

# A side-by-side comparison of filter-based PM<sub>2.5</sub> measurements at a suburban site: A closure study

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## Abstract

Assessing the effects of air quality on public health and the environment requires reliable measurement of PM<sub>2.5</sub> mass and its chemical components. This study seeks to evaluate PM<sub>2.5</sub> measurements that are part of a newly established national network by comparing them with more versatile sampling systems. Experiments were carried out during 2002 at a suburban site in Maryland, United States, where two samplers from the US Environmental Protection Agency (US EPA) Speciation Trends Network: Met One Speciation Air Sampling System—STN<sub>S</sub> and Thermo Scientific Reference Ambient Air Sampler—STN<sub>R</sub>, two Desert Research Institute Sequential Filter Samplers—DRI<sub>F</sub>, and a continuous TEOM monitor (Thermo Scientific Tapered Element Oscillating Microbalance, 1400a) sampled air in parallel. These monitors differ not only in sampling configuration but also in protocol-specific laboratory analysis procedures. Measurements of PM<sub>2.5</sub> mass and major contributing species (i.e., sulfate, ammonium, organic carbon, and total carbon) were well correlated among the different methods with *r*-values >0.8. Despite the good correlations, daily concentrations of PM<sub>2.5</sub> mass and major contributing species were significantly different at the 95% confidence level from 5% to 100% of the time. Larger values of PM<sub>2.5</sub> mass and individual species were generally reported from STN<sub>R</sub> and STN<sub>S</sub>. These differences can only be partially accounted for by known random errors. Variations in flow design, face velocity, and sampling artifacts possibly influenced the measurement of PM<sub>2.5</sub> speciation and mass closure. Statistical tests indicate that the current uncertainty estimates used in the STN and DRI network may underestimate the actual uncertainty.

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**Keywords:** Aerosol sampling; Chemical speciation; PM<sub>2.5</sub>; Comparison study; Filter sampling

## 1. Introduction

Elevated levels of PM<sub>2.5</sub> mass (the mass concentration of fine aerosol with aerodynamic diameter

less than 2.5 μm, hereafter referred to as PM<sub>2.5</sub>) have been associated with cardiovascular and respiratory problems and even increased mortality rates (Laden et al., 2000; Schwartz and Neas, 2000; Peters et al., 2001a). The 1997 National Ambient Air Quality Standards (NAAQS) address the long-term (annual average concentration of 15 μg m<sup>-3</sup>)

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and short-term (24-h average concentration of  $65\ \mu\text{g m}^{-3}$ ) maximum allowable  $\text{PM}_{2.5}$ . US EPA recently lowered the short-term NAAQS to  $35\ \mu\text{g m}^{-3}$  (effective 17/12/06) to reflect new scientific studies of the  $\text{PM}_{2.5}$  health effects (Federal Register, 2006; US EPA, 2006). NAAQS calls for the use of a Federal Reference Method, FRM (Code of Federal Regulations (CFR), 1997) for the measurement of filter-based gravimetric  $\text{PM}_{2.5}$  mass to determine compliance. However, other sampling and analytical protocols have been used extensively in air quality monitoring projects, such as the Speciation Trends Network (STN, US EPA, 1999), the Interagency Monitoring and Protective Visual Environment network (IMPROVE, Malm et al., 1994, 2002, 2004, 2005; Ames and Malm, 2001) and the California Regional  $\text{PM}_{10}/\text{PM}_{2.5}$  air quality study (Chow et al., 2006a), to assess human exposure, health risks, visibility degradation and climate change related to  $\text{PM}_{2.5}$ .

Comparability among the FRM and more-versatile PM samplers must be established for studies using those samplers to describe  $\text{PM}_{2.5}$  spatial and temporal trends. A reasonable estimate of measurement uncertainties is also critical for  $\text{PM}_{2.5}$  source apportionment tasks based on chemical mass balance and/or multivariate receptor models (Hopke, 1984; Watson et al., 1984; Kim and Hopke, 2005; Kim et al., 2005; Ogulei et al., 2005; Chen et al., 2007). Equivalence of  $\text{PM}_{2.5}$  mass determined with different protocols is currently under evaluation (Peters et al., 2001b; Watson and Chow, 2002; Solomon et al., 2003; Chow et al., 2005a). An FRM for  $\text{PM}_{2.5}$  speciation has not yet been established by the US EPA.

The 2002 intensive sampling periods at Fort Meade, Maryland allowed for an evaluation of STN speciation samplers and filter analyses under typical and elevated  $\text{PM}_{2.5}$  events. Fort Meade, Maryland (FME:  $39.10^\circ\text{N}$ ,  $76.74^\circ\text{W}$ ), a suburban site located in the Baltimore–Washington urban corridor, approximately 3 km east of the Baltimore–Washington Parkway (I-295) and 10 km east of Interstate 95, was the anchor site for the Maryland Aerosol Characterization (MARCH-Atlantic) study (Chen, 2002; Chen et al., 2002) and part of the nationwide STN. It also served as one of the satellite sites for the Baltimore Supersite experiment during 2001–2003 (Lake et al., 2003; Harrison et al., 2004; Lee et al., 2005a; Ogulei et al., 2005; Park et al., 2005a, b; Ondov et al., 2006). Previous studies indicate that FME observations often reflect regio-

nal haze episodes in summer and local accumulation under stagnant conditions in winter. Major sources include regional and local sulfate, wood smoke, industrial and mobile emissions as well as secondary nitrate (Chen, 2002; Chen et al., 2001, 2002, 2003). Chen et al. (2002) report an average  $\text{PM}_{2.5}$  concentration of  $13.0 \pm 7.7\ \mu\text{g m}^{-3}$  across eight sampling months between July 1999 and 2001.

During January and July 2002,  $\text{PM}_{2.5}$  speciation monitors from two different protocols (STN and Desert Research Institute—DRI) were installed at FME to concurrently measure atmospheric aerosol on a 24-h basis. Two sequential filter samplers (SFS, Desert Research Institute, Reno, NV) from DRI were deployed in both January and July, while a reference ambient air sampler (RAAS  $\text{PM}_{2.5}$ , Thermo Scientific, Waltham, MA) and a Met One speciation air sampling system (SASS, Met One Instruments Inc., Grants Pass, OR) represented the STN operation in January and July, respectively. The change of STN sampling systems (from January to July) was made with the understanding that both samplers had been equally approved by EPA for the STN application (US EPA, 1999). However, in this study, their performances are not the same with respect to the DRI sampler. The SFS samples were analyzed by DRI and the RAAS and SASS samples were analyzed at the Research Triangle Institute (RTI, Research Triangle Park, NC) using methods described in Chow et al. (1996) and US EPA (1999). We will refer to the SFS samplers as  $\text{DRI}_F$  and the RAAS and SASS samplers as  $\text{STN}_R$  and  $\text{STN}_S$  ( $\text{STN}_{RS}$  denotes both instruments) hereafter. Components quantified by both DRI and RTI include gravimetric  $\text{PM}_{2.5}$  mass, 35 trace elements, elemental carbon (EC), organic carbon (OC), total carbon (TC), and water soluble ions such as sulfate, nitrate and ammonium. DRI and RTI often used different techniques and instruments for the analyses. Continuous measurements of  $\text{PM}_{2.5}$  mass were made in July with a tapered element oscillating microbalance (TEOM 1400a, Thermo Scientific, Waltham, MA).

Field performance of the  $\text{STN}_R$  and performance of the  $\text{STN}_{RS}$  size-selective inlet were assessed during the early stage of  $\text{STN}_{RS}$  development (Peters et al., 2001b, c), but up-to-date evaluations of the  $\text{STN}_{RS}$  speciation data under real-world operation are limited. This paper compares the  $\text{STN}_{RS}$  data from FME with collocated DRI measurements and investigates the  $\text{PM}_{2.5}$  chemical composition and mass closure within the context of uncertainty analysis. Approaches and conclusions

herein can be tested in other studies facilitating a weight of evidence approach (e.g., Burton et al., 2002; Weed, 2005) to improve the design of ambient PM<sub>2.5</sub> networks. The objective and results of this study are coordinated with others in the region including Lee et al. (2005a, b), Flanagan et al. (2006) and the EPA-sponsored Eastern Supersites program (Solomon et al., 2003; Rees et al., 2004; Ondov et al., 2006).

