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Evaluation of the RAMS Continuous Monitor for Determination of $PM_{2.5}$ Mass Including Semi-Volatile Material in Philadelphia, PA

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ABSTRACT

The real-time ambient mass sampler (RAMS) is a continuous monitor based on particle concentrator, denuder, drier, and tapered element oscillating microbalance (TEOM) monitor technology. It is designed to measure $PM_{2.5}$ mass, including the semi-volatile species NH_4NO_3 and semi-volatile organic material, but not to measure $PM_{2.5}$ water content. The performance of the RAMS in an urban environment with high humidity was evaluated during the July 1999 NARSTO-Northeast Oxidant and Particles Study (NEOPS) intensive study at the Baxter water treatment plant in Philadelphia, PA. The results obtained with the RAMS were compared to mass measurements made with a TEOM monitor and to constructed mass obtained with a Particle Concentrator-Brigham Young University Organic Sampling System (PC-BOSS) sampler designed to determine the chemical composition of fine particles, including the semi-volatile species. An average of 28% of the fine particulate material present during the study was semi-volatile organic material lost from a filter during particle collection, and 1% was NH_4NO_3 that was also lost from the particles during sampling. The remaining mass was dominantly nonvolatile $(NH_4)_2SO_4$ (31%) and organic material (37%), with minor amounts of soot, crustal material, and nonvolatile NH_4NO_3. Comparison of the RAMS and PC-BOSS results indicated that the RAMS correctly monitored for fine particulate mass, including the semi-volatile material. In contrast, the heated filter of the TEOM monitor did not measure the semi-volatile material. The comparison of the RAMS and PC-BOSS data had a precision of ±4.1 μg/m^3 (±9.6%). The precision of the RAMS data was limited by the uncertainty in the blank correction for the reversible adsorption of water by the charcoal-impregnated cellulose sorbent filter of the RAMS monitor. The precision of the measurement of fine particulate components by the PC-BOSS was ±6–8%.

IMPLICATIONS

The RAMS is specifically designed to measure total fine particulate material, including the semi-volatile components. Comparison of the RAMS, TEOM monitor, and integrated sampler results during the summer in Philadelphia indicated that an average of 28% of the fine particulate material present during the study was semi-volatile organic material that was lost from a filter during particle collection, and 1% was NH_4NO_3 that was also lost from the particles during sampling. Sampling with a TEOM monitor or a conventional single-filter sample will tend to underestimate the importance of these semi-volatile species to total fine particulate mass. Correspondingly, the fractional contribution of stable fine particulate species, such as SO_4^{2-}, will be overestimated.

INTRODUCTION

Recent epidemiologic studies have implied that fine particles (<2.5 μm aerodynamic diameter) are strongly associated with observed health effects. This may be because of their composition and because they can deposit deep in the lung.[1-5] In an analysis of data from 151 U.S. metropolitan areas, controlling for smoking, education, and other risk factors, Pope et al.[4] concluded that increased risk for cardiopulmonary disease, lung cancer, and mortality was associated with SO_4^{2-} and fine particulate air pollution at concentrations commonly found in U.S. cities. On July 18, 1997, the U.S. Environmental Protection Agency (EPA) published a $PM_{2.5}$ standard based on research available at that time.[5] The new standard included two new primary $PM_{2.5}$ standards: an annual standard for $PM_{2.5}$ of 15 μg/m^3 and a daily, or 24 hr, standard of 65 μg/m^3. A Federal Reference Method (FRM) for fine particulate monitoring was also instituted to implement the new $PM_{2.5}$ standard.[6-8] The $PM_{2.5}$ FRM is an integrated, single-filter sampling method with gravimetric determination of the collected mass.

Fine particles in urban atmospheres contain substantial amounts of semi-volatile materials [such as NH_4NO_3 and semi-volatile organic compounds (SVOCs)], which are lost from particles during sampling on a filter.[9-13] The extent to which these species will be lost during sampling with conventional integrated and continuous single-filter samplers, such as the FRM and tapered element oscillating microbalance (TEOM) monitor, is not well known. However, it can be expected that these samplers will

undermeasure $PM_{2.5}$ in any environment where a significant concentration of semi-volatile particulate material is present. These semi-volatile fine particulate components can be sampled more accurately using diffusion denuder techniques.

The hypothesis of the study reported here was that fine particulate mass would be significantly underdetermined in urban environments using the traditional methods, such as the $PM_{2.5}$ FRM sampler and the TEOM monitor, because of the loss of semi-volatile material from particles during sampling. It is postulated that fine particulate mass, including the semi-volatile fine particulate species, is an appropriate surrogate for the components of fine particles that have been associated with observed mortality and morbidity effects in epidemiologic studies. Underdetermination of these semi-volatile species will tend to overemphasize the importance of nonvolatile fine particulate components such as SO_4^{2-}. Real-time sampling methods not only reduce the operating costs as compared with integrated samplers, but they also provide hourly information for use in evaluating control strategies and in epidemiologic studies. The need is recognized for real-time sampling methods that accurately measure $PM_{2.5}$, including the semi-volatile constituent NH_4NO_3 and semi-volatile organic material, for use in $PM_{2.5}$ research or exposure monitoring.

A $PM_{2.5}$ real-time ambient mass sampler (RAMS) has been developed for the determination of fine particulate mass, including particulate semi-volatile material.[14-17] The RAMS combines diffusion denuder, Nafion drier, and TEOM monitor technologies whereby particles are collected on a sorbent "sandwich" filter on the tip of the TEOM monitor. Because the RAMS can determine total particulate mass including the semi-volatile components, total $PM_{2.5}$ mass determined by the RAMS[13-16] was higher than concentrations determined by a collocated TEOM monitor. The $PM_{2.5}$ mass determined by the RAMS was also higher than $PM_{2.5}$ FRM results and was consistent with Particle Concentrator-Brigham Young University Organic Sampling System (PC-BOSS) data.[14-17]

