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A side-by-side comparison of filter-based $PM_{2.5}$ measurements at a suburban site: A closure study

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Received 28 September 2006; received in revised form 8 April 2007; accepted 9 April 2007

Abstract

Assessing the effects of air quality on public health and the environment requires reliable measurement of $PM_{2.5}$ mass and its chemical components. This study seeks to evaluate $PM_{2.5}$ 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_S and Thermo Scientific Reference Ambient Air Sampler—STN_R, two Desert Research Institute Sequential Filter Samplers—DRI_F, and a continuous TEOM monitor (Thermo Scientific Tapered Element Oscillating Microbalance, 1400a) were sampling air in parallel. These monitors differ not only in sampling configuration but also in protocol-specific laboratory analysis procedures. Measurements of $PM_{2.5}$ 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 $PM_{2.5}$ mass and major contributing species were significantly different at the 95% confidence level from 5% to 100% of the time. Larger values of $PM_{2.5}$ mass and individual species were generally reported from STN_R and STN_S. 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 $PM_{2.5}$ speciation and mass closure. Statistical tests indicate that the current uncertainty estimates used in the STN network may underestimate the actual uncertainty.

Keywords: Aerosol sampling; Chemical speciation; $PM_{2.5}$; Comparison study; Filter sampling

1. Introduction

Elevated levels of $PM_{2.5}$ mass (the mass concentration of fine aerosol with aerodynamic diameter less than 2.5 μm, hereafter referred to as $PM_{2.5}$) 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^{-3})

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1352-2310/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2007.04.008

Please cite this article as: Hains, J.C., et al., A side-by-side comparison of filter-based $PM_{2.5}$ measurements at a suburban site: A closure study, Atmospheric Environment (2007), doi:10.1016/j.atmosenv.2007.04.008

and short-term (24-h average concentration of 65 μg m^{-3}) maximum allowable $PM_{2.5}$. US EPA recently lowered the short-term NAAQS to 35 μg m^{-3} (effective 17/12/06) to reflect new scientific studies of the $PM_{2.5}$ 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 $PM_{2.5}$ 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 $PM_{10}/PM_{2.5}$ air quality study (Chow et al., 2006a), to assess human exposure, health risks, visibility degradation and climate change related to $PM_{2.5}$.

Comparability among the FRM and more-versatile PM samplers must be established for studies using those samplers to describe $PM_{2.5}$ spatial and temporal trends. A reasonable estimate of measurement uncertainties is also critical for $PM_{2.5}$ 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 $PM_{2.5}$ 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 $PM_{2.5}$ 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 $PM_{2.5}$ events. Fort Meade, Maryland (FME: 39.10°N, 76.74°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 regional 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., 2002, 2003). Chen et al. (2002) report an average $PM_{2.5}$ concentration of 13.0 ± 7.7 μg m^{-3} across eight sampling months between July 1999 and 2000.

During January and July 2002, $PM_{2.5}$ 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 $PM_{2.5}$, 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 DRI_F and the RAAS and SASS samplers as STN_R and STN_S (STN_{RS} denotes both instruments) hereafter. Components quantified by both DRI and RTI include gravimetric $PM_{2.5}$ 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 $PM_{2.5}$ mass were made in July with a tapered element oscillating microbalance (TEOM 1400a, Thermo Scientific, Waltham, MA).

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

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tested in other studies facilitating a weight of evidence approach (e.g., Burton et al., 2002; Weed, 2005) to improve the design of ambient $PM_{2.5}$ 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_{RS} and DRI_F 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_R 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_F is designated as FRM for PM_{10} (aerosol with aerodynamic diameter $\leqslant 10\,\mu m$) when equipped with a PM_{10} inlet (Code of Federal Regulations (CFR), 1997) and has been successfully deployed in many air quality studies for sampling $PM_{10}/PM_{2.5}$ since 1988 (Chow et al., 1992, 1996, 2006a; Chen, 2002; Chen et al., 2002; Watson and Chow, 2002).

STN_{RS} samplers use a critical orifice to set the flow rate and monitor it with a mass flow sensor. STN_{RS} record ambient temperature and pressure and this is 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_R flow was calibrated with a flow audit device (BGI deltaCal) and the STN_S flow was calibrated with a bubble meter (Sensidyne/Gilian Gilibrator 2). The DRI_F 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_F, 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_{RS} record the total volume sampled, which is calculated from the mass flow sensor, temperature and pressure readings.

The sample flow rates for $PM_{2.5}$ mass were 20, 16.7, and 6.7 $L\,min^{-1}$ in DRI_F, STN_R, and STN_S, respectively. Since all the samplers used 47-mm filters, DRI_F imposed an approximately 20% larger face velocity than the STN_R and a face velocity that was two times larger than the STN_S around the filter. The STN_R sample flow rate was 7.3 $L\,min^{-1}$ for ions and carbon (similar to the STN_S) and the DRI_F imposed a 64% larger face velocity than the STN_R.