## 2. Experiment

STN<sub>RS</sub> and DRI<sub>F</sub> differ in filter types used to collect aerosol as well as flow rates required by the specific cyclone to maintain a stable cut-point at 2.5 μm. Fig. 1 illustrates all the sampler configurations and Table 1 summarizes the specifications of the samplers along with analytical methods for determining all species reported. STN<sub>R</sub> samplers are considered FRM equivalent (Solomon et al., 2003) and have been compared with other samplers (Peters et al., 2001b, c; Solomon et al., 2003), while DRI<sub>F</sub> is designated as FRM for PM<sub>10</sub> (aerosol with aerodynamic diameter ≤ 10 μm) when equipped with a PM<sub>10</sub> inlet (Code of Federal Regulations (CFR), 1997) and has been successfully deployed in many air quality studies for sampling PM<sub>10</sub>/PM<sub>2.5</sub> since 1988 (Chow et al., 1992, 1996, 2006a; Chen, 2002; Chen et al., 2002; Watson and Chow, 2002).

STN<sub>RS</sub> samplers use a critical orifice to set the flow rate and monitor it with a mass flow sensor. STN<sub>RS</sub> record ambient temperature and pressure and they are used to convert the mass flow to volumetric flow. The average volumetric flow rate and total volume sampled are recorded for every 24-h sampling period (Thermo Anderson, 2001; US EPA, 2001). The STN<sub>R</sub> flow was calibrated with a flow audit device (BGI deltaCal) and the STN<sub>S</sub> flow was calibrated with a bubble flow meter (Sensidyne/Gilian Gilibrator 2). The DRI<sub>F</sub> also uses a critical orifice to maintain constant flow, but the flow was measured and adjusted only once every third day using a rotameter (calibrated against a NIST-traceable Roots meter). The flow rate is recorded before and after each 3-day sampling period for the DRI<sub>F</sub>, and it can drop by 4% due to buildup of water and particles on the filter. DRI uses the average flow rate (from the initial and final flow) to calculate the total volume sampled and the resultant mass concentration. STN<sub>RS</sub> record the total volume sampled, which is calculated from the mass flow sensor, temperature and pressure readings.

The sample flow rates for PM<sub>2.5</sub> mass were 20, 16.7, and 6.7 L min<sup>-1</sup> in DRI<sub>F</sub>, STN<sub>R</sub>, and STN<sub>S</sub>, respectively. Since all the samplers used 47-mm filters, DRI<sub>F</sub> imposed an approximately 20% larger face velocity than the STN<sub>R</sub> and a face velocity that was three times larger than the STN<sub>S</sub> around the filter. The STN<sub>R</sub> sample flow rate was 7.3 L min<sup>-1</sup> for ions and carbon (similar to the STN<sub>S</sub>) and the DRI<sub>F</sub> imposed a 64% larger face velocity than the STN<sub>R</sub>.

Cyclones used by STN<sub>R</sub> and STN<sub>S</sub> (Table 1) exhibit different size-selection curves at their specified flow, but Peters et al. (2001c) found that only sites dominated by crustal material had significantly different PM<sub>2.5</sub> mass collected by the two samplers. Chen (2002) showed a minor crustal material contribution at FME, ~3% of PM<sub>2.5</sub> mass on average, and therefore strong biases resulting from imperfect size cut are not expected in this study. There may also be diffusion losses of ultrafine particles between the sampler inlet and filter, which vary with the different flow rates used by DRI<sub>F</sub>, STN<sub>R</sub> and STN<sub>S</sub>. Ultrafine particles (<0.1 μm in diameter) typically contribute little to PM<sub>2.5</sub> mass in this environment (e.g., Tolocka et al., 2005; Ondov et al., 2006) and strong biases resulting from diffusion losses are unlikely.

The DRI<sub>F</sub> used a front quartz–fiber filter with a sodium–chloride-impregnated cellulose backup filter to collect nitrate. The backup filter captured nitrate volatilized from the front filter (Zhang and McMurry, 1992). These filters were located behind a bundle of aluminum-oxide-coated denuders to remove gaseous nitric acid. Specifications of the denuders are described in Chow et al. (1993a). The STN<sub>R</sub> and STN<sub>S</sub> collected nitrate particles behind a magnesium-oxide denuder on a single nylon filter (Fig. 1). Specifications of the denuders are described in Research Triangle Institute (2000). Frank (2006) found that denuded nylon filters captured more nitrate than undenuded Teflon filters. The different denuders and filter types used by the STN<sub>RS</sub> and DRI<sub>F</sub> in this study could affect the nitrate collection efficiency as suggested by Solomon et al. (2003) and Frank (2006).

Quartz–fiber filters were used in all the samplers to collect carbonaceous material. DRI<sub>F</sub> included backup filters (i.e., the sequential quartz–quartz filter setup) to assess sampling artifacts from volatile organic compounds (McDow and Huntzicker, 1990; Turpin et al., 1994; Chow et al., 1996, 2001). Carbon concentrations determined from the DRI<sub>F</sub>

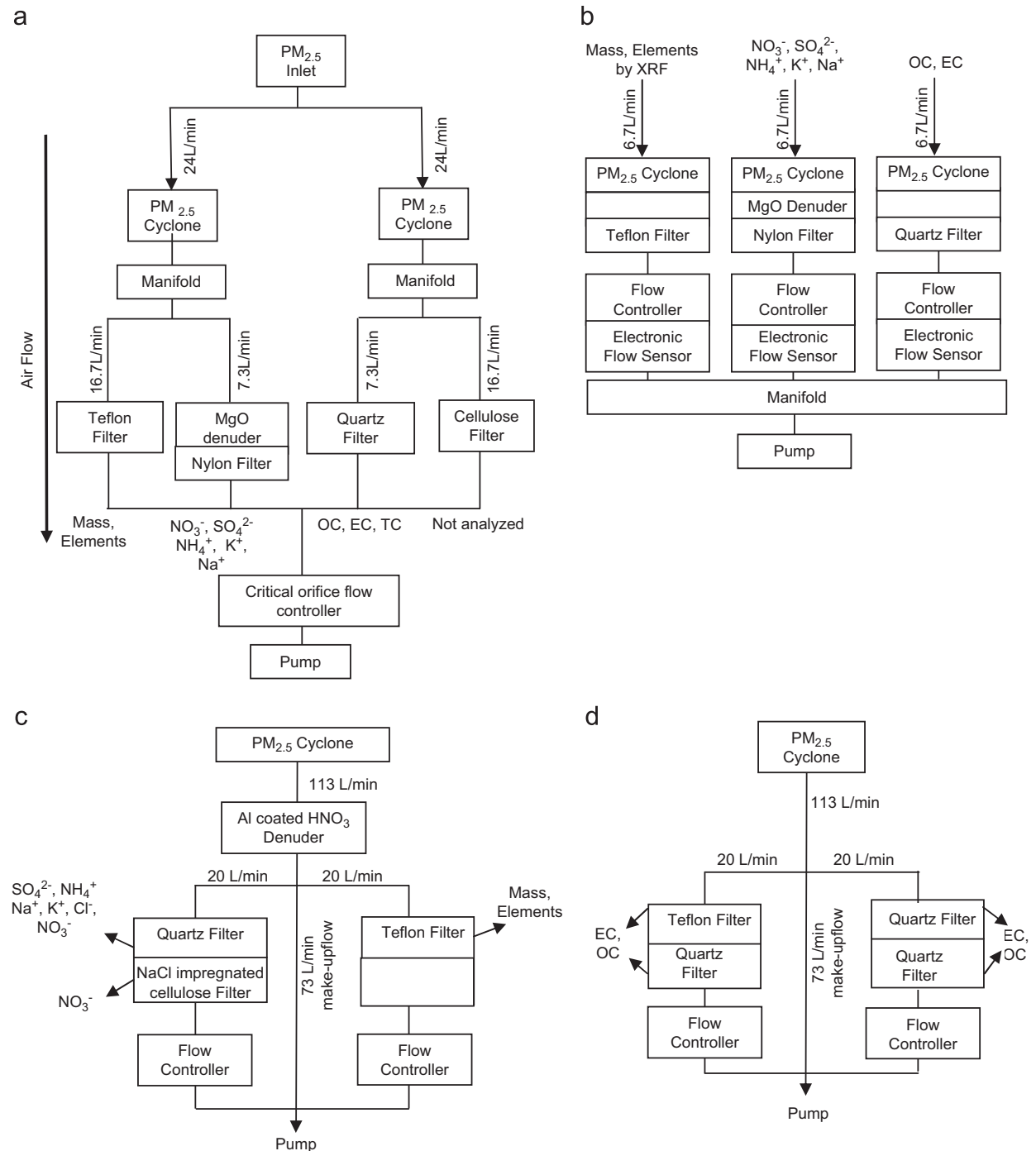


Fig. 1. Sampler configuration for (a) STN<sub>R</sub> (Anderson RAAS) (b) STN<sub>S</sub> (Met-One SASS) (c) DRI<sub>F</sub> for elements and ions (d) DRI<sub>F</sub> for carbonaceous material.

