ , or just over 6% of the FRM mass.

These results illustrate seasonal variation in the volatilization losses. In the summer months, OC losses are more important than nitrate losses, with the total volatilization losses amounting to 5% of FRM mass. In the winter months, nitrate losses rise to 15% of FRM mass which in combination with the OC losses (3% of FRM mass) representative a significant negative discrepancy. Therefore, there is a strong seasonal variation to the relative importance of the volatilization losses.

### 3.2.4. Uncertainty from estimation of the organic PM concentrations from the OC measurements

Uncertainty in the OC multiplier used to estimate organic mass alone cannot explain the observed mass balance discrepancy. For example, during the episodes of significant positive discrepancy in August 2001, the OC multiplication factor required to close the mass balance is 3.5 for the 31 July–4 August period, and 4.4 for the 7–11 August period. Accounting for expected losses of nitrate and organics due to volatilization, increases the OC multiplication factor required to close the mass balance during those periods to 4.1 and 5.2, respectively. These values are significantly above the range considered appropriate for urban aerosol (Turpin and Lim, 2001); therefore, the OC multiplier value is not the cause the periods of significant positive mass balance discrepancy. (In the winter the OC multiplication factor is within the upper range of acceptable values, after accounting for volatilization.)

### 3.2.5. Uncertainty from estimation of crustal components

The sum of the oxides method is the most common method used to estimate the crustal component of  $\text{PM}_{2.5}$  mass (Andrews et al., 2000). The actual crustal contribution can deviate from this estimate due to underlying assumptions for the estimate or analytical uncertainty; for example, all the metals may not be in the form of oxides. Andrews et al. (2000) concluded that the estimate from the sum of component method represents the lower bound of the crustal estimate, underestimating the crustal component by as much as 50%.

A second issue is that we only have data to estimate the daily crustal contribution for July 2001 and January 2002. As previously discussed, for the other periods we assumed a crustal contribution of  $1 \mu\text{g m}^{-3}$ , the average value for the periods for which we have complete set of trace element data. Using an assumed, constant value does not cause the mass balance discrepancy for the periods for which we do not have crustal data. First, the day-to-day variations in the crustal  $\text{PM}_{2.5}$  were relatively small; the standard deviation of  $\text{PM}_{2.5}$  crustal for the 54 days for which we have a complete set of data is  $0.4 \mu\text{g m}^{-3}$ , less than the uncertainty assigned to the crustal component. Second, even the largest measured crustal contribution,  $2.1 \mu\text{g m}^{-3}$ , is not nearly large enough to close the mass balance for periods such as that shown in Fig. 6. Finally, it is unlikely that using an average value for crustal would cause the persistent negative mass balance discrepancy observed in February 2002 (see Fig. 6).

There are clearly large uncertainties regarding the potential contribution of the crustal component; however, the crustal material in Pittsburgh is a relatively small fraction of overall  $\text{PM}_{2.5}$  mass. This large uncertainty has been incorporated into the uncertainty analysis (Table 1), and the uncertainty in the crustal estimate alone would not be sufficient to close the observed mass balance discrepancy on days with significant positive discrepancies.

### 3.3. Estimation of bound water by aerosol thermodynamic models

Thermodynamic aerosol models are available that estimate ambient aerosol water using aerosol composition data, ambient temperature and RH. Since aerosol composition data are often available modeling aerosol water could provide a way to estimate aerosol water effects in other areas. Evaluating the suitability of these models to estimate the aerosol bound water is important because many monitoring networks do not have the sophisticated instrumentation like the DAASS.

We used the GFEMN model (Ansari and Pandis, 1999) with PAQS speciation data to compare modeled aerosol water results to those measured by the DAASS (Fig. 10). The GFEMN estimates compare well with the DAASS measured water. Overall for the summer, the DAASS measured an average of  $3.8 \mu\text{g m}^{-3}$ , while the GFEMN results were 13% lower at  $3.3 \mu\text{g m}^{-3}$  of water. In January, modeled results are a little greater than those measured, averaging  $1.3 \mu\text{g m}^{-3}$  while measured results average  $0.8 \mu\text{g m}^{-3}$ . Based on these results, the GFEMN model provides reasonable estimates of bound aerosol water. Using this model in conjunction with measured volatilization effects allows further examination of the mass discrepancy effect in other areas.