Cyclones used by STN_R and STN_S (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 $PM_{2.5}$ mass collected by the two samplers. Chen (2002) showed a minor crustal material contribution at FME, ~3% of $PM_{2.5}$ 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_F, STN_R and STN_S. Ultrafine particles ($<0.1\,\mu m$ in diameter) typically contribute little to $PM_{2.5}$ 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_F used a front quartz–fiber filter with a sodium–chloride-impregnated cellulose backup filter to collect nitrate. The backup filter captured nitrate volatized 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_R and STN_S 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 and Neil (2006) found that denuded nylon filters captured more nitrate than undenuded Teflon filters. The different denuders and filter types used by the STN_{RS} and DRI_F in this study likely affect the nitrate collection efficiency as suggested by Solomon et al. (2003) and Frank and Neil (2006).

Quartz–fiber filters were used in all the samplers to collect carbonaceous material. DRI_F 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_F

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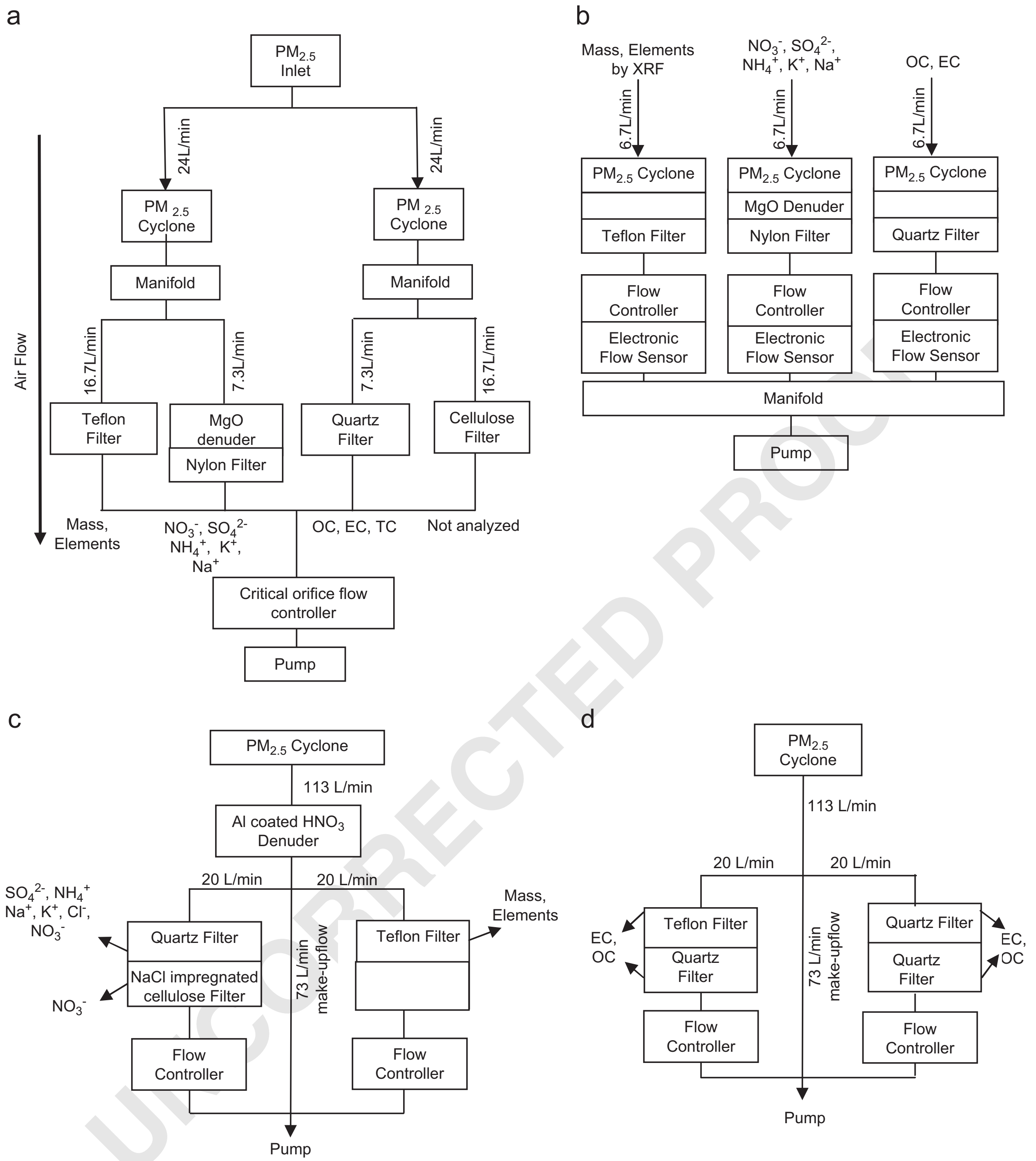

Fig. 1. Sampler configuration for (a) STN_R (Anderson RAAS) (b) STN_S (Met-One SASS) (c) DRI_F for elements and ions (d) DRI_F for carbonaceous material.

front quartz–fiber filters were used to compare with the STN_{RS} 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.,

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Table 1
Analytical methods for species collected by DRI_F (analyzed by DRI) and STN_{RS} (analyzed by RTI) and instrument specifications

	DRI analysis[a]	RTI analysis[b]
$PM_{2.5}$	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)	Thermal optical transmittance (NIOSH[c])
OC	Thermal optical reflectance (IMPROVE)	Thermal optical transmittance (NIOSH[c])

	Instrument specifications		
	DRI_F	STN_R	STN_S
Flow ($L\ min^{-1}$)	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 $\pm 1{-}\sigma$.