front quartz–fiber filters were used to compare with the STN<sub>RS</sub> data based on single quartz–fiber filters. For carbon analysis, RTI adopted the STN-thermal optical transmission (STN-TOT) method (Peterson

and Richards, 2002; OC/EC Laboratory, 2003), while DRI used the interagency monitoring of protected visual environments-thermal optical reflectance (IMPROVE-TOR) method (Chow et al.,

Table 1  
Analytical methods for species collected by DRI<sub>F</sub> (analyzed by DRI) and STN<sub>RS</sub> (analyzed by RTI) and instrument specifications

	DRI analysis <sup>a</sup>	RTI analysis <sup>b</sup>		
		DRI <sub>F</sub>	STN <sub>R</sub>	STN <sub>S</sub>
PM <sub>2.5</sub>	Mass gravimetry		Mass gravimetry	
Trace elements	X-ray fluorescence		X-ray fluorescence	
Sulfate	Ion chromatography		Ion chromatography	
Nitrate	Ion chromatography		Ion chromatography	
Ammonium	Automated colorimetry		Ion chromatography	
Chloride	Ion chromatography		Chlorine is measured with XRF	
Sodium ion	Atomic absorption		Ion chromatography	
Potassium ion	Atomic absorption		Ion chromatography	
EC	Thermal optical reflectance (IMPROVE-TOR)		Thermal optical transmittance (STN-TOT)	
OC	Thermal optical reflectance (IMPROVE-TOR)		Thermal optical transmittance (STN-TOT)	
Instrument specifications				
		DRI <sub>F</sub>	STN <sub>R</sub>	STN <sub>S</sub>
Flow (L min <sup>-1</sup> )		20 ± 0.8	16.7 ± 0.3 (mass and elements) 7.3 ± 0.1 (ions and carbon)	6.7 ± 0.1
Cyclone	Bendex 240		AN 3.68	SC 2.141
Nitric acid denuder coating	Aluminum oxide		Magnesium oxide	Magnesium oxide
Sample inlet height (m)	10		15	15
Filter diameter (mm)	47		47	47

Flow rate uncertainties are  $\pm 1 - \sigma$ .

<sup>a</sup>DRI operating procedure (1990); Chow et al. (1993c, 2001).

<sup>b</sup>US EPA (2001); Thermo Anderson (2001).

1993b). The IMPROVE-TOR and STN-TOT differ in temperature steps used to extract OC and EC and in optical charring corrections. They usually yield equivalent TC but different OC and EC concentrations (Chow et al., 2001, 2004, 2005a; Schmid et al., 2001; Subramanian et al., 2004). The IMPROVE-TOR method generally assigns less OC and more EC to a filter sample than the STN-TOT method.

DRI quantified water-soluble potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>) with atomic absorption spectroscopy (AAS) and RTI quantified the species with ion chromatography (IC). AAS has a lower detection limit (Chow et al., 1993c; Technology Transfer Network Air Quality System, 2006). There were also differences in blank collection. A field blank was collected every third day for the DRI<sub>F</sub> sampler and once every 2 weeks for the STN<sub>S</sub> sampler. Only one field blank was collected for the STN<sub>R</sub> sampler. DRI corrected for field blanks as part of their analysis (Watson et al., 1989a, b), but RTI did not. To correct STN<sub>RS</sub> samples for field blanks, we averaged all STN<sub>RS</sub> blank values obtained during the sampling period, converted them from mass per filter to mass m<sup>-3</sup> using the volume sampled by the

instrument, and subtracted the blanks from the mass measurement.

Sample recovery was scheduled for different time periods. The DRI<sub>F</sub> filters were collected from the site every 3 days, so that used filters remained in the sampler for up to 2.5 days (an average of 1.5 days). The STN<sub>R</sub> filters were collected every day, immediately after the sampling finished, so that used filters remained in the sampler for less than 30 min. The STN<sub>S</sub> filters were collected every other day, so that used filters remained in the sampler for about 12 h. Chen (2002) performed an audit experiment in summer 2001 at FME with the DRI<sub>F</sub> samplers, to determine how filters left in the sampler may be affected by volatile losses and/or passive collection. He found that OC and TC mass (measured on the front quartz-fiber filters) decreased (by 38% and 29%, respectively) during a 2.5-day period after sampling. Total PM<sub>2.5</sub> mass (measured on Teflon filters) and sulfate mass (measured on quartz-fiber filters) varied less than their respective uncertainties.

A TEOM measures near real-time continuous PM<sub>2.5</sub> mass. The TEOM at FME drew ambient air in at 3 L min<sup>-1</sup> through a PM<sub>2.5</sub> cyclone inlet.

A constant volumetric flow was achieved using a mass flow controller corrected for ambient temperature and pressure. The air stream was heated to 50 °C to maintain a low relative humidity. This heating likely increased volatilization of nitrate and semi-volatile organic compounds. The TEOM measurements were adjusted with a scaling factor of 1.03 and an offset of +3.0  $\mu\text{g m}^{-3}$  to account for loss of semi-volatile material. Although this empirical adjustment allows the TEOM to be a federal equivalent method (FEM) for  $\text{PM}_{10}$  measurements (Patashnick and Rupprecht, 1991), the effects on  $\text{PM}_{2.5}$  measurements in different environments has not been fully evaluated. The mean mass concentration was recorded every 30 min, every hour, and every 8 h. All 1-h measurements made in a day were averaged to compare with the  $\text{DRI}_F$  and  $\text{STN}_S$  data.

### 3. Results and discussion

#### 3.1. Uncertainty analysis

Uncertainties associated with flow control and sample analysis need to be accounted for to determine the uncertainty in total  $\text{PM}_{2.5}$  and each reported species concentration. For  $\text{STN}_{RS}$ , the species concentration (with units of  $\text{mass m}^{-3}$  at ambient temperature and pressure) is calculated using the equation below:

$$\begin{aligned} \text{Species concentration} &= m(t \times \text{mass flow} \\ &\times \text{MM}^{-1} \times R \times T \times P^{-1})^{-1}. \end{aligned} \quad (1)$$

Here  $m$  is the mass of a given species on the filter,  $t$  is the time over which sampling occurred, mass flow has units of  $\text{mass time}^{-1}$ ,  $\text{MM}$  is the molar mass of the air sampled,  $R$  is the gas constant (0.08314  $\text{L atm K}^{-1} \text{mol}^{-1}$ ),  $T$  is ambient temperature (K) and  $P$  is the ambient pressure (atm). Uncertainties in the calculated concentration reflect uncertainties in the laboratory analysis, the mass flow sensor reading, the temperature reading and the pressure reading. Uncertainties associated with the integration time appear to be less than 1% and are therefore not included in the error analysis. US EPA (2001) states that  $\text{STN}_{RS}$  temperature readings must be within  $\pm 4 \text{ K}$  of the actual temperature and pressure readings must be within  $\pm 0.013 \text{ atm}$  of the actual pressure. These ranges represent part of the uncertainty associated with the measurements. The precision associated with a commercial mass flow

sensor for the maximum allowable mass flow, i.e.,  $\pm 2\%$  at the  $1-\sigma$  level, is used as an estimate of the mass flow sensor uncertainty (Table 1). Flanagan et al. (2006) report the percentage difference in laboratory replicates of  $\text{PM}_{2.5}$  and speciated masses. We adopt their values of laboratory uncertainty to calculate the overall uncertainty. The resultant  $\pm 2-\sigma$  uncertainty,  $u$ , (i.e., the 95% confidence level) associated with  $\text{PM}_{2.5}$  mass, sulfate, ammonium, OC or elemental concentration is given by

$$\begin{aligned} u &= \text{mass concentration} \\ &\times [(\delta A/A)^2 + (\delta \text{mf}/\text{mf})^2 + (\delta T/T)^2 + (\delta P/P)^2]^{1/2}. \end{aligned} \quad (2)$$

Here  $\delta A/A$  represents fractional uncertainty associated with the laboratory determination of the mass of a species (uncertainties from Flanagan et al., 2006 were used),  $\delta \text{mf}/\text{mf}$  represents the fractional uncertainty associated with the mass flow meter measurements, and  $\delta T/T$  and  $\delta P/P$  represent the fractional uncertainty associated with temperature and pressure measurements, respectively. Eq. (2) represents idealized conditions, neglecting the sample handling and variability among different instruments and operators. RTI did not report uncertainties for samples analyzed in 2002, however they did report uncertainties for samples measured in the US in 2005 to the EPA's Air Quality System database (AQS, Technology Transfer Network Air Quality System, 2006). The uncertainties reported by RTI include laboratory analysis ( $\pm 1-\sigma$  uncertainty) and a 5% uncertainty associated with flow control and shipment of the samples (RTI, 2004). Using their uncertainties associated with concentrations that were similar to (within  $\pm 1\%$  of) the FME samples, and multiplying them by two to obtain the  $\pm 2-\sigma$  uncertainties, we found the resultant uncertainties are on average 2.5 times larger than those calculated from Eq. (2) for most species except  $\text{PM}_{2.5}$  mass (Table 2). This suggests an underestimate of analytical uncertainties by Flanagan et al. (2006), a substantial uncertainty from sample handling, or both. For this paper we adopt the RTI reported  $\pm 2-\sigma$  uncertainties. Kim et al. (2005) report fractional uncertainty associated with measurements made in New York, New Jersey and Vermont. Uncertainties they reported for sulfate, ammonium and calcium agreed within 20% of the uncertainties used in this paper.