The PC-BOSS[14,18] is an integrated diffusion denuder sampler developed to routinely chemically characterize fine particulate material, including semi-volatile components.[9-11] Previous studies using the PC-BOSS at Riverside, CA,[9,10] and Bakersfield, CA,[11] indicated that the PC-BOSS can accurately determine $PM_{2.5}$ total mass including semi-volatile material, and that the $PM_{2.5}$ FRM undermeasured total $PM_{2.5}$ mass in these studies by 20–40%. The loss of semi-volatile material from particles collected on filters during sampling in these studies was dominated by the loss of SVOCs, which accounted for ~80% of the total loss. The efficiency of the particle concentration in the PC-BOSS particle concentrator in these studies was obtained with data from other samplers.[9-11] A new configuration of the PC-BOSS[12,13] that directly determines the collection efficiency of and particle loss in the particle concentrator was developed to solve this problem. Any water present in ambient particles was expected to be lost from the Teflon filter of the PC-BOSS (or an FRM sampler). Water also would be lost from the particles collected on the heated TEOM filter and from the RAMS filter after operation of the Nafion driers of the RAMS. Thus, the $PM_{2.5}$ composition results given in this paper do not include water present in the particles in the ambient atmosphere.

The initial version of the RAMS[14] was tested in the field in Riverside and Bakersfield.[16] Based on the results obtained there, the RAMS was modified and then tested in Provo, UT.[15] These studies indicated that a continuous blank measurement was needed and that the blank would be expected to be sensitive to relative humidity. Philadelphia, PA, was selected as a field-sampling site to further evaluate the modified RAMS because Philadelphia is a typical polluted eastern city with high humidity in the summer. Reported $PM_{2.5}$ concentrations in Philadelphia are generally above the $PM_{2.5}$ standard annual average, with generally high SO_4^{2-}, moderate carbon, and low NO_3^- concentrations.[19,20] In addition, the modified RAMS was tested in Atlanta, GA, during the Supersite study.[17] This paper reports the evaluation of the continuous total $PM_{2.5}$ mass monitor (RAMS) by comparison with data from the PC-BOSS and TEOM monitors during July 1999, in Philadelphia, PA, during the NARSTO-NEOPS study.[21]

EXPERIMENTAL

RAMS

The configuration of the modified RAMS has been previously detailed,[15] as shown in Figure 1. The RAMS has both a monitor and an active blank sampler. The monitor has eight parts:

(1) a combined impactor-particle concentrator inlet to separate the fine particles (2.5 µm) from coarse particles and from 70% of the sampled gas stream;
(2) two triethanolamine-coated annular denuders to remove O_3 and NO_2;
(3) a Nafion drier to remove gas-phase water;
(4) a charcoal-impregnated multi-parallel filter diffusion denuder (small BOSS denuder) to remove gas-phase semi-volatile organic material, HNO_3, NH_3, SO_2, and oxidants (such as O_3 and H_2O_2), which can interfere with the measurement of fine particulate mass. This denuder was heated (to ~30 °C) to minimize the absorption of water by the charcoal-impregnated cellulose filter (CIF) strips that formed the denuder surface;
(5) one triethanolamine-coated annular denuder to remove any NO_2 formed from nitric oxide on the charcoal of the BOSS denuder;

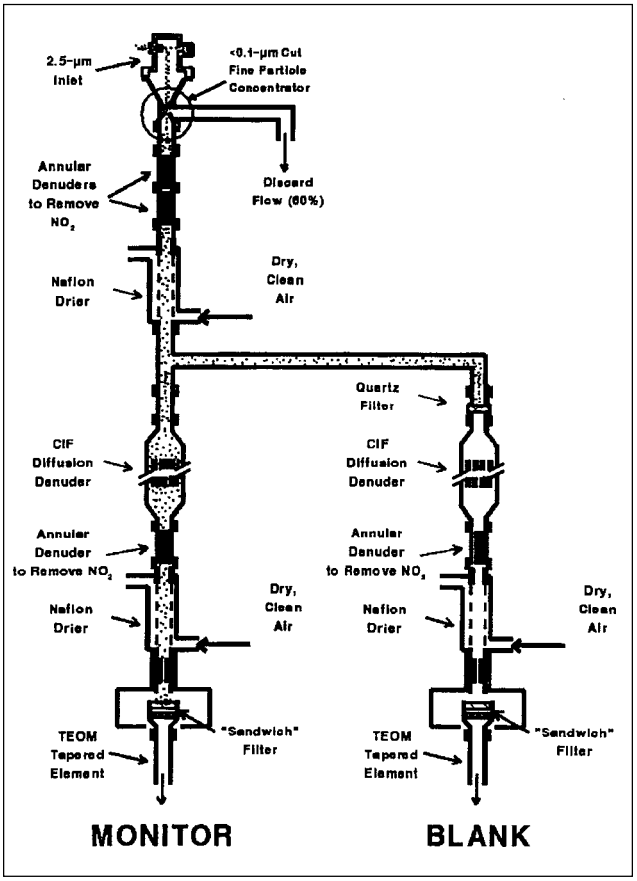

Figure 1. The RAMS, showing both the monitor and active blank samplers, taken from Obeidi and Eatough.[15]

(6) a final Nafion drier to remove gas-phase water from the sampled air stream;

(7) a sandwich filter (a Teflon-coated quartz filter followed by a CIF) to collect fine particles and semi-volatile species that can be lost from the particles during sampling. The temperature of the sandwich filter was maintained at 30 °C. The ability of the RAMS to accurately monitor a nonvolatile aerosol $[(NH_4)_2SO_4]$[22] and the ability of the CIF to trap semi-volatile material in both chamber[22] and field studies[9-12,19] have been previously published; and

(8) a TEOM monitor to measure the rate of collection of fine particulate material by the sandwich filter.

The first three components of the sampler were identical for both the active blank sampler and the monitor. After the first Nafion drier, the flow stream was split, half entering the remainder of the monitor system. The second half passed through a 47-mm quartz fiber filter to remove particles and then through components identical to components 4–8 of the monitor to provide a particle-free sample steam for the active blank sampler. The RAMS monitor data were corrected for this active blank measurement.[15,17] The blank correction measured in Philadelphia varied from 81 to –22 µg/m^3 and averaged 9 µg/m^3. This corresponded to from 270 to 0% of the RAMS measurement, averaging 79% of the RAMS value. Subsequent to the research reported here, it has been shown that the blank variability can be reduced by one order of magnitude using a glass, rather than a cellulose, charcoal-impregnated filter.[17] This alteration to the RAMS design has been made in subsequent applications of the RAMS.