[a] DRI operating procedure (1990); Chow et al. (1993c, 2001).

[b] US EPA (2001); Thermo Anderson (2001).

[c] National Institute for Occupational Safety and Health.

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^+) and sodium (Na^+) 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_F sampler and once every 2 weeks for the STN_S sampler. Only one field blank was collected for the STN_R sampler. DRI corrected for field blanks as part of their analysis (Watson et al., 1989a, b), but RTI did not. To correct STN_{RS} samples for field blanks, we averaged all STN_{RS} blank values obtained during the sampling period, converted them from mass per filter to mass m^{-3} 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_F 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_R 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_S 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_F 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 $PM_{2.5}$ mass (measured on Teflon

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filters) and sulfate mass (measured on quartz–fiber filters) varied less than their respective uncertainties.

A TEOM measures near real-time continuous $PM_{2.5}$ mass. The TEOM at FME drew ambient air in at $3\,L\,min^{-1}$ through a $PM_{2.5}$ 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 $+3.0\,\mu g\,m^{-3}$ to account for loss of semi-volatile material. Although this empirical adjustment allows the TEOM to be a federal equivalent method (FEM) for PM_{10} measurements (Patashnick and Rupprecht, 1991), the effects on $PM_{2.5}$ 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 DRI_F and 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 $PM_{2.5}$ and each reported species concentration. For STN_{RS}, the species concentration (with units of mass m^{-3} at ambient temperature and pressure) is calculated using the equation below:

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

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 mass time^{-1}, MM is the molar mass of the air sampled, R is the gas constant ($0.08314\,L\,atm\,K^{-1}\,mol^{-1}$), T is ambient temperature and P is the ambient pressure. 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 STN_{RS} temperature readings must be within $\pm 4\,K$ of the actual temperature and pressure readings must be within ± 0.013 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., ±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 $PM_{2.5}$ 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 $PM_{2.5}$ mass, sulfate, ammonium, OC or elemental concentration is given by

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

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), $\delta mf/mf$ 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 ±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 $PM_{2.5}$ 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,

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

	Calculated 2σ uncertainty (%)	RTI reported 2σ uncertainty (%)
$PM_{2.5}$	10	10
OC	12	27
Sulfate	9	16
Ammonium	4	14
Iron	6	16

ammonium and calcium agreed within 20% of the uncertainties used in this paper.

The DRI_F measures the flow rate using a pressure drop across a critical orifice. Ambient temperature 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 ±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_{RS} versus DRI_F 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_R and STN_S $PM_{2.5}$ with DRI_F $PM_{2.5}$ 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_R and DRI_F and between STN_S and DRI_F with respect to $PM_{2.5}$ mass, though both the STN_R and STN_S measurements are generally larger than the DRI_F 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 $PM_{2.5}$ from STN_R and DRI_F and from −38% to 67% between STN_S and DRI_F. To determine whether the daily differences were statistically significant we calculated the z-test values for each day using the standard formula (Wilks, 1995)

$$z = \frac{(x\mathrm{bar}_1 - x\mathrm{bar}_2) - E[x\mathrm{bar}_1 - x\mathrm{bar}_2]}{(s_1^2/n_1 + s_2^2/n_2)^{1/2}}. \tag{3}$$

Here $x\mathrm{bar}_1$ and $x\mathrm{bar}_2$ are the individual measurement of $PM_{2.5}$ from STN_{RS} and DRI_F, respectively. The $s_{1(2)}$ represents the STN_{RS} $(DRI_F)\pm 1-\sigma$ uncertainty value for the specified day. It is assumed that $n=1$ and the expected value of the difference between $x\mathrm{bar}_1$ and $x\mathrm{bar}_2$, i.e., $E[x\mathrm{bar}_1 - x\mathrm{bar}_2]$, 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 $PM_{2.5}$ were significantly different, and in July this percentage was lowered slightly to 50%.

Watson and Chow (2002) and Chow et al. (2006b) compared mass concentrations obtained with the STN_R and DRI_F (both analyses were performed at DRI) in central California and found similar results. They attribute the discrepancies between the DRI_F and the STN_R 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 ~0.2 μm in this study.