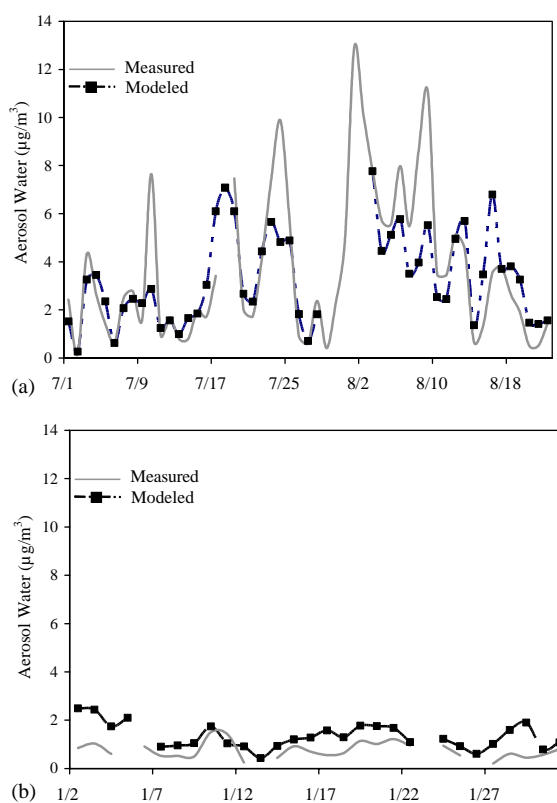


Fig. 10. Comparison of measured and predicted daily average aerosol water for (a) summer 2001 and (b) January 2002. Measured water results are based on DAASS measurements extrapolated to 35% RH, and the predicted results are from the GFEMN model using aerosol composition data. Results shown are at 35% RH.

### 3.4. Closing the mass balance

Our analysis suggests that the FRM mass can be estimated by summing measurements of individual chemical components, adding estimated aerosol water and subtracting volatilization effects. Using this approach we can reconstruct the FRM mass based on measurements of the individual  $\text{PM}_{2.5}$  components in the atmosphere. Results for the August episodes are summarized in Fig. 11a. Including water brings the mass balance within measurement uncertainty for the August episodes; eliminating the 19% positive discrepancy ( $8.7 \mu\text{g m}^{-3}$ ) for the 31 July–4 August period and reducing the 32% positive discrepancy ( $10.5 \mu\text{g m}^{-3}$ ) to an 8% positive discrepancy ( $2.6 \mu\text{g m}^{-3}$ ) for the 7–11 August period. Water accounted for  $8.3 \mu\text{g m}^{-3}$  or 18% of the FRM mass for the 31 July–4 August period, and  $6.4 \mu\text{g m}^{-3}$  or 20% of the FRM mass for the 7–11 August period. Volatilization losses had substantially less impact on the mass balance than aerosol water

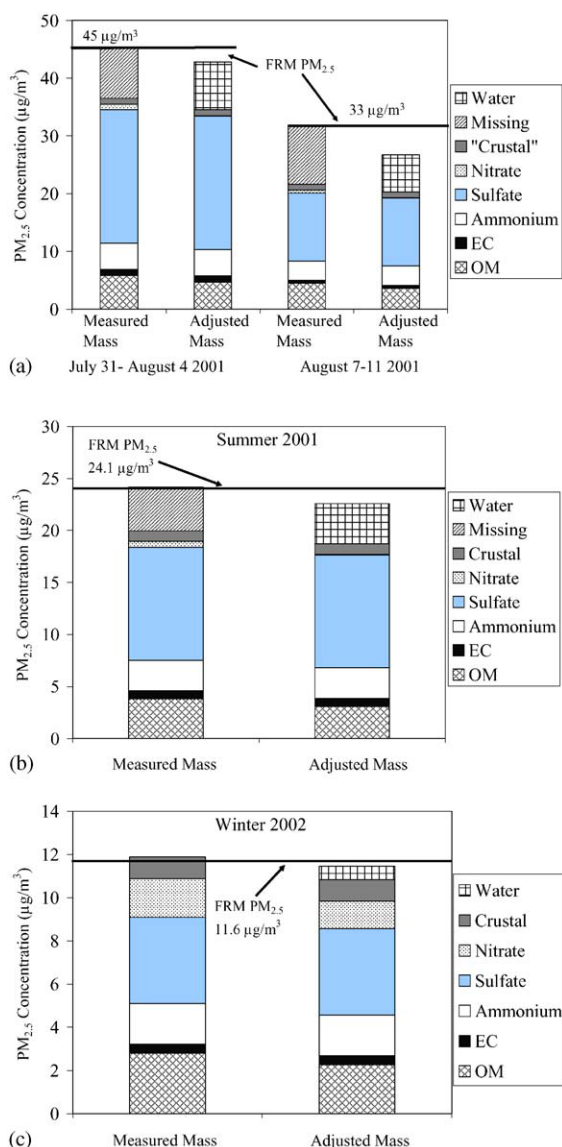


Fig. 11. Mass balances adjusted for water and volatilization. In the column labeled "adjusted mass", estimated water is added to sum of the chemical components, and measured nitrate and OM are corrected for volatilization losses. (a) Average data for two episodes in the summer of 2001. (b) Average daily mass balance for July and August 2001. (c) Average daily mass balance for January and February 2002. OM is defined as  $1.8 \times \text{OC}$ .

during these periods, impacting  $<2\%$  of the FRM-measured mass for these periods.