TEOM

The TEOM monitor is a commercial product of Rupprecht and Patashnick, Inc., based on the design of Rupprecht and Patashnick.[23] The TEOM monitor uses a single heated filter (50 °C in this study) for the continuous determination of $PM_{2.5}$ mass. Data from the TEOM monitor were provided by the Harvard School of Public Health.

PC-BOSS

Combining the technology used in the BOSS and the Harvard particle concentrator has helped develop the PC-BOSS.[9-12,18] The PC-BOSS configuration used in this study[12] is shown schematically in Figure 2. The inlet to the sampler was a Bendix cyclone with a particle cut of 2.3 µm aerodynamic diameter at an inlet flow of 150 L/min.[24] After the cyclone, the flow was split into two channels,

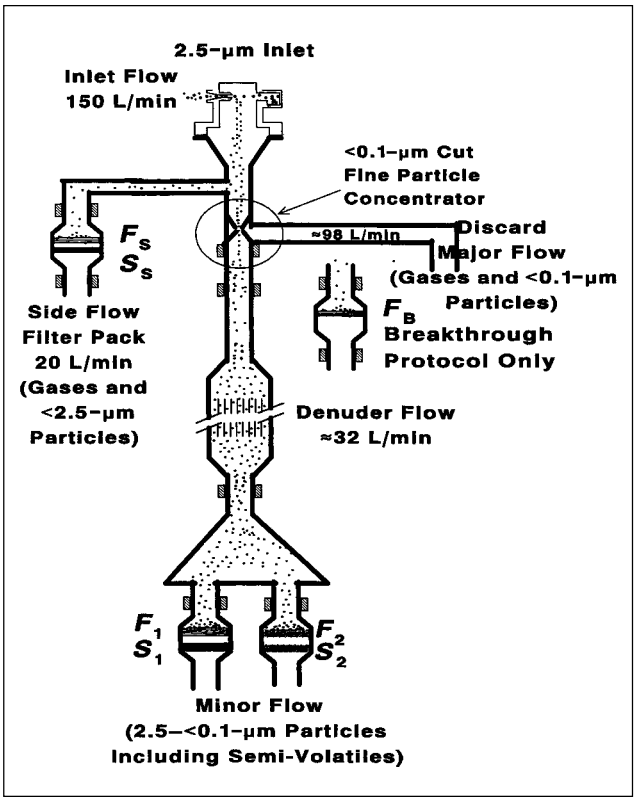

Figure 2. The PC-BOSS. F_S/S_S is the side-flow filter pack containing a Nuclepore or Teflon filter followed by a CIF sorbent filter. F_1/S_1 and F_2/S_2 are the quartz and CIF filter pack and Teflon and Nuclepore filter pack, respectively, of the minor flow. The F_B filter pack was used for diffusion denuder breakthrough experiments.

one a side flow of 20 L/min. The 20-L/min side-flow channel entered a filter pack containing a Teflon or Nuclepore filter (F_s in Figure 2) to collect particles, followed by a CIF (S_s) to determine gas-phase organic material. The data obtained with this filter pack were used to evaluate the collection efficiency of and losses in the particle concentrator of the PC-BOSS, total gas-phase SVOC concentrations, and crustal material in particles. Nuclepore filters were used to determine particulate crustal material using proton-induced X-ray emission (PIXE) analysis. The remainder of the flow (130 L/min) entered a slotted virtual impactor particle concentrator. The design[25] and evaluation[18] of the particle concentrator have been described previously. The particle concentrator removed 75% of the gas-phase material into the major flow and left particles larger than the cut point (~0.1 μm)[18] along with a significantly reduced fraction of the gas-phase material in the minor flow. The concentrator had a 9.5-cm-long slit with a distance between the accelerator and receiver slits 1.5 times the acceleration slit width of 0.32 mm.

The minor flow (25% of the total 130 L/min flow) containing concentrated particles entered the BOSS diffusion denuder,[26,27] composed of 15 (4.5 × 58 cm) strips of Schleicher and Schuell, Inc. CIF paper, which were separated at the long edges by 2-mm glass rods. The denuder was followed by two parallel filter packs (see Figure 2). The F_1/S_1 filter pack, containing a 47-mm quartz filter (Pallflex, prefired) followed by a 47-mm CIF (Schleicher and Schuell, Inc.), was used to determine fine particulate SO_4^{2-}, NO_3^-, and carbonaceous material including SVOCs and NO_3^- lost from particles during sampling. The second filter pack (F_2/S_2) contained 47-mm Teflon (Gelman, Zefluor) and Nylon (Gelman Nylasorb) filters to determine mass, SO_4^{2-}, and NO_3^-, including any NO_3^- lost from particles during sampling.[9-12]

Sample Collection

Samples were collected from July 2 to July 31, 1999, at the NARSTO-NEOPS site at the Philadelphia Baxter water treatment plant.[21] Samples were collected each day from 8:00 a.m. to 10:00 a.m. EST, from 10:00 a.m. to 8:00 p.m. EST, and from 10:00 p.m. to 8:00 a.m. EST the next day using a PC-BOSS (see Figure 2). A RAMS and a TEOM monitor were operated continuously during the study. A collocated second PC-BOSS was used for several purposes during the sampling program. For four days of the study, the second PC-BOSS was used to measure the gas-phase SVOCs not removed by the denuder. In these experiments, a quartz filter was placed in the minor flow past the particle concentrator but before the denuder (F_B in Figure 2). During these days, filter samples for the determination of gas-phase SVOCs were also collected in the side-flow filter pack. For the remaining collocated samples, both PC-BOSSes were run with the configuration shown in Figure 2. Samples were collected on the same schedule as the main PC-BOSS for 5 days. For an additional 8 forecast episode days, samples were collected with the second PC-BOSS on a more frequent schedule. During these episode sampling periods, five samples (8:00 a.m. to 10:00 a.m. EST, 10:00 a.m. to 3:00 p.m. EST, 3:00 p.m. to 8:00 p.m. EST, 10:00 p.m. to 3:00 a.m. EST the next day, and 3:00 a.m. the next day to 8:00 a.m. EST the next day) were collected with the second PC-BOSS. Sample flows were all audited with calibrated mass flow meters, rotameters, and dry gas meters. Precision of the flow data was ±5%. The sample volumes and concentrations were calculated for standard concentrations at 25 °C and 1 atm. Field blank samples were obtained for 10% of all collected samples.