The TEOM data are available for half of July 2002, and comparisons were made between the TEOM and the DRI_F and STN_S data. Only TEOM data with full 24-h coverage were used. The DRI_F

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Table 3
January average concentrations and uncertainties for $PM_{2.5}$, sulfate, ammonium, nitrate, OC, EC, TC, bromine, calcium, potassium, iron, silicon and titanium measured with the STN_{RS} and DRI_F

	Deming slope	Deming intercept	Correlation (r)	Average difference (STN_R–DRI_F)	RMS difference	STN_R species average ($\pm 2\sigma$ uncertainty)	STN_R signal-to-MDL	DRI_F species average ($\pm 2\sigma$ uncertainty)	DRI_F signal-to-MDL
(a) *January (13 days of measurements)*									
$PM_{2.5}$	0.76	0.62	0.98	1.47	1.66	8.77±0.94	11.9	7.30±0.98	8.58
Sulfate	0.89	−0.01	0.94	0.28	0.35	2.32±0.40	193	2.04±0.27	240
Ammonium	0.98	−0.03	0.92	0.05	0.14	1.02±0.14	60.2	0.98±0.12	115
Nitrate (with backup[a])	0.80	−0.22	0.97	0.52	0.57	1.49±0.29	171	0.97±0.11	115
Nitrate (no backup)	0.89	−0.71	0.93	0.88	0.93	1.49±0.29	171	0.61±0.04	72
OC	0.68	0.72	0.80	−0.12	0.73	1.88±0.63	7.82	2.00±0.53	58.7
EC	2.72	−0.20	0.65	−0.40	0.49	0.35±0.45	1.45	0.75±0.18	22.2
TC	0.91	0.60	0.80	−0.52	0.97	2.23±0.78	9.28	2.74±0.61	80.7
Bromine	0.66	1.62	0.88	−0.61	1.10	2.95±1.52	5.46	3.56±1.66	21.0
Calcium	0.75	1.25	0.85	3.20	4.72	17.8±4.79	2.40	14.6±9.40	19.2
Potassium	0.92	5.46	0.97	−1.59	5.06	47.4±7.94	6.59	49.0±10.5	64.5
Iron	0.82	3.45	0.95	4.78	9.51	46.4±6.68	22.12	41.7±5.63	245.1
Silicon	2.06	−25.01	0.50	−6.72	16.71	29.9±12.7	2.98	36.6±10.7	24.4
Titanium	0.71	−0.25	0.48	1.08	1.95	2.84±2.72	0.57	1.76±52.2	3.5
(b) *July (28 days of measurements)*									
$PM_{2.5}$	0.88	−0.50	0.96	3.75	5.59	27.8±2.82	37.62	24.4±1.29	28.3
Sulfate	0.89	−0.20	0.97	1.29	2.28	9.72±1.43	810.10	8.44±0.43	992
Ammonium	1.08	0.10	0.95	−0.32	0.73	2.61±0.36	153.51	2.93±0.24	344
Nitrate (with backup[a])	0.62	0.17	0.54	0.06	0.25	0.60±0.17	68.89	0.54±0.05	63.5
Nitrate (no backup)	0.01	0.03	0.13	0.57	0.63	0.60±0.17	68.89	0.03±0.04	3.5
OC	0.93	−0.14	0.99	0.64	1.14	6.97±1.35	29.05	6.33±0.63	186
EC	2.02	0.03	0.58	−0.51	0.62	0.47±0.48	1.98	0.98±0.33	29.0
TC	0.97	0.12	0.98	0.13	1.03	7.45±1.45	31.03	7.32±0.72	215
Bromine	0.82	1.06	0.88	−0.42	1.15	3.58±1.45	6.63	4.00±0.52	23.5
Calcium	0.79	−2.92	0.89	14.95	26.73	56.1±8.39	7.57	41.1±3.79	54.1
Potassium	0.92	3.00	0.94	7.51	54.82	135±12.3	18.87	128±7.64	168.9
Iron	0.98	−6.39	0.88	7.85	44.62	91.0±15.7	43.35	83.2±5.85	489.3
Silicon	0.84	9.51	0.88	19.61	148.55	175±26.7	17.65	157±17.0	104.6
Titanium	0.45	1.47	0.58	2.73	8.68	7.68±3.21	1.54	4.95±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_R and DRI_F in January and STN_S and DRI_F in July are presented. Slopes and intercepts were calculated with the y-axis = DRI_F and the x-axis = STN_{RS}. Bromine, calcium, potassium, iron, silicon and titanium are reported in units of $ng\,m^{-3}$ and shaded in grey. All other species are reported in units of $\mu g\,m^{-3}$.

[a] Only DRI_F collected nitrate with a front and backup filter.

and STN_S 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 $3.0\,\mu g\,m^{-3}$ offset to the TEOM measurements has brought them closer to those from the STN_S and DRI_F. However, an intercept of -2.24 to $-2.64\,\mu g\,m^{-3}$ (Table 5) indicates that the empirical adjustment for PM_{10} may not fully address volatile losses of $PM_{2.5}$ from the heated inlet at this site. The RMS difference is greater for STN_S–TEOM than DRI_F–TEOM. The STN_S–TEOM average difference is positive and about half of the RMS difference, while the DRI_F–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_S and TEOM measurements. In contrast, deviations between the DRI_F and TEOM