The  $\text{DRI}_F$  measures the flow rate using a pressure drop across a critical orifice. Ambient temperature

Table 2  
Comparison of  $2-\sigma$  uncertainty in concentration calculated using Eq. (2) and RTI reported  $2-\sigma$  uncertainty (from 2005 AQS database)

	Calculated $2\sigma$ uncertainty (%)	RTI reported $2\sigma$ uncertainty (%)
PM <sub>2.5</sub>	10	10
OC	12	27
Sulfate	9	16
Ammonium	4	14
Iron	6	16

and pressure can alter this flow rate. DRI calculates the uncertainty for each measurement by accounting for the variability between the initial and final flow tests through 24-h sampling (typically  $\pm 4\%$ ), as well as precision in laboratory analyses (Chow et al., 1993c). The monthly average concentration of species and the average uncertainty (i.e., the average of all  $2-\sigma$  uncertainty values for the month) for STN<sub>RS</sub> versus DRI<sub>F</sub> are shown in Table 3 along with the signal-to-minimum detection limit (MDL) ratio, where the MDL was obtained from Chow et al. (1993c) for the DRI samplers and the median of all 2005 MDL values reported by RTI (to the EPA's AQS database) for the STN samplers. The signal-to-noise ratio for each species can be calculated from Table 3 by dividing the species average by the  $2-\sigma$  uncertainty.

### 3.2. Gravimetric mass comparisons

Comparisons of daily STN<sub>R</sub> and STN<sub>S</sub> PM<sub>2.5</sub> with DRI<sub>F</sub> PM<sub>2.5</sub> are shown in Fig. 2 and their error bars (representing the  $\pm 2-\sigma$  uncertainty) overlap only part of the time. Table 3 shows the Deming slope and intercept, which reduces variance in both independent ( $x$ ) and dependent ( $y$ ) variables (Cornbleet and Gochman, 1979), as well as the correlation coefficient, monthly average difference and monthly RMS difference between the two pairs of measurements. Good correlations ( $r \sim 0.95$ ) are found between STN<sub>R</sub> and DRI<sub>F</sub> and between STN<sub>S</sub> and DRI<sub>F</sub> with respect to PM<sub>2.5</sub> mass, though both the STN<sub>R</sub> and STN<sub>S</sub> measurements are generally larger than the DRI<sub>F</sub> measurements. The only exception occurred on 5th July when the sample was contaminated by the annual 4th of July fireworks held at FME (close to the samplers). The percentage differences  $\{[STN_{RS} - DRI_F]/([STN_{RS} + DRI_F]/2) \times 100\}$  ranged from 8% to 31% between

daily PM<sub>2.5</sub> from STN<sub>R</sub> and DRI<sub>F</sub> and from  $-38\%$  to  $67\%$  between STN<sub>S</sub> and DRI<sub>F</sub>. To determine whether the daily differences were statistically significant we calculated the  $z$ -test values for each day using the standard formula (Wilks, 1995)

$$z = \frac{(\bar{x}_{1} - \bar{x}_{2}) - E[\bar{x}_{1} - \bar{x}_{2}]}{(s_1^2/n_1 + s_2^2/n_2)^{1/2}} \quad (3)$$

Here  $\bar{x}_{1}$  and  $\bar{x}_{2}$  are the individual measurement of PM<sub>2.5</sub> from STN<sub>RS</sub> and DRI<sub>F</sub>, respectively. The  $s_{1(2)}$  represents the STN<sub>RS</sub> (DRI<sub>F</sub>)  $\pm 1-\sigma$  uncertainty value for the specified day. It is assumed that  $n = 1$  and the expected value of the difference between  $\bar{x}_{1}$  and  $\bar{x}_{2}$ , i.e.,  $E[\bar{x}_{1} - \bar{x}_{2}]$ , is zero. A  $z$ -value less than  $-1.96$  or greater than  $1.96$  indicates the two measurements are significantly different at the 95% confidence level. Table 4 shows the percentage of days when the paired measurements were significantly different under this test. In January, 62% of the daily measurements of PM<sub>2.5</sub> were significantly different, and in July this percentage was lowered to 50%.

Watson and Chow (2002) and Chow et al. (2006b) compared mass concentrations obtained with the STN<sub>R</sub> and DRI<sub>F</sub> (both analyses were performed at DRI) in central California and found similar results. They attribute the discrepancies between the DRI<sub>F</sub> and the STN<sub>R</sub> to different instrument inlet designs, flow controls, and resulting cyclone cutoff efficiencies. As discussed in the experimental section above, large particle intrusion is not expected to be a major issue at FME despite the uncertainty in the flow and size cut. Other reasons for the inter-sampler discrepancies include differences in face velocity, which may result in losses of volatile material. For submicrometer particles, the overall filter collection efficiency decreases with increasing face velocity (Liu et al., 1983; Lippmann, 1995; McDow and Huntzicker, 1990). The overall efficiency of membrane filters, however, is close to 100% for particles larger than the pore size (Lippmann, 1995), which is  $\sim 0.2 \mu\text{m}$  in this study.

The TEOM data are available for half of July 2002, and comparisons were made between the TEOM and the DRI<sub>F</sub> and STN<sub>S</sub> data. Only TEOM data with full 24-h coverage were used. The DRI<sub>F</sub> and STN<sub>S</sub> versus TEOM have  $r$ -values of 0.95 and slopes within 11% of unity (Table 5). The addition of the 1.03 scaling factor and the  $3.0 \mu\text{g m}^{-3}$  offset to the TEOM measurements has brought them closer to those from the STN<sub>S</sub> and DRI<sub>F</sub>. However,

Table 3

January average concentrations and uncertainties for PM<sub>2.5</sub>, sulfate, ammonium, nitrate, OC, EC, TC, bromine, calcium, potassium, iron, silicon and titanium measured with the STN<sub>RS</sub> and DRI<sub>F</sub>