Sample Analysis

All quartz filters were prefired by heating to 800 °C for 4 hr prior to use. The Zefluor (Gelman Science), Teflon (Whatman Inc.), Nuclepore, and Nylasorb (Gelman Science) filters were used as received from the manufacturers. The Teflon filters in the minor flow of the PC-BOSS and in the side flow of the PC-BOSS (see Figure 2) were weighed before and after sampling to determine collected fine particulate mass. The Nuclepore, CIF, Teflon, and quartz filters were stored in individual petri dishes (Millipore) at 0 °C in the field and at –30 °C after being returned to Brigham Young University (BYU). Nylasorb filters were stored in a monovette (Starstedt) under the same temperature storage conditions.

One 2-cm^2 punch of the PC-BOSS quartz filters was extracted by ultrasonication with 5 mL deionized water. The extraction solution was analyzed by ion chromatography (IC) for SO_4^{2-} and NO_3^-. Half of each Nuclepore filter and all of the Teflon and Nylasorb filters were extracted by ultrasonication with 10 mL deionized water or IC eluent (for the Nylasorb filter) and analyzed by IC for NO_3^- and SO_4^{2-} using a Dionex 500 with IonPac AS 14+IonPac AG14E columns; analytic conditions were 3.5-mM $NaHCO_3$/1.0-mM $NaHCO_3$ eluent and a flow rate of 1.2 mL/min. The suppressor was an anion self-regeneration suppressor-1, and ions were measured with a CD20 conductivity detector.

One 2-cm^2 punch of each quartz and CIF filter was analyzed for total carbonaceous material by temperature-programmed volatilization (TPV). CIF filter samples were continuously heated from 40 to 300 °C in an N_2 atmosphere at a temperature ramp rate of 10 °C/min. Quartz filters were heated from 40 to 800 °C in an N_2/O_2 (80/20) atmosphere at a temperature ramp rate of 28 °C/min. Soot was estimated as the high temperature peak (>450 °C) in the TPV thermgram[10,27] for samples where the soot peak could be resolved from other evolved carbon peaks. Blank

corrections were applied for each type of filter. The SO_4^{2-} data were used to evaluate the efficiency of and losses in the PC-BOSS particle concentrator.[9-12]

Analysis of data obtained in Atlanta during August 1999[13] indicated that the distance between the transition from the inlet to the point where the side flow was removed (see Figure 2) was not great enough to allow for complete equilibration across the sample stream. As a result, the side-flow SO_4^{2-} concentrations were high by 15%.[13] This factor was used to correct the side-flow date for the Philadelphia study. This problem has been corrected in subsequent studies with the PC-BOSS by adding a flow equilibration chamber before the side flow is removed.

Concentrations of trace elements in collected particles on the Nuclepore filter were determined using PIXE analysis. The half of the Nuclepore filter not used for the determination of anions by IC was placed directly in the proton beam, which covered an area corresponding to ~10% of the total collected sample. Details of the PIXE analysis and data reduction techniques have been published.[28]

RESULTS AND DISCUSSION

The concentrations of nonvolatile particulate species collected by the PC-BOSS may be calculated two ways:[12] from the side-flow data or from the minor flow data and the overall concentrator efficiency for a given species

$$C = C_{\text{Minor}}/E_{\text{pc}} \tag{1}$$

where C_{Minor} is the concentration of the species determined from the minor flow filters, F_1 or F_2 in Figure 2, and E_{pc} is the efficiency for concentration of the species in the minor flow. A small (4–8%) percentage of particles is lost by deposition in the particle concentrator during sampling[9,11] and must be corrected for. The side-flow channel in the new PC-BOSS configuration (see Figure 2) is designed to independently determine nonvolatile particulate material, such as SO_4^{2-} and soot, to obtain the combination of the particle concentrator collection efficiency and the particle loss correction. The side-flow data were adjusted by 15%, as discussed previously. The combination of particle concentrator efficiency and losses was calculated by a linear regression fit of the data to

$$E_{\text{pc}} = C_{\text{Minor}}/C_{\text{Side}} \tag{2}$$

where C_{Side} is the concentration determined on the F_S filter in the side flow, as shown in Figure 2. The concentrations of particulate semi-volatile species could only be calculated using eq 2 because the positive and negative artifacts present in the particulate material measurement in the side flow were unknown. Pang et al.[10] and Lewtas et al.[12] concluded that the use of the concentrator efficiency and the PC-BOSS minor-flow concentration to calculate the total $PM_{2.5}$ concentration is generally applicable. The concentrations of all $PM_{2.5}$ species determined with the PC-BOSS given in this paper are based on eq 1.

The precision and accuracy of the data obtained with the PC-BOSS were evaluated by comparing both the results obtained for the two minor-flow filter packs and for two collocated PC-BOSSes and the results obtained with the PC-BOSS and the other samplers used in the study. The standard deviation between each compared data set was calculated by

$$\sigma = \left[\frac{1}{2N}\sum_{i=1}^{N}\left(C_{1,i} - C_{2,i}\right)^2 - \left(\overline{C}_1 - \overline{C}_2\right)^2\right]^{\frac{1}{2}} \tag{3}$$

where $C_{1,i}$ and $C_{2,i}$ are concentrations of the chemical species of interest and $\overline{C}_1$ and $\overline{C}_2$ are the average for each replicate set. The $(\overline{C}_1 - \overline{C}_2)^2$ term corrects the standard deviation for bias between the two replicate data sets. The percent precision for the replicate sets was calculated from

$$\sigma_{\%} = \frac{\sigma}{\frac{1}{2}\left(\overline{C}_1 - \overline{C}_2\right)} \times 100 \tag{4}$$

Each data set was also compared by linear regression analysis. In these analyses, both the regression-calculated intercept and a slope with a zero intercept were calculated. The results of these various statistical analyses are given in Table 1.