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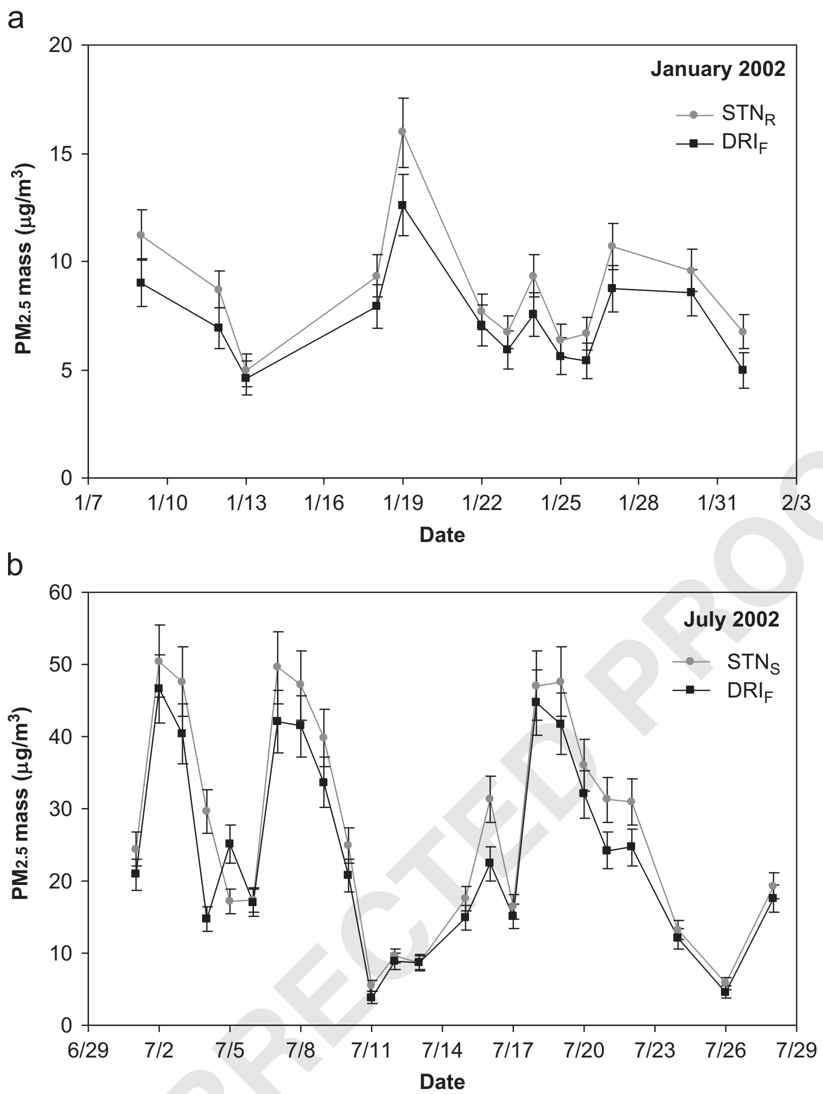

Fig. 2. Time series of $PM_{2.5}$ concentrations measured with STN_{RS} and DRI_F for January (a) and July (b). Error bars represent $\pm 2-\sigma$ uncertainty.

appear to be random in nature (Fig. 3a) and generally fall within 10% of the Deming regression line. Chen (2002); Chen et al. (2002) found similar results when comparing the DRI_F to the TEOM in summer months from 1999 to 2001.

3.3. *Chemical compositions*

Besides gravimetric mass, Tables 3 and 4 show the statistics and comparisons of major contributing species to $PM_{2.5}$ 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_{RS} consistently report higher values than the DRI_F. Since the average deviation is 14–17% for both $PM_{2.5}$ 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., 2006). Chen (2002) show that sulfate mass from DRI_F

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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_F and STN_{RS} for sulfate and mass.

DRI_F and STN_{RS} measure nitrate on different filter substrates behind different denuder configurations (Fig. 1). Comparisons between the front only DRI_F filters and front plus backup DRI_F filters with STN_{RS} have both been made. The nitrate concentrations are well correlated in the winter (without or with backup filter concentrations added), although DRI_F measures only 3–65% of the average 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 STN_R appear to retain much more nitrate than single quartz–fiber filters. Moreover, the DRI_F filters remained in the field for up to 2.5 days longer, and this led to more nitrate loss through volatilization. The DRI_F July average nitrate (on the front filter) is below the $2-\sigma$ uncertainty and most of the nitrate (above the $2-\sigma$ uncertainty) 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 DRI_F nitrate accounts for 6 to 90% of the STN_S (without or with backup filters added). When the DRI_F front and backup nitrate are compared with STN_S, there are no significant differences for the July period (Tables 3b and 4).

Table 4
Percentage of days when the species measured with STN_{RS} and DRI_F were significantly different at the 95% confidence level

	Percentage of significantly different values January (%)	Percentage of significantly different values July (%)
$PM_{2.5}$	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.