	Deming slope	Deming intercept	Correlation (r)	Average difference (STN <sub>R</sub> –DRI <sub>F</sub> )	RMS difference	STN <sub>R</sub> species average ( $\pm 2\sigma$ uncertainty)	STN <sub>R</sub> signal-to-MDL	DRI <sub>F</sub> species average ( $\pm 2\sigma$ uncertainty)	DRI <sub>F</sub> signal-to-MDL
<b>(a) January (13 days of measurements)</b>									
PM <sub>2.5</sub>	0.76	0.62	0.98	1.47	1.66	8.77 $\pm$ 0.94	11.9	7.30 $\pm$ 0.98	8.58
Sulfate	0.89	–0.01	0.94	0.28	0.35	2.32 $\pm$ 0.40	193	2.04 $\pm$ 0.27	240
Ammonium	0.98	–0.03	0.92	0.05	0.14	1.02 $\pm$ 0.14	60.2	0.98 $\pm$ 0.12	115
Nitrate	0.80	–0.22	0.97	0.52	0.57	1.49 $\pm$ 0.29	171	0.97 $\pm$ 0.11	115
(with backup <sup>a</sup> )									
Nitrate (no backup)	0.89	–0.71	0.93	0.88	0.93	1.49 $\pm$ 0.29	171	0.61 $\pm$ 0.04	72
OC	0.68	0.72	0.80	–0.12	0.73	1.88 $\pm$ 0.63	7.82	2.00 $\pm$ 0.53	58.7
EC	2.72	–0.20	0.65	–0.40	0.49	0.35 $\pm$ 0.45	1.45	0.75 $\pm$ 0.18	22.2
TC	0.91	0.60	0.80	–0.52	0.97	2.23 $\pm$ 0.78	9.28	2.74 $\pm$ 0.61	80.7
Bromine	0.66	1.62	0.88	–0.61	1.10	2.95 $\pm$ 1.52	5.46	3.56 $\pm$ 1.66	21.0
Calcium	0.75	1.25	0.85	3.20	4.72	17.8 $\pm$ 4.79	2.40	14.6 $\pm$ 9.40	19.2
Potassium	0.92	5.46	0.97	–1.59	5.06	47.4 $\pm$ 7.94	6.59	49.0 $\pm$ 10.5	64.5
Iron	0.82	3.45	0.95	4.78	9.51	46.4 $\pm$ 6.68	22.12	41.7 $\pm$ 5.63	245.1
Silicon	2.06	–25.01	0.50	–6.72	16.71	29.9 $\pm$ 12.7	2.98	36.6 $\pm$ 10.7	24.4
Titanium	0.71	–0.25	0.48	1.08	1.95	2.84 $\pm$ 2.72	0.57	1.76 $\pm$ 52.2	3.5
<b>(b) July (28 days of measurements)</b>									
PM <sub>2.5</sub>	0.88	–0.50	0.96	3.75	5.59	27.8 $\pm$ 2.82	37.62	24.4 $\pm$ 1.29	28.3
Sulfate	0.89	–0.20	0.97	1.29	2.28	9.72 $\pm$ 1.43	810.10	8.44 $\pm$ 0.43	992
Ammonium	1.08	0.10	0.95	–0.32	0.73	2.61 $\pm$ 0.36	153.51	2.93 $\pm$ 0.24	344
Nitrate	0.62	0.17	0.54	0.06	0.25	0.60 $\pm$ 0.17	68.89	0.54 $\pm$ 0.05	63.5
(with backup <sup>a</sup> )									
Nitrate (no backup)	0.01	0.03	0.13	0.57	0.63	0.60 $\pm$ 0.17	68.89	0.03 $\pm$ 0.04	3.5
OC	0.93	–0.14	0.99	0.64	1.14	6.97 $\pm$ 1.35	29.05	6.33 $\pm$ 0.63	186
EC	2.02	0.03	0.58	–0.51	0.62	0.47 $\pm$ 0.48	1.98	0.98 $\pm$ 0.33	29.0
TC	0.97	0.12	0.98	0.13	1.03	7.45 $\pm$ 1.45	31.03	7.32 $\pm$ 0.72	215
Bromine	0.82	1.06	0.88	–0.42	1.15	3.58 $\pm$ 1.45	6.63	4.00 $\pm$ 0.52	23.5
Calcium	0.79	–2.92	0.89	14.95	26.73	56.1 $\pm$ 8.39	7.57	41.1 $\pm$ 3.79	54.1
Potassium	0.92	3.00	0.94	7.51	54.82	135 $\pm$ 12.3	18.87	128 $\pm$ 7.64	168.9
Iron	0.98	–6.39	0.88	7.85	44.62	91.0 $\pm$ 15.7	43.35	83.2 $\pm$ 5.85	489.3
Silicon	0.84	9.51	0.88	19.61	48.55	175 $\pm$ 26.7	17.65	157 $\pm$ 17.0	104.6
Titanium	0.45	1.47	0.58	2.73	8.68	7.68 $\pm$ 3.21	1.54	4.95 $\pm$ 18.6	9.7

The  $\pm 2\text{-}\sigma$  uncertainty is just the average of all uncertainties for the month. Deming slope, intercept, correlation coefficient, monthly average difference and RMS difference for species measured with STN<sub>R</sub> and DRI<sub>F</sub> in January and STN<sub>S</sub> and DRI<sub>F</sub> in July are presented. Slopes and intercepts were calculated with the  $y$ -axis = DRI<sub>F</sub> and the  $x$ -axis = STN<sub>RS</sub>. Bromine, calcium, potassium, iron, silicon and titanium are reported in units of ng m<sup>–3</sup> and shaded in grey. All other species are reported in units of  $\mu\text{g m}^{-3}$ .

<sup>a</sup>Only DRI<sub>F</sub> collected nitrate with a front and backup filter.

an intercept of  $-2.24$  to  $-2.64 \mu\text{g m}^{-3}$  (Table 5) indicates that the empirical adjustment for PM<sub>10</sub> may not fully address volatile losses of PM<sub>2.5</sub> from the heated inlet at this site. The RMS difference is greater for STN<sub>S</sub>–TEOM than DRI<sub>F</sub>–TEOM. The STN<sub>S</sub>–TEOM average difference is positive and about half of the RMS difference, while the DRI<sub>F</sub>–TEOM average difference is slightly negative and about 1/8 of the RMS difference (Table 5). The

magnitude of these differences is consistent with a systematic bias (in addition to random noise) between the STN<sub>S</sub> and TEOM measurements. In contrast, deviations between the DRI<sub>F</sub> and TEOM appear to be random in nature (Fig. 3a) and generally fall within 10% of the Deming regression line. Chen et al. (2002) found similar results when comparing the DRI<sub>F</sub> to the TEOM in summer months from 1999 to 2001.

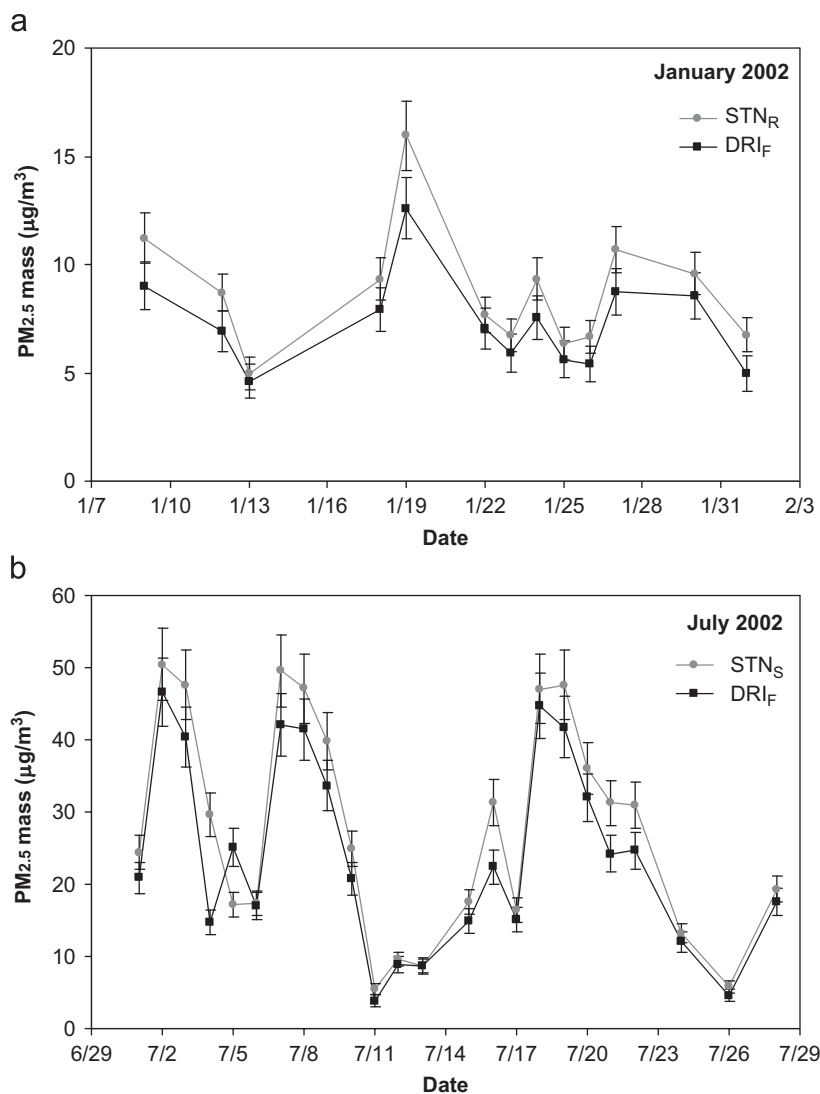


Fig. 2. Time series of PM<sub>2.5</sub> concentrations measured with STN<sub>RS</sub> and DRI<sub>F</sub> for January (a) and July (b). Error bars represent  $\pm 2\text{-}\sigma$  uncertainty.

### 3.3. Chemical compositions

Besides gravimetric mass, Tables 3 and 4 show the statistics and comparisons of major contributing species to PM<sub>2.5</sub> including sulfate, ammonium, nitrate, OC, EC, TC and trace elements including bromine and potassium, and crustal mass made of calcium, iron, silicon and titanium. In January, 15% of the paired sulfate measurements were found to be significantly different, but in July this fraction increased to 33%. Although sulfate measurements from the different instruments are well correlated with  $r$ -values greater than 0.94, the STN<sub>RS</sub> consistently report higher values than the DRI<sub>F</sub>. Since the

average deviation is 13–18% for both PM<sub>2.5</sub> and sulfate (Table 3), there appears to be a bias in the flow control, allowing more or less sample volume than specified. It should be noted that sulfate concentration is not sensitive to a small difference in the size cut because most sulfate is in submicron particles (Cabada et al., 2004; Tolocka et al., 2005). Chen (2002) shows that sulfate mass from DRI<sub>F</sub> increases by 4% when filters are exposed for 72 h after sampling while total mass may either increase (by 1%) or decrease (by 3%). This suggests that the different filter exposure times had minimal effects on the differences between DRI<sub>F</sub> and STN<sub>RS</sub> for sulfate and mass.