Collection Efficiency of the Particle Concentrator

The collection efficiency of the particle concentrator should be evaluated for each sampling site because different environmental conditions and particle size distributions will affect the performance of the particle concentrator.[13,18,25] SO_4^{2-} is a stable species in particles and is easily and accurately determined by IC. The collection efficiency (includes particle losses in the concentrator) of the concentrator of the main PC-BOSS (A) for SO_4^{2-} was 50 ± 1%. The collection efficiency of the concentrator for the other collocated PC-BOSS sampler, PC-BOSS (B), was comparable, at 52 ± 1%. These results also agreed with results reported by Lewtas et al.[12] and Modey et al.[13] with the same configuration of the PC-BOSS.

The NO_3^- and SVOCs on the backup filters (Nylasorb and CIF, see Figure 2) were assumed to originate only from losses from the collected particulate matter on the front Teflon (F_2) and quartz (F_1) filters in the minor flow of the PC-BOSS samplers because the removal efficiency of the combination of the particle concentrator and BOSS denuder for gas-phase SVOCs, SO_2, and HNO_3 was expected

Table 1. Results of the statistical analysis of 10-, 5-, and 2-hr samples during the 4-week study.

X vs. *Y*	*n*[a]	r^2	Slope[b]	Intercept µg/m³[a]	*X* Average µg/m³	*X-Y* Bias µg/m³	σ µg/m³	σ%
PC-BOSS A $PM_{2.5}$	70	0.98	1.00 ± 0.01	0 ± 0.8	8.3	0.1	0.5	6.3
Teflon vs. quartz SO_4^{2-}	(1)	0.99	1.01 ± 0.02	0.2 ± 0.8				
PC-BOSS A vs. B	17	0.98	1.03 ± 0.02	0 ± 1.0	8.9	0.2	0.7	8.1
SO_4^{2-} $PM_{2.5}$	(1)	0.98	1.10 ± 0.04	–0.9 ± 0.9				
PC-BOSS vs. Harvard	75	0.89	1.00 ± 0.02	0 ± 1.9	7.4	–0.4	1.3	17.
$PM_{2.5}$ SO_4^{2-}	(5)	0.90	0.91 ± 0.04	1.0 ± 1.8				
PC-BOSS minor nonvolatile	36	0.63	0.86 ± 0.03	0 ± 6.3	30.1	3.8	NA[d]	NA[d]
mass vs. TEOM mass[c]	(7)	0.64	0.76 ± 0.10	3.4 ± 6.3				
PC-BOSS nonvolatile	53	0.85	1.04 ± 0.03	0 ± 5.7	27.9	–1.2	3.9	13.8
constructed vs. Teflon	(5)	0.85	1.05 ± 0.06	–0.1 ± 5.7				
measured mass								
PC-BOSS mass vs. RAMS	46	0.72	0.99 ± 0.02	0 ± 6.0	43.2	0.4	4.1	9.6
$PM_{2.5}$ mass[e]	3	0.74	0.88 ± 0.08	4.8 ± 5.9				

[a]Number of data pairs in statistical analysis. The value in ( ) is the number of samples not included in the analysis, because of identifiable problems with the data or missing dates, which did not allow calculation of constructed mass; [b]Slopes are given for (1) zero intercept and (2) calculated intercept; [c]PC-BOSS minor nonvolatile mass is nonvolatile $PM_{2.5}$ constructed mass and TEOM mass is $PM_{2.5}$ measured mass; [d]σ could not be calculated because the sampler bias was greater than σ; [e]PC-BOSS mass is $PM_{2.5}$ constructed mass and RAMS mass is $PM_{2.5}$ measured mass.

to be essentially 100%.[9-12,18] The removal efficiency of the particle concentrator and BOSS denuder for gas-phase organic material in this study was 99.6 ± 0.9%.

Determination of SO_4^{2-}

The probable precision and accuracy of the PC-BOSS could be evaluated from appropriate comparisons of the SO_4^{2-} data. SO_4^{2-} was determined on both the quartz and Teflon minor-flow filters of the PC-BOSS (see Figure 2). These data were in agreement (see Table 1) with a precision of ±0.5 µg/m³, ±6.3%. Similarly, the SO_4^{2-} determined from the collocated PC-BOSS agreed (see Table 1) with a precision of 0.7 µg/m³, ±8.1%. The slope for the comparison of PC-BOSS SO_4^{2-} with SO_4^{2-} determined by the Harvard School of Public Health using a Harvard-EPA Annular Denuder Sampler (HEADS) was unity (see Table 1) with a somewhat higher uncertainty, ±1.3 µg/m³, ±17%.

Contribution of Crustal Material

The contribution of crustal material (Si, Al, Ca, Fe, Mn, Ba, K, Ti, Sr, etc.) to $PM_{2.5}$ fine particulate mass is generally expected to be small. The $PM_{2.5}$ crustal material was estimated from the Fe and Si data using crustal abundance data. The estimated concentration of crustal material varied from 0.4 to 4.5 µg/m³ and averaged 0.8 µg/m³.

Chemical Composition of Fine Particles

The major components of the $PM_{2.5}$ fine particles— SO_4^{2-} compounds, NO_3^- compounds, organic material (including any SVOCs and NO_3^- lost from the particles during sampling), and elemental carbon (soot)—were determined by TPV and IC analysis of the collected PC-BOSS samplers. The average pH of the extracts of collected particles in the Philadelphia study was 5.6 and varied from 4.3 to 7.5. This corresponded to negligible acid SO_4^{2-} compounds in the samples. Therefore, the SO_4^{2-} and NO_3^- were assumed to be present as $(NH_4)_2SO_4$ and NH_4NO_3, respectively. The TPV-determined soot was assumed to contain only C. The remaining carbonaceous material was assumed to be 62.5% C.[29] The results of these compositional analyses are given in Figures 3 and 4.