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 DRI_F and the STN_R-measured ammonium is negligible. In July the DRI_F monthly average is slightly greater than the 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 STN_S concentration is similar to that of the DRI_F, although the STN_S is slightly larger than the DRI_F. In January, the STN_R concentration is less than 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 DRI_F and STN_S is good in July with an *r*-value of 0.98, much better than the *r*-value of 0.80 between the DRI_F and 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

Table 5
Deming slope, intercept, correlation, and average and RMS difference ($\mu g\,m^{-3}$) for the STN_S versus TEOM, and the 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*
STN_S	TEOM	0.97	16	−2.64	0.95	2.96	5.35	24.06	21.10
DRI_F	TEOM	1.11	16	−2.24	0.95	−0.48	4.28	20.62	21.10

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

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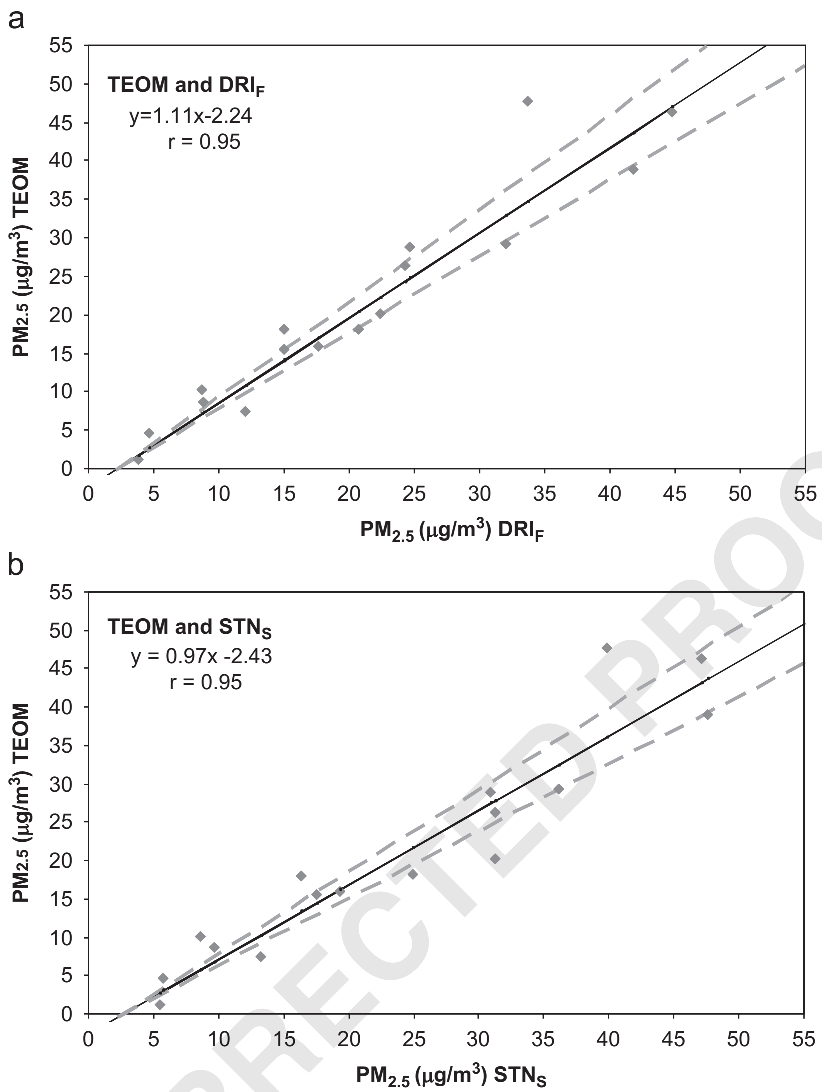

Fig. 3. Comparisons of $PM_{2.5}$ total mass between TEOM and (a) DRI$_F$ and (b) STN$_S$. Deming regression line shown in black, ±10% (of the regression line) shown in broken gray. The TEOM and DRI$_F$ generally agree within experimental error.

be expected. The OC/EC ratio was 5.4 in January, compared with 14.8 in July (based on STN$_{RS}$). This reflects larger secondary organic 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$_{RS}$ EC are generally only ~50% of the DRI$_F$ 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$_{RS}$ 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$_F$ and STN$_{RS}$ 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$_F$ has the largest face velocity (with a flow rate of $20\,\mathrm{L\,min^{-1}}$) for OC collection, followed by STN$_R$ and STN$_S$ (with flow rates of $\sim 7\,\mathrm{L\,min^{-1}}$). In July the average DRI$_F$ OC and TC are smaller than the

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STN_S, 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_F filters that were left in the field for a longer time period. However, in January the DRI_F TC is larger than the STN_R. 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_R sampler showed relatively high OC. The STN_R field blank OC was on average 50% of the non-blank corrected OC, while the STN_S and DRI_F field blank OC was on average 20% of the non-blank corrected OC. The winter STN_R 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_S generally reports larger crustal species concentrations than DRI_F does, consistent with the situation for $PM_{2.5}$ mass and sulfate. The smaller DRI_F concentration could be reflected by either a small DRI_F/STN_S slope (<1) or a negative intercept (Table 3). STN_{RS} and DRI_F 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 and Neil, 2006). To reconstruct the $PM_{2.5}$ 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 and Neil, 2006) as shown below:

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

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_F reconstructed mass. The carbon concentration is not corrected by backup filters (but is blank corrected).