$\text{DRI}_F$  and  $\text{STN}_{RS}$  measure nitrate on different filter substrates behind different denuder configurations (Fig. 1). Comparisons between the front only  $\text{DRI}_F$  filters and front plus backup  $\text{DRI}_F$  filters with  $\text{STN}_{RS}$  have both been made. The nitrate concentrations are well correlated in the winter (without or with backup filter concentrations added), although  $\text{DRI}_F$  measures only 41–65% of the average  $\text{STN}_R$  nitrate (without or with backup filter concentration added; see Table 3). All differences were found statistically significant (Table 4). The nylon filters used by  $\text{STN}_R$  appear to retain much more nitrate than single quartz-fiber filters. Moreover, the  $\text{DRI}_F$  filters remained in the field for up to 2.5 days longer, and this potentially led to more nitrate loss through volatilization. The  $\text{DRI}_F$  July average nitrate (on the front filter) is below the detection limit and most

of the nitrate (above the detection limit) was found on the backup filter. The July measurements of nitrate do not correlate well ( $r = 0.13$  front filter only,  $r = 0.54$  front and backup filter), and the  $\text{DRI}_F$  nitrate accounts for 6 to 90% of the  $\text{STN}_S$  (without or with backup filters added). When the  $\text{DRI}_F$  front and backup nitrate are compared with  $\text{STN}_S$ , there are no significant differences for the July period (Tables 3b and 4).

Ammonium shows good inter-sampler correlation with  $r$ -values greater than 0.92 for both sampling months (Table 3), but there were significant differences in 15–38% of the daily measurements in January and July, respectively (Table 4). In January, the average difference as well as the RMS difference between the  $\text{DRI}_F$  and the  $\text{STN}_R$  measured ammonium is negligible. In July the  $\text{DRI}_F$  monthly average is slightly greater than the  $\text{STN}_S$  average, but within 11% (Table 3b). Like nitrate, ammonium can also be volatilized readily (Appel and Tokiwa, 1981; Appel et al., 1984; Chow et al., 2005b; Pathak et al., 2004). Pathak et al. (2004) found that there were substantially less losses of ammonium than nitrate on filter samplers. Ammonium is less volatile when it is in the form of ammonium sulfate.

For TC, which is independent of thermal/optical method, the  $\text{STN}_S$  concentration is similar to that of the  $\text{DRI}_F$ , although the  $\text{STN}_S$  is slightly larger than the  $\text{DRI}_F$ . In January, the  $\text{STN}_R$  concentration is less than  $\text{DRI}_F$ , but within 20%. Inter-sampler differences of TC were significant 8% of the time in July and 69% in January (Table 4). Correlation between the  $\text{DRI}_F$  and  $\text{STN}_S$  is good in July with an  $r$ -value of 0.98, better than the  $r$ -value of 0.80 between the  $\text{DRI}_F$  and  $\text{STN}_R$  in January. Since the TC concentration was low in January ( $< 1/3$  of that in July) and close to the MDL, more scatter could be expected. The OC/EC ratio was 5.4 in January, compared with 14.8 in July (based on  $\text{STN}_{RS}$ ). This reflects larger secondary organic

Table 4  
Percentage of days when the species measured with  $\text{STN}_{RS}$  and  $\text{DRI}_F$  were significantly different at the 95% confidence level

	Percentage of significantly different values January (%)	Percentage of significantly different values July (%)
$\text{PM}_{2.5}$	62	50
Nitrate	100	0
Sulfate	15	33
Ammonium	15	38
OC	36	8
EC	NA	NA
TC	69	8
Bromine	0	5
Calcium	NA	65
Potassium	0	26
Iron	15	29
Silicon	29	30
Titanium	NA	NA

Only species with concentrations greater than three times the MDL were compared. Comparisons could not be made for EC, calcium (January), nitrate (July) or titanium because over half of the measurements were too small.

Table 5  
Deming slope, intercept, correlation, and average and RMS difference ( $\mu\text{g m}^{-3}$ ) for the  $\text{STN}_S$  versus TEOM, and the  $\text{DRI}_F$  versus TEOM as well as  $N$ , number of days comparisons were made

$X$	$y$	Slope	$N$	Intercept	Correlation ( $r$ )	Average difference ( $x-y$ )	RMS difference	Monthly average $x$	Monthly average $y$
$\text{STN}_S$	TEOM	0.97	16	-2.64	0.95	2.96	5.35	24.06	21.10
$\text{DRI}_F$	TEOM	1.11	16	-2.24	0.95	-0.48	4.28	20.62	21.10

The averages ( $\mu\text{g m}^{-3}$ ) for each sampler for the second half of July are also given.

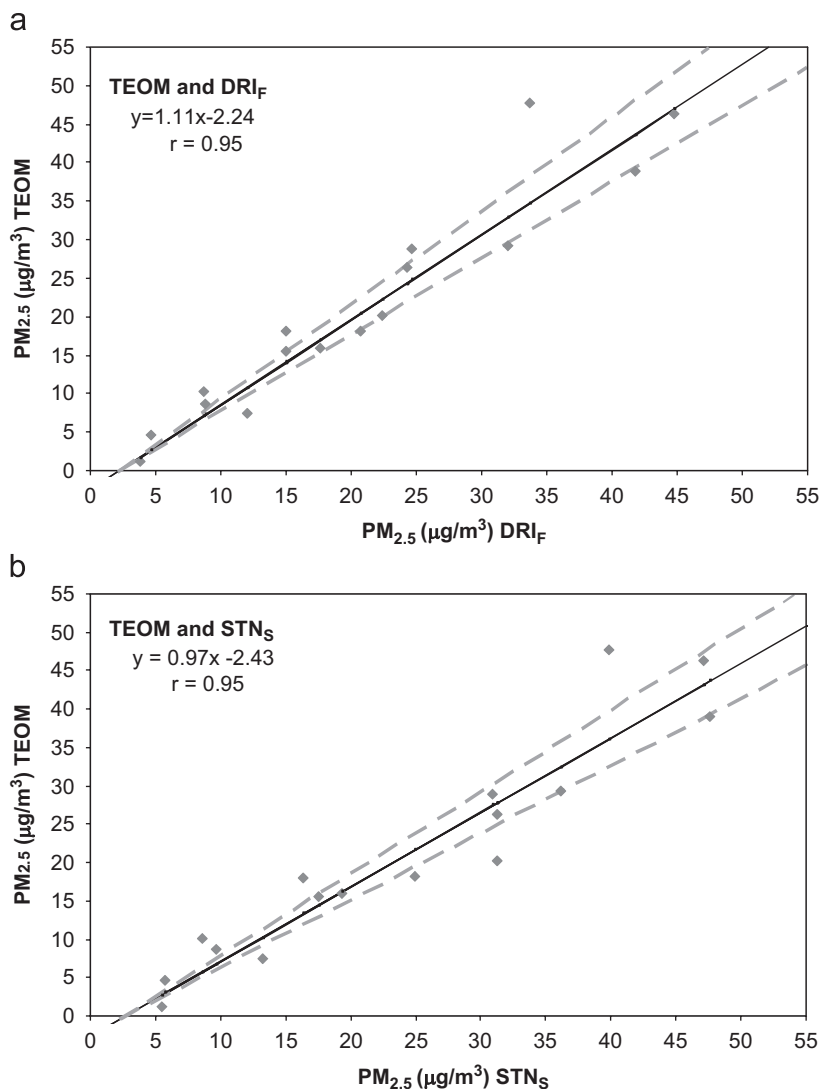


Fig. 3. Comparisons of PM<sub>2.5</sub> total mass between TEOM and (a) DRI<sub>F</sub> and (b) STN<sub>S</sub>. Deming regression line shown in black,  $\pm 10\%$  (of the regression line) shown in broken gray. The TEOM and DRI<sub>F</sub> generally agree within experimental error.

aerosol contributions in the summer (Polidori et al., 2006). OC correlation was similar to that of TC with an  $r$ -value of 0.99 in July and an  $r$ -value of 0.80 in January. OC is the dominant fraction of TC in both seasons and this explains the similar relationship. EC correlation is poor between the paired measurements both in winter and summer and the STN<sub>RS</sub> EC are generally only  $\sim 50\%$  of the DRI<sub>F</sub> EC, likely because of the different ways STN-TOT and IMPROVE-TOR define EC (Chow et al., 1993b; Peterson and Richards, 2002; OC/EC Laboratory, 2003). STN<sub>RS</sub> EC concentrations were generally less than three times the MDL and for this reason the  $z$ -test comparison was not performed.