The dominant components of the $PM_{2.5}$ were $(NH_4)_2SO_4$ and organic material. These components accounted for 43 and 51% of the nonvolatile $PM_{2.5}$ mass, respectively. An average of 44% of the particulate organic material was lost from collected particles on the Teflon or quartz filters during sampling, which would cause a significant negative artifact in single-filter results. This result is comparable to previously published results.[9-12,17,26,27] The sample-to-sample loss of particulate semi-volatile organic material during sampling (see Figure 3) varied from

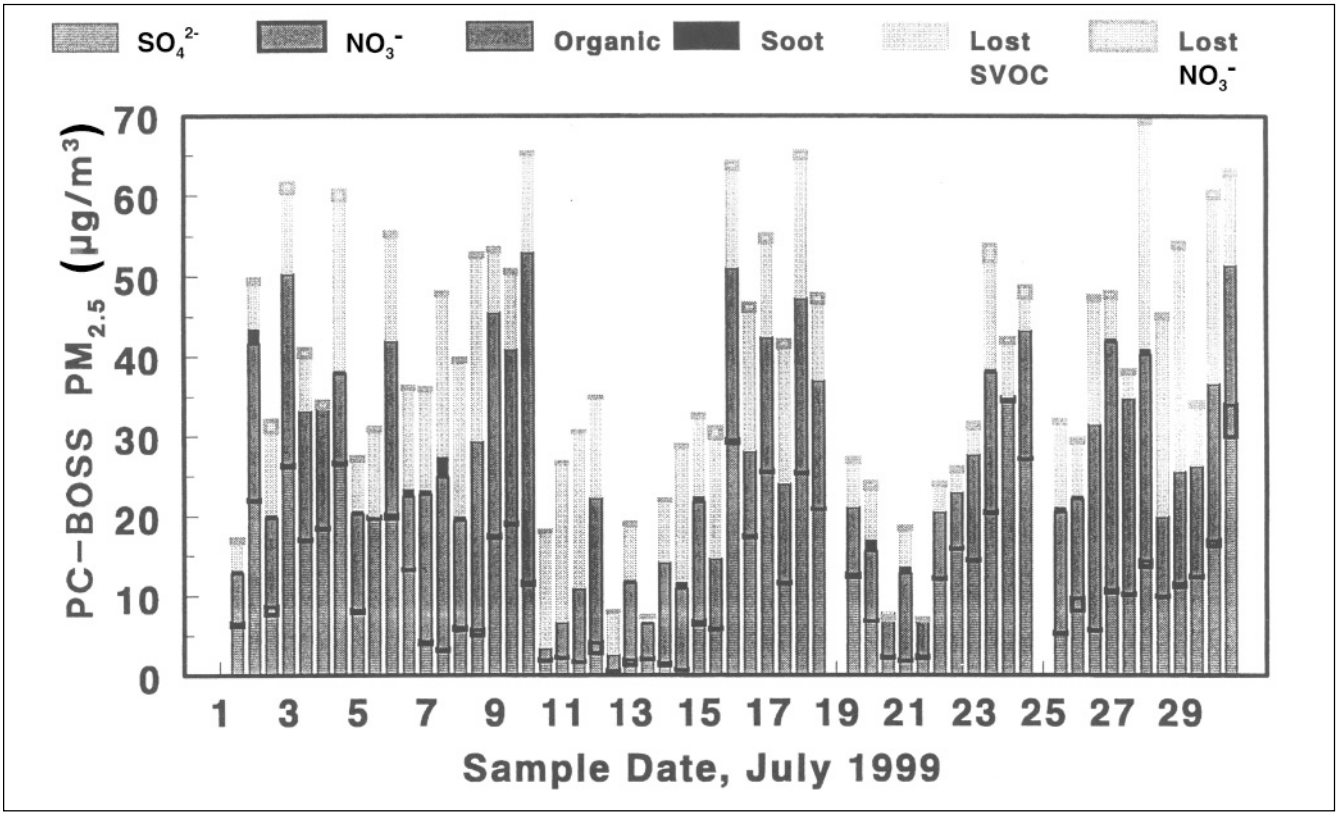

Figure 3. Composition of $PM_{2.5}$ for PC-BOSS 10-hr samples. SO_4^{2-} and NO_3^- were assumed to be present as the NH_4^+ salts, and organic material was assumed to be 62.5% C; see text. Crustal material is not included because it was only measured for samples where RAMS data were available. For these samples, crustal material averaged 0.8 µg/m³.

negligible to 28 µg/m³. Concentrations of particulate NO_3^- were low. However, an average of 60% of the particulate NO_3^- was lost from collected particles during sampling.

Comparison of TEOM and PC-BOSS Nonvolatile $PM_{2.5}$ Mass

The TEOM monitor was expected to determine only nonvolatile $PM_{2.5}$ mass because the single filter used in the TEOM was heated to 50 °C. The PC-BOSS sampler is suitable for use with sampling periods as short as 2 hr. The TEOM monitor can obtain half-hour data. During the Philadelphia episode study periods, one 2-hr and four 5-hr PC-BOSS samples were collected each day. The PC-BOSS nonvolatile filter retained mass was constructed based on the assumptions that SO_4^{2-} and NO_3^- were present as $(NH_4)_2SO_4$ and NH_4NO_3, respectively; soot was assumed to contain only C; the remaining carbonaceous material was assumed to be 62.5% C;[30] and crustal material was estimated from Fe and Si data. There was a consistent bias between TEOM $PM_{2.5}$ mass and the PC-BOSS constructed nonvolatile mass. The TEOM $PM_{2.5}$ measurements were biased an average of 13% lower than the PC-BOSS measurements. This was also reflected in the zero intercept slope of 0.86 in the PC-BOSS retained mass versus the TEOM comparison (see Table 1). This difference presumably reflected the increased loss of organic material (and possibly a small amount of NO_3^-) from the heated filter of the TEOM, as compared with the unheated filters of the PC-BOSS—it suggests that an average of 26% of the organic material retained on the PC-BOSS filter was lost from the heated TEOM filter. The PC-BOSS constructed nonvolatile $PM_{2.5}$ mass agreed well with the PC-BOSS $PM_{2.5}$ filter mass (see Table 1 and Figure 5) determined by either the Teflon filter (F_s) in the side flow or F_2 in the minor flow of the PC-BOSS (see Figure 2). The bias of the constructed nonvolatile $PM_{2.5}$ mass and the mass directly determined on a Teflon