Closure of the mass balance for the summer averaged data is shown in Fig. 11b. The 17% positive discrepancy ( $4.5 \mu\text{g}/\text{m}^3$ ) disappears and the mass balance is within measurement uncertainty when adjusted for water and

volatilization. Water accounts for  $3.9 \mu\text{g}/\text{m}^3$  or 16% of the FRM mass, while volatilization losses account for  $1.3 \mu\text{g}/\text{m}^3$  or 5% of total mass.

Fig. 11c shows similar success in accounting for the mass balance in the winter months. During the winter the average mass balance between the FRM and the sum of the chemical components was closed. In the winter, the loss of mass due to volatilization is offset by the gain of mass due to water; on average, volatilization losses were  $1 \mu\text{g}/\text{m}^3$  (8.6%) and water contributed  $0.9 \mu\text{g}/\text{m}^3$  (7.8%) to the FRM mass.

Many studies that reconstruct an FRM mass balance do not observe the positive artifact in the summer months, and instead find a consistent negative artifact (e.g., Tanner and Parkhurst, 2000; Modey et al., 2001; Pang et al., 2002a, b). The presence of a significant negative discrepancy is dependent on aerosol composition. Studies conducted in the western US, where aerosol composition is dominated by nitrates and organics, suggest that FRM  $PM_{2.5}$  measurements may be up to 30% less than the reconstructed aerosol mass, with the losses resulting from volatilization of nitrates and organic species (Hering and Cass, 1999; Pang et al., 2002a, b). As previously discussed, we also observe significant volatilization losses of these species. However, the aerosol in Pittsburgh is dominated by sulfates, and in the summer it is often subjected to acidic atmospheric conditions, inducing hygroscopic behavior at low RH. These conditions result in a significant positive discrepancy between the FRM and the sum of the chemical components caused by water retained on the FRM filter after conditioning. This positive artifact due to water may be more of a regional phenomenon, more prevalent in the eastern US which is characterized by high sulfate levels and acidic conditions, than the western US. Indeed, data from the 1995 SEAVS experiment in Tennessee and from IMPROVE data taken in the southeast US show that up to 42% of  $PM_{2.5}$  mass was not accounted for by the measured chemical components, and that aerosol water was suspected to contribute significantly to that discrepancy (Andrews et al., 2000; Jansen et al., 2002).

#### 4. Summary and conclusions

FRM measurements of  $PM_{2.5}$  mass are used for determining compliance with the recently revised National Ambient Air Quality Standards. In this context, it is important to understand what the FRM is measuring and how this relates to atmospheric  $PM_{2.5}$  concentrations. Episodes of high  $PM_{2.5}$  mass in August 2001 left around 19–32% of the mass measured by the FRM unaccounted for by summing the mass of the chemical components. Overall for the summer 2001, approximately 17% of the mass measured by the FRM

was not accounted for by the sum of the mass of the chemical components. This positive mass discrepancy observed is greater than the estimated measurement uncertainty. The winter average FRM mass was  $11.6 \mu\text{g m}^{-3}$ , roughly equal to the mass of the sum of the aerosol chemical components.

Bound water remaining on the FRM filter can explain most of the observed positive discrepancy in the summer. Water is present when the inorganic PM component is dominated by ammonium bisulfate, which does not effloresce at the RH of filter conditioning. The presence of bound water occurs simultaneously with losses of nitrates and organics from sampling volatilization. Accounting for these positive and negative artifacts closes the mass balance.

Both water and volatilization effects occur simultaneously throughout the year in western Pennsylvania, with relative importance of each effect varying seasonally. In the summer months, contributions of water dominate, resulting in an overall positive discrepancy. In the winter, volatilization effects become more pronounced, resulting in a negative or net balance. In the summer months, the FRM measured on average  $4.5 \mu\text{g m}^{-3}$  (17%) more mass than the sum of the chemical components. Water accounted for  $3.9 \mu\text{g m}^{-3}$  (16%) of the FRM mass, while volatilization losses are estimated to reduce the FRM mass by  $1.3 \mu\text{g m}^{-3}$  (5%). Accounting for these artifacts closes the mass balance between the FRM and the sum of the chemical components, and the large contribution of water during the summer appears related to acidic conditions that favor retention of water at low relative humidity. In the winter months there is on average no mass balance discrepancy; with the contribution of water ( $0.9 \mu\text{g m}^{-3}$ ) offsetting volatilization losses ( $1 \mu\text{g m}^{-3}$ ). Although the mass balance closed on average in the winter, the negative discrepancy occurred more frequently than the positive discrepancy. The seasonal variation in the mass balance discrepancy is directly attributable to changes in aerosol composition. The application of aerosol thermodynamic models, such as GFEMN, provides a method to estimate bound aerosol water from chemical speciation data.

#### Acknowledgements

This research was conducted as part of the Pittsburgh Air Quality Study which was supported by US Environmental Protection Agency under contract R82806101 and the US Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This paper has not been subject to EPA's peer and policy review, and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

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