McDow and Huntzicker (1990) demonstrate that a larger face velocity leads to increases in volatilization of organic species. The DRI<sub>F</sub> and STN<sub>RS</sub> all use 47-mm filters. Assuming that the filter holder has negligible effects on the area of the filter impacted by the flow, the face velocity can be approximated by the flow rates such that the DRI<sub>F</sub> has the largest face velocity (with a flow rate of  $20 \text{ L min}^{-1}$ ) for OC collection, followed by STN<sub>R</sub> and STN<sub>S</sub> (with flow rates of  $\sim 7 \text{ L min}^{-1}$ ). In July the average DRI<sub>F</sub> OC and TC are smaller than the STN<sub>S</sub>, and these differences may be partly attributed to the effects of face velocity. The higher temperatures in July might facilitate OC

volatilization, especially from the DRI<sub>F</sub> filters that were left in the field for a longer time period. However, in January the DRI<sub>F</sub> TC is larger than the STN<sub>R</sub>. This is explained neither by flow control differences nor by face velocity. A problem specific to the TC and OC measurement is the blank correction and the only field blank collected for the STN<sub>R</sub> sampler showed relatively high OC. The STN<sub>R</sub> field blank OC was on average 50% of the non-blank corrected OC, while the STN<sub>S</sub> and DRI<sub>F</sub> field blank OC was on average 20% of the non-blank corrected OC. The winter STN<sub>R</sub> TC and OC might have been overcorrected. The quantification of OC mass might also be affected by different thermal analysis protocols that define the OC and EC split differently.

Inter-sampler comparisons of crustal species, including silicon (in July), calcium and iron, as well as trace elemental species that are >3 times the MDL (bromine and potassium) all have *r*-values greater than 0.85. STN<sub>S</sub> generally reports larger crustal species concentrations than DRI<sub>F</sub> does, consistent with the situation for PM<sub>2.5</sub> mass and sulfate. The smaller DRI<sub>F</sub> concentration could be reflected by either a small DRI<sub>F</sub>/STN<sub>S</sub> slope (<1) or a negative intercept (Table 3). STN<sub>RS</sub> and DRI<sub>F</sub> differences for silicon, calcium, iron and potassium concentrations were significant 0–30% of the time in January and 25–65% of the time in July. Calcium (in January), and Titanium, were below three times the MDL and thus the *z*-test was not performed for these species.

### 3.4. Mass closure

Reconstructed mass from the sum of individual species determines the degree to which the gravimetrically measured total mass is explained by the

measured species (Chow et al., 1996; Andrews et al., 2000; Malm et al., 2005; Frank, 2006). To reconstruct the PM<sub>2.5</sub> mass, the crustal mass, organic mass and mass of all other species are added together. The crustal mass is the sum of silicon, calcium, iron and titanium multiplied by factors to account for oxygen associated with them (Frank, 2006) as shown below:

$$\begin{aligned} \text{Crustal mass} = & 3.73 \times \text{silicon} + 1.63 \times \text{calcium} \\ & + 2.42 \times \text{iron} + 1.94 \times \text{titanium}. \end{aligned} \quad (4)$$

There is much debate over what factor should be used to determine the oxygen, nitrogen and hydrogen associated with OC, and this factor can range from 1.2 to 2.5 (Turpin and Lim 2001; Rees et al., 2004; El-Zanan et al., 2005). We multiply the OC by a factor of 1.8, similar to Rees et al. (2004), because the area is highly influenced by regional sources. Front and backup filter nitrate are included in the DRI<sub>F</sub> reconstructed mass. The carbon concentration is not corrected by backup filters (but is blank corrected).

The reconstructed mass from the DRI<sub>F</sub> samplers is well correlated with the measured gravimetric mass in both January and July (*r* = 0.94–0.99, see Table 6), and a good correlation is also found for STN<sub>S</sub>. The July DRI<sub>F</sub> reconstructed PM<sub>2.5</sub> mass overestimates the gravimetric mass by 6% while the STN<sub>S</sub> reconstructed mass underestimates the gravimetric mass by just 3%. For STN<sub>R</sub> in January, the average measured and reconstructed mass differ by less 2%, although their correlation is not as good (*r* = 0.80). Histograms of the difference between the gravimetric and reconstructed masses (i.e., the residuals) are shown in Fig. 4. In January, the DRI<sub>F</sub> residuals are shifted negatively from the

Table 6  
Average reconstructed mass for STN<sub>RS</sub> and DRI<sub>F</sub> for January and July (units are in  $\mu\text{g m}^{-3}$ )

	Average gravimetric mass	Average reconstructed mass	RMS difference	Average difference (gravimetric-reconstructed)	Slope	Intercept	Correlation ( <i>r</i> )
<i>January</i>							
DRI <sub>F</sub>	7.3	8.8	1.7	−1.5	1.2	0.38	0.94
STN <sub>R</sub>	8.8	8.9	1.7	−0.12	0.93	0.73	0.80
<i>July</i>							
DRI <sub>F</sub>	24.1	25.5	2.1	−1.4	0.99	1.5	0.99
STN <sub>S</sub>	27.8	27.3	3.2	0.57	0.99	−0.37	0.98

Also shown is the Deming slope, intercept, and correlation for the gravimetric (*x*-axis) and reconstructed mass (*y*-axis).

normal distribution, with a mode at  $-1 \mu\text{g m}^{-3}$ . The  $\text{STN}_R$  residuals have a mode at zero and an apparent outlier, which explains the poorer correlation. There is better overlap between the  $\text{DRI}_F$  and  $\text{STN}_S$  residuals in July, but the  $\text{DRI}_F$  residuals are still less than  $\text{STN}_S$  residuals.

Fig. 5 shows the contributions of sulfate, organic matter ( $\text{OM} = \text{OC} \times 1.8$ ), EC, ammonium, nitrate, crustal mass and the sum of all other species, to total mass (the relative contribution) as well as the ratios of  $\text{DRI}_F/\text{STN}_{RS}$  relative contribution. Here nitrate from the front and backup filter of  $\text{DRI}_F$  was used. In January and July,  $\text{STN}_{RS}$  report larger sulfate concentrations, but the relative contribution of sulfate to total mass is similar for  $\text{STN}_{RS}$  and  $\text{DRI}_F$  (shown by the ratios of relative contribution

$[\text{DRI}_F/\text{STN}_{RS}]$  being close to unity in Fig. 5). A systematic bias would explain why the difference between the sulfate concentrations does not show up in the relative contributions. This bias can result from differences in how the two instruments record volume as described in the experimental section. In January,  $\text{DRI}_F$  reports more OM concentration than  $\text{STN}_R$  and the relative contribution of OM to total mass from  $\text{DRI}_F$  is greater than that from  $\text{STN}_R$ . In July,  $\text{DRI}_F$  reports less OM concentration than  $\text{STN}_S$  and the relative contribution of OM to total mass from  $\text{DRI}_F$  is greater than that from  $\text{STN}_S$ . This should not negate the above argument that there is a systematic bias between the two instruments, since the relative contribution of OM to total mass is affected by artifacts in both mass