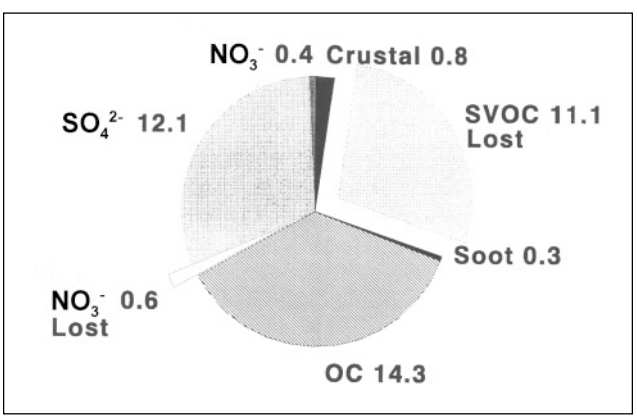

Figure 4. Average composition of $PM_{2.5}$, µg/m³. SVOCs lost from particles during collection in a filter averaged 28% of the total $PM_{2.5}$ mass.

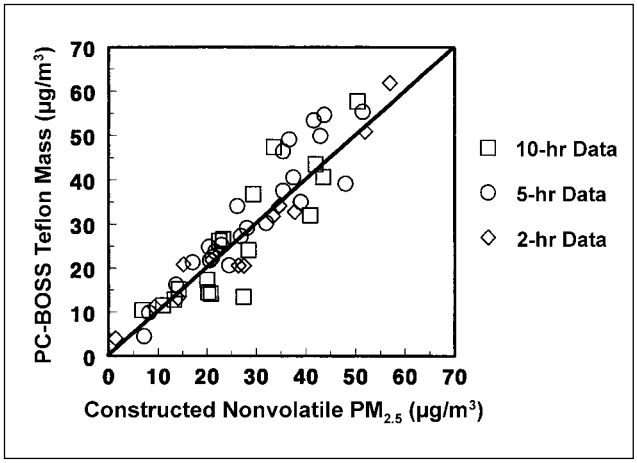

Figure 5. Comparison of PC-BOSS constructed and measured nonvolatile mass retained on the quartz and Teflon filters.

filter, either F_s in the side flow or F_2 in the minor flow of the PC-BOSS, was only –1.2 µg/m³, which is smaller than the standard deviation of the comparison of ±3.9 µg/m³ (±13%).

Comparison of RAMS and TEOM

The capability of the RAMS and TEOM monitors to determine total $PM_{2.5}$ mass, including semi-volatile material, has been outlined by Eatough et al.[14,15,17] RAMS data, plotted every hour (Figure 6), are given as 5-hr running averages to minimize the effect of the blank correction uncertainty in the RAMS.[17] This blank correction uncertainty is dominated by the absorption and loss of water from the CIF of the RAMS sandwich filter.[17] The uncertainty in the blank for the sandwich filter used in the Philadelphia study has been significantly reduced in more recent studies using a glass fiber (rather than cellulose) charcoal-impregnated filter.[17] The hourly, 5-hr running average TEOM monitor results obtained during the study are also given in Figure 6. The TEOM data were obtained by the Harvard School of Public Health with the filter at 50 ºC and no correction to the data. As shown in Figure 6, the RAMS $PM_{2.5}$ mass measurements were equal to or greater than the $PM_{2.5}$ mass measured by the TEOM monitor. The only exception was during the second day of the