The reconstructed mass from the DRI_F 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_S. The July DRI_F reconstructed $PM_{2.5}$ mass overestimates the gravimetric mass by 6% while the STN_S reconstructed mass underestimates the gravimetric mass by just 3%. For STN_R in January, the average measured and reconstructed mass differ by less 2%, although their correlation is not as good

Table 6
Average reconstructed mass for STN_{RS} and DRI_F for January and July (units are in $\mu g\,m^{-3}$)

	Average gravimetric mass	Average reconstructed mass	RMS difference	Average difference (gravimetric-reconstructed)	Slope	Intercept	Correlation (r)
January							
DRI_F	7.3	8.8	1.7	−1.5	1.2	0.38	0.94
STN_R	8.8	8.9	1.7	−0.12	0.93	0.73	0.80
July							
DRI_F	24.1	25.5	2.1	−1.4	0.99	1.5	0.99
STN_S	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).

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($r = 0.80$). Histograms of the difference between the gravimetric and reconstructed masses (i.e., the residuals) are shown in Fig. 4. In January, the DRI_F residuals are shifted negatively from the normal distribution, with a mode at $-1\,\mu g\,m^{-3}$. The STN_R residuals have a mode at zero and an apparent outlier, which explains the poorer correlation. There is better overlap between the DRI_F and STN_S residuals in July, but the DRI_F residuals are still less than STN_S residuals.

Fig. 5 shows the contributions of sulfate, organic matter ($OM = OC \times 1.8$), EC, ammonium, nitrate, crustal mass and the sum of all other species, to total mass (the relative contribution) as well as the ratios of DRI_F/STN_{RS} relative contribution. Here nitrate from the front and backup filter of DRI_F was used. In January and July, STN_{RS} report larger sulfate concentrations, but the relative contribution of sulfate to total mass is similar for STN_{RS} and DRI_F (shown by the ratios of relative contribution [DRI_F/STN_{RS}] being close to unity in Fig. 5). A systematic bias explains 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, DRI_F reports more OM concentration than STN_R and the relative contribution of OM to total mass from DRI_F is greater than that from STN_R. In July, DRI_F reports less OM concentration than STN_S and the relative contribution of OM to total mass from DRI_F is greater than that from

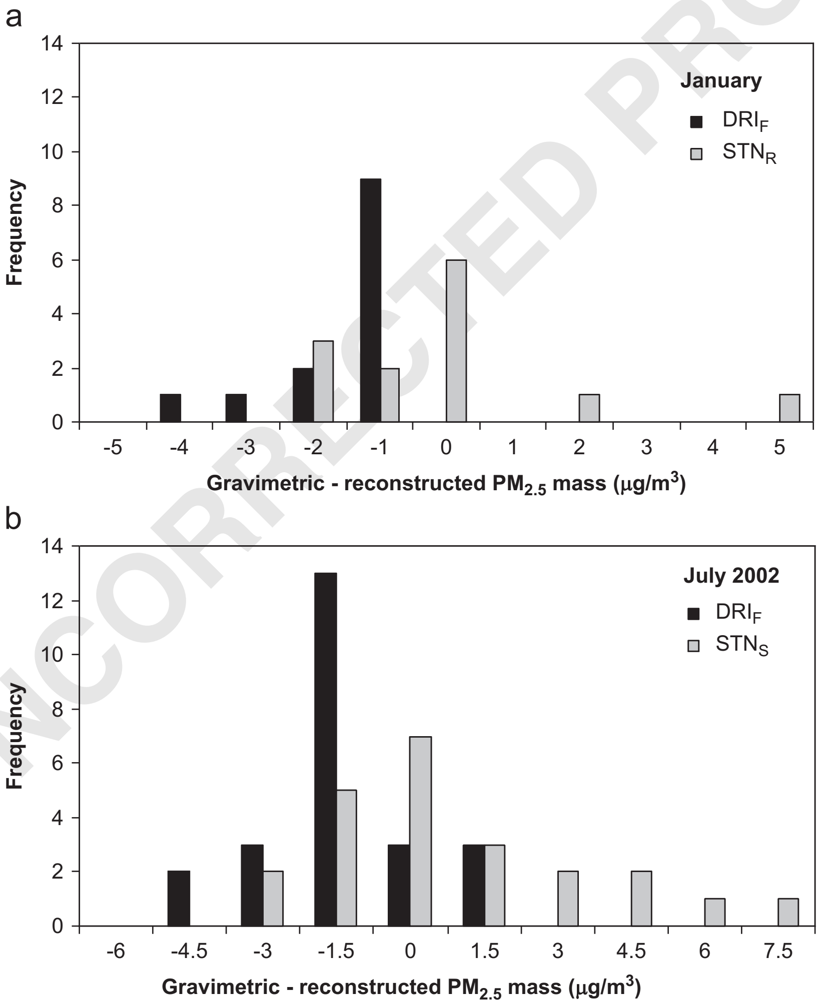

Fig. 4. Frequency distribution of gravimetric—reconstructed differences (residuals), for January DRI_F and STN_R and July DRI_F and STN_S.