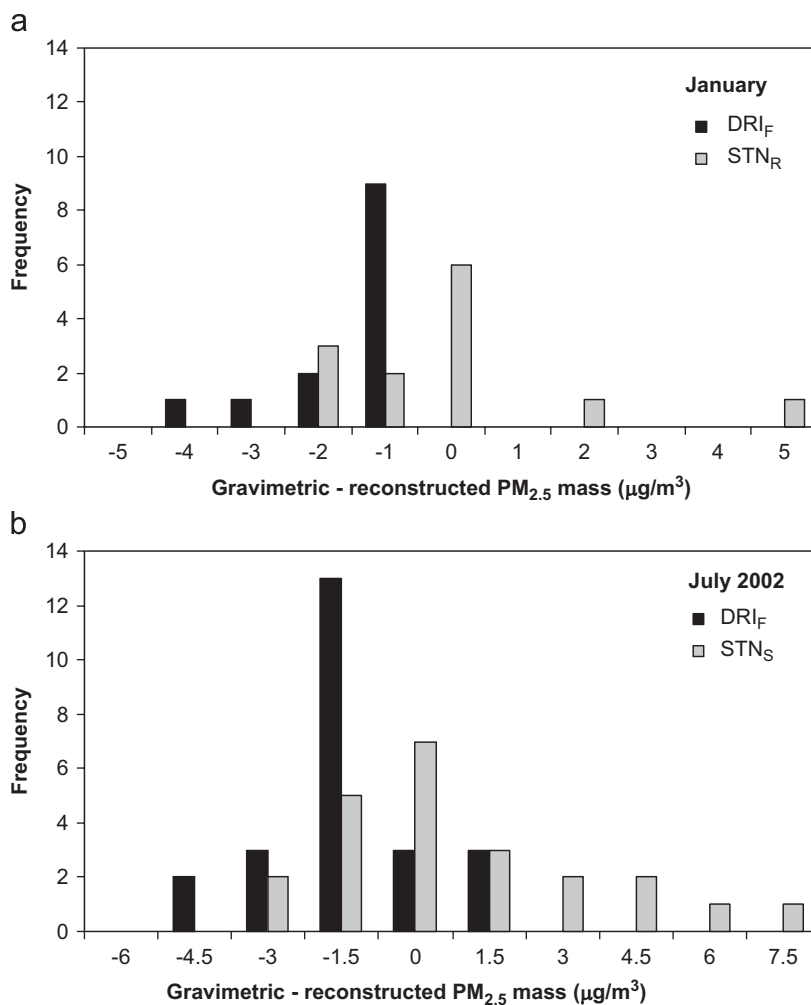


Fig. 4. Frequency distribution of gravimetric—reconstructed differences (residuals), for January  $\text{DRI}_F$  and  $\text{STN}_R$  and July  $\text{DRI}_F$  and  $\text{STN}_S$ .

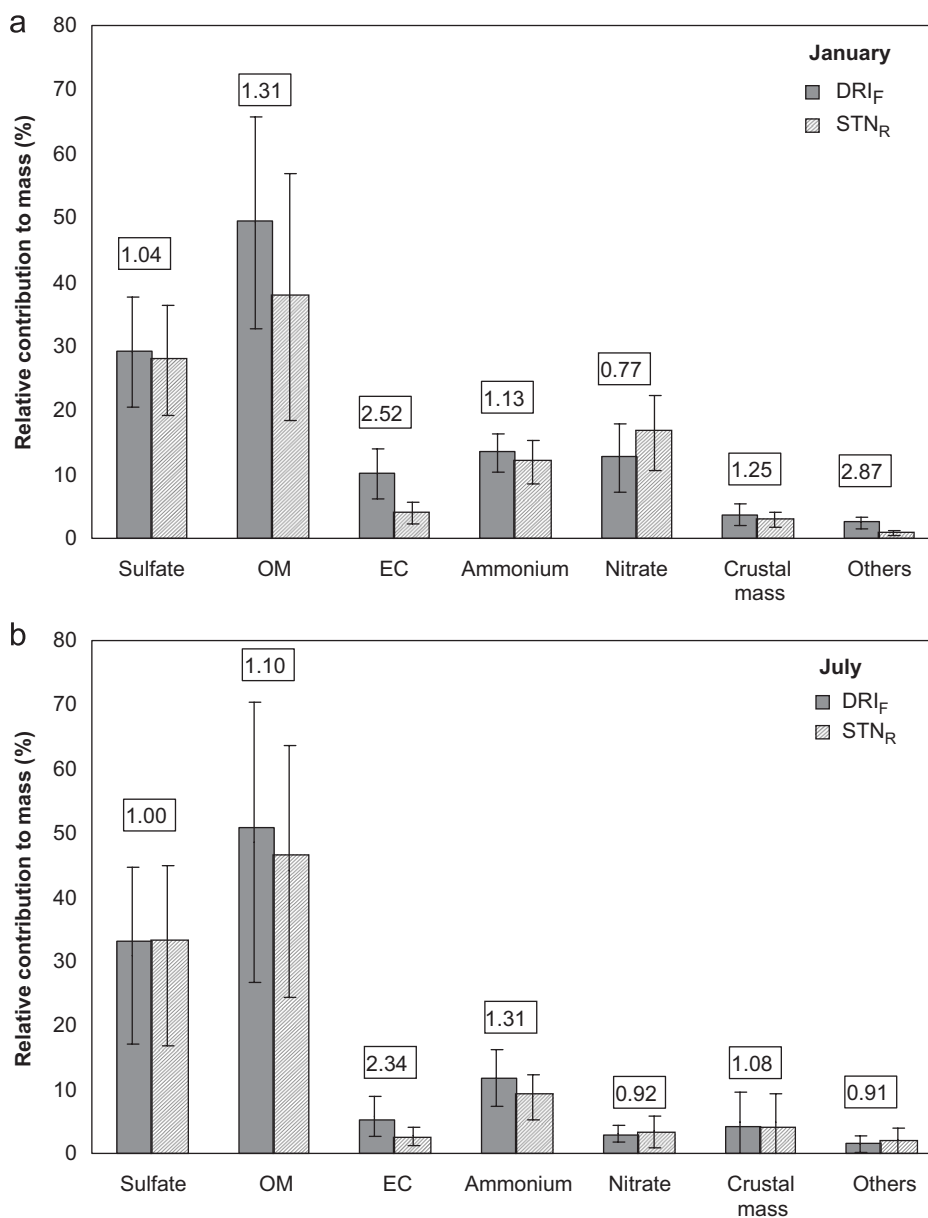


Fig. 5. Contributions of individual species to  $PM_{2.5}$  mass (relative contribution) for (a) January and (b) July. Numbers in boxes are the  $DRI_F$  relative contribution divided by  $STN_{RS}$  relative contribution. Error bars represent the standard deviation of the relative contributions.

and OC measurements. The differences in OM relative contribution are not the same as the differences in sulfate relative contribution because of issues related to organic sampling artifacts, blank correction and analysis protocols. The mass closure of  $DRI_F$  usually exceeds 100%, consistent with a positive organic sampling artifact that is not corrected. For  $STN_R$ , however, the problem associated with organic sampling artifacts has been

offset by a relatively high blank subtraction in this study. The organic sampling artifact is a major issue regarding  $PM_{2.5}$  mass closure, particularly for low PM-loaded samples.

#### 4. Conclusions

Measurements from the DRI and RTI analyzed samplers ( $DRI_F$  versus  $STN_R$  and  $DRI_F$  versus

STN<sub>S</sub>) at Fort Meade, MD were generally well correlated. PM<sub>2.5</sub>, sulfate, OC, TC and ammonium all had *r*-values in excess of 0.8. The STN method, however, reported larger PM<sub>2.5</sub> mass than the DRI method by 13–18%. Possible causes for this bias include differences in sampling, flow design and loss of volatile species (because of different face velocities and durations filters remained in the field after sampling). Considering the characteristics of PM<sub>2.5</sub> at FME and the fact that sulfate showed the same bias, the differences in the flow monitoring strategies that allow a sampler to collect more or less volume than specified is the probable explanation.

Even though the PM<sub>2.5</sub> mass measurements were well correlated, differences between the measurements were statistically significant more than 50% of the time under the current uncertainty estimates. The uncertainty associated with PM<sub>2.5</sub> mass must be raised from 10% to 20% for January measurements, and from 10% to 28% for July measurements, to make the differences statistically significant only 5% of the time (using a *z*-test and assuming only random errors). Even though the measurements of speciated mass were well correlated, the differences between the samplers are statistically significant at the 95% confidence level from 5% to 100% of the time. Particularly, measurements of EC did not compare well. Two different analysis methods, IMPROVE-TOR and STN-TOT, were used, and these two methods are known to define EC differently. In addition, EC was a minor fraction of TC and frequently found below or near the MDL at FME. Nitrate correlated well between the two samplers in January, however the DRI<sub>F</sub> measurements were substantially smaller than those from the STN<sub>R</sub> and all the measurements were significantly different using a *z*-test. In July, the nitrate correlation was weaker, possibly because of the increased volatility and lower concentration of the nitrate aerosol. It is likely that the STN<sub>RS</sub> nylon filters retained more nitrate than the DRI<sub>F</sub> quartz filters (e.g. Frank, 2006). At FME this problem was mitigated somewhat because DRI<sub>F</sub> used backup filters. Residuals of gravimetric—reconstructed mass were generally small and negative for both DRI<sub>F</sub> and STN<sub>RS</sub>. The differences possibly result from the organic sampling artifact and/or conversion factor between the mass of OC and OM.

Overall, the uncertainty estimates used by either the STN (i.e., from AQS) or DRI are likely too low to account for the potential variability in the PM<sub>2.5</sub>

measurements, and to some extent this will impact the conclusions of trend analyses and receptor modeling based on these data. With the current state of ambient monitoring it is reasonable to expect uncertainties of at least 20% (at the 95% confidence level) for PM<sub>2.5</sub>, sulfate, ammonium, and OM concentration. Further evaluation for these sampling systems is recommended through side-by-side measurements at more locations and for longer periods of time.

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