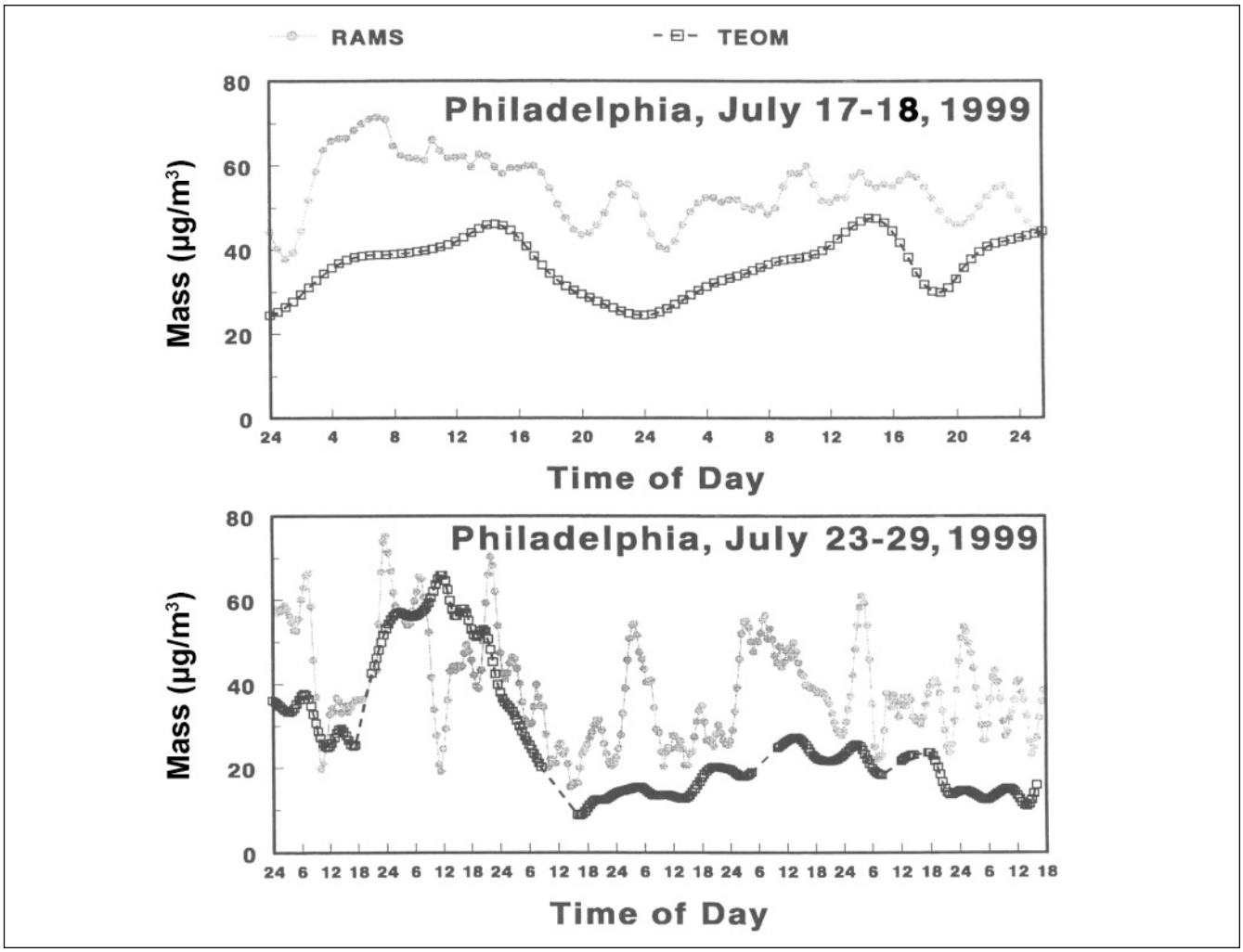

Figure 6. Five-hour running averages of RAMS and TEOM monitor data. The data are plotted as 5-hr running averages to minimize the short-term blank correction noise in the RAMS results.

July 23–July 29 period, as shown in Figure 6. However, the PC-BOSS data during this time period were consistent with the lower concentrations reported by the RAMS. The consistently higher RAMS $PM_{2.5}$ mass, as compared with that of the TEOM monitor, can be attributed to the presence of semi-volatile particulate material (see Figure 3) that was measured by the RAMS but not by the TEOM monitor.[14-17] The highest concentrations of semi-volatile fine particulate species (dominated by semi-volatile organic material, see Figures 3 and 4) were observed during the evening hours. This may reflect the role of automotive emissions, the inversion depth being high during the summer daytime period, resulting in dilution of the relative importance of nearby urban pollutants as compared with regional pollutants. In contrast, evening inversions would be expected to increase the relative importance of nearby emissions.

The relative undermeasurement of $PM_{2.5}$ total mass by the TEOM monitor as compared with the RAMS can be affected not only by temperature and relative humidity,[7-9] but also by the importance of SO_4^{2-} concentrations in $PM_{2.5}$ fine particles. Regional sources of SO_2 are major contributors to $PM_{2.5}$ SO_4^{2-} in Philadelphia. For the first two days of the July 23–July 29 period for which both TEOM and RAMS data were obtained in Philadelphia, the $(NH_4)_2SO_4$ concentrations averaged 25 µg/m^3 and varied from 13 to 41 µg/m^3 during the various PC-BOSS A and B sampling periods. The importance of regional source contributions during those two days was expected. The average fraction of total $PM_{2.5}$ not detected by the TEOM monitor was only 12% of the total during those two days. In contrast, the average concentration of $(NH_4)_2SO_4$ present during the last five days of this period was much lower, averaging 7 µg/m^3 and varying from 3 to 9 µg/m^3, and the fraction of the total $PM_{2.5}$ not measured by the TEOM monitor increased to 46%. The contribution of regional SO_2 sources to $PM_{2.5}$ fine particle mass during the first two days of this period was much more important than that during the last five days. Therefore, fine particles from the regional source included more nonvolatile material, such as SO_4^{2-}, than semi-volatile material, such as SVOCs from Philadelphia.

Comparison of RAMS with PC-BOSS $PM_{2.5}$

The RAMS is a continuous sampler designed to accurately determine total $PM_{2.5}$ mass, including semi-volatile material.[14-17] The PC-BOSS is a denuder sampler designed to accurately determine total $PM_{2.5}$ mass, including semi-volatile material.[9-13,18] The evaluation of the RAMS in Philadelphia was conducted by comparison with the PC-BOSS results. The total $PM_{2.5}$ mass, obtained for the PC-BOSS sampler, was calculated as the sum of the average $(NH_4)_2SO_4$ obtained from the Teflon (F_2) and quartz (F_1) filters (see Figure 2), the average NH_4NO_3 from the same

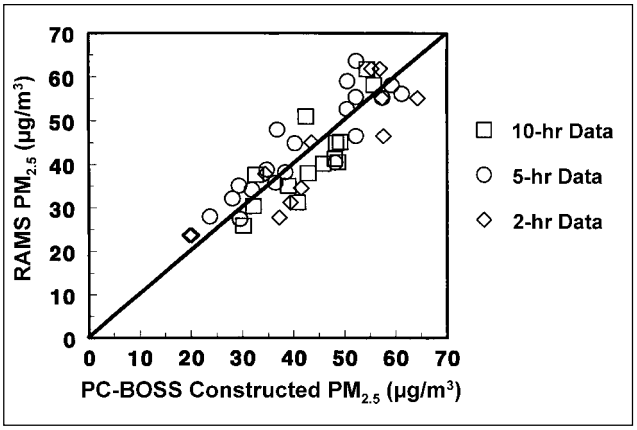

Figure 7. Comparison of PC-BOSS constructed $PM_{2.5}$ mass, including the semi-volatile components, and RAMS measured mass.

Teflon and quartz filters, volatile NH_4NO_3 obtained from the Nylasorb (S_2) filter, the soot collected on the quartz (F_1) filter, and the total organic carbonaceous material (OC), which is the sum of the particle-retained organic material on the quartz filter and the SVOCs lost from collected particles on the quartz filters during sampling and subsequently collected on the CIF (S_1, Figure 2). The particle-retained organic compounds were calculated from the difference between the total C and soot determined on the minor-flow quartz filter by TPV. The result of statistical analysis (see Table 1) indicated that there was no statistical difference between the RAMS-measured $PM_{2.5}$ and PC-BOSS constructed total $PM_{2.5}$ mass, including semi-volatile material (Figure 7). The bias between the two methods (0.4 µg/m^3) was smaller than the sigma for the comparison of these two collocated samplers for the determination of $PM_{2.5}$ total mass, ±4.1 µg/m^3 (±9.6%). In addition, both the R^2 value for the regression analysis and zero intercept regression slope indicated that comparable results are obtained with the two samplers.

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