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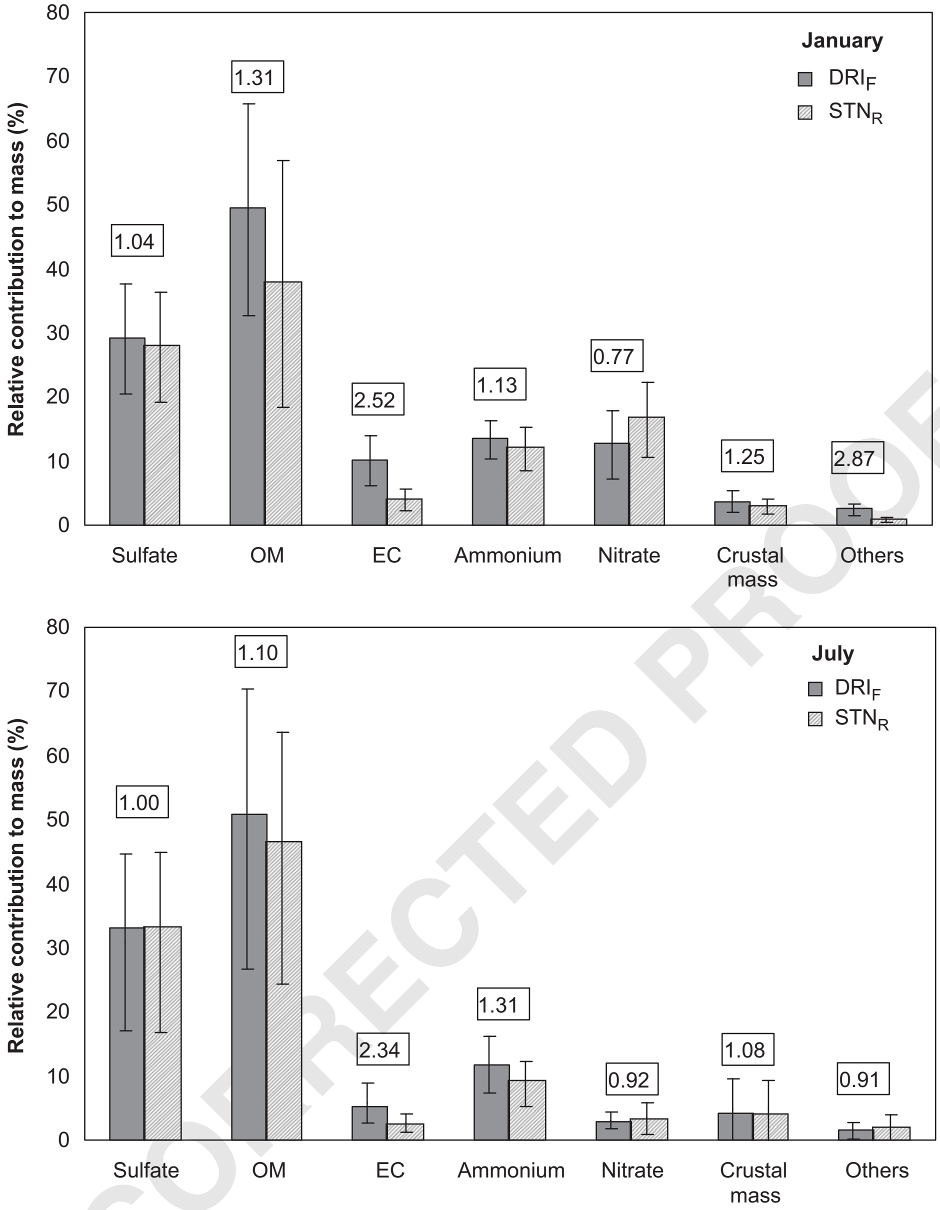

Fig. 5. Contributions of individual species to $PM_{2.5}$ mass (relative contribution) for (a) January and (b) July. Numbers in boxes are the DRI_F relative contribution divided by STN_{RS} relative contribution. Error bars represent the standard deviation of the relative contributions.

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 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.

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4. Conclusions

Measurements from the DRI and RTI analyzed samplers (DRI_F versus STN_R and DRI_F versus STN_S) at Fort Meade, MD were generally well correlated. $PM_{2.5}$, sulfate, OC, TC and ammonium all had *r*-values in excess of 0.8. The STN method, however, reported larger $PM_{2.5}$ mass than the DRI method by 14–17%. 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 $PM_{2.5}$ 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 $PM_{2.5}$ 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 $PM_{2.5}$ 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_F measurements were substantially smaller than those from the STN_R 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_{RS} nylon filters retained more nitrate than the DRI_F quartz filters (e.g. Frank and Neil, 2006). At FME this problem was mitigated somewhat because DRI_F used backup filters. Residuals of gravimetric—reconstructed mass were generally small and negative for both DRI_F and STN_{RS}. 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 $PM_{2.5}$ 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 $PM_{2.5}$, 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.

5. Uncited reference

Chen et al., 2001.

Acknowledgments

This work was supported in part by the Constellation Energy Group, Baltimore Gas and Electric Company and Potomac Electric Power Company through the Electric Power Research Institute and Maryland Industrial Partnerships. From the initiation to the end of the MARCH-Atlantic study Dr. Peter K. Mueller of EPRI and TropoChem contributed to its design and accomplishments. The authors thank Maryland Department of the Environment for support at the sampling site and Dr. Judith C. Chow and Mr. Steve Kohl at DRI and Dr. R.K.M. Jayanty at RTI for organizing chemical analysis. Reviewers' comments are greatly appreciated.

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