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Intercomparison and evaluation of four semi-continuous PM_{2.5} sulfate instruments

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Abstract

The development and evaluation of time-resolved (minutes) measurement technologies to characterize the physical and chemical make up of ambient aerosols/particulate matter in the atmosphere are essential to our improved understanding of aerosol process science, source attribution, and population exposure. During the PMTACS-NY summer 2001 campaign in Queens/New York, a wide variety of on-line aerosol analysis instruments were deployed together with gas-phase and filter sampling techniques. Here, we report on the intercomparison of four semi-continuous PM_{2.5} sulfate instruments and evaluation of these instruments with one set of 6 h and three sets of 24-h filter measurements, collected at the same site. The semi-continuous instruments were an aerosol mass spectrometer, a particle-into-liquid sampler coupled with ion chromatograph, a Rupprecht & Patashnick Sulfate Monitor (R&P 8400S), and a continuous sulfate monitor developed by George Allen at Harvard School of Public Health and built in the field by one of us (J.J.S.). We found an excellent almost one-to-one correlation between the four semi-continuous instruments with typical multiple *R*-squared values > 0.9. In addition, the correlations of the semi-continuous data with the filter measurements are also highly linear (*R*² 0.86–0.98) but the semi-continuous instruments recover only about 85% of the sulfate mass collected by the filter techniques. The most likely explanation for this deviation is a combination of positive sampling artifacts on the filters (collection of particles with diameter greater than 2.5 μm, oxidation/condensation processes on the filters) with negative biases of the semi-continuous measurements (inlet line losses, limited collection efficiency for small particles below ca. 0.1 μm).

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1. Introduction

Atmospheric aerosol particles play an important role in physical and chemical processes in the atmosphere such as climate forcing, heterogeneous chemistry and cloud formation (Andreae et al., 1997; Ravishankara, 1997; Jacob, 2000; Hizenberger et al., 1999). In addition, their possible impact on air quality and human health causes increasing concern (Pope et al., 2002; Kuenzli et al., 2000; Samet et al., 2000; US Environmental Protection Agency, 1996). Despite the increasing interest in solving the problem of fine particulate pollution,

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many questions concerning the nature, generation, transport and transformation of particles remain largely unanswered. In order to solve many of these questions, reliable real-time measurements of the aerosol chemical composition are required with increasing specificity and precision.

The PM_{2.5} Technology Assessment and Characterization Study—New York (PMTACS-NY) is one of several US EPA ‘Supersites’ intended to provide enhanced measurement data on chemical and physical composition of fine particulate matter and its associated precursors. One of the primary objectives of this study is to test and evaluate new measurement techniques for particulate matter and to demonstrate the operational robustness of these technologies for routine monitoring applications.

To achieve this objective, a wide variety of state-of-the-art on- and off-line techniques for physical and chemical aerosol analysis were deployed in a common field intensive in New York City during July 2001 for the purpose of in-field instrument testing, intercomparison and evaluation by comparison with well-accepted techniques (i.e. filter-based measurements).

It is widely recognized that sulfate, either acidic or neutralized, is a major component of fine particulate (PM_{2.5}) mass. In the last couple of years a number of new techniques for real-time measurement of this important aerosol component have been developed. Four of these semi-continuous sulfate instruments have been deployed during PMTACS-NY 2001: An aerosol mass spectrometer (AMS), developed and manufactured by Aerodyne Research Inc. (Jayne et al., 2000), a particle-into-liquid sampler coupled with ion chromatograph (PILS-IC), developed and built by Georgia Tech (Weber et al., 2001), a Rupprecht & Patashnick 8400S Particulate Sulfate Monitor (Stolzenburg et al., 2000) and a continuous sulfate monitor (Allen et al., 2001), designed by Harvard School of Public Health (HSPH instrument) and built on a license basis by one of us (J.J.S.) in the field.

A brief description of the instruments deployed including sampling, collection and analysis techniques, operational parameters as well as the datasets, obtained with each of these instruments during the field study is provided in the section below. Intercomparison of the instruments is performed by linear regression analysis of the sulfate mass concentrations, averaged on a common 1-h time basis. Evaluation of the instruments against filter measurements are based on correlations of the averaged semi-continuous instrument data with one set of 6-h and three sets of 24-h filter data.

2. Instrument descriptions and field deployment

The measurement site of the PMTACS-NY 2001 summer intensive was located at the edge of parking

field #6 of Queens College in Queens/New York, right next to a running track. Queens College is located in the heart of Queens, a few hundred meters south of Long Island Expressway and ca. 1 km east of Van Wyck Expressway, two of the busiest highways in eastern New York City.

The primary measurement period of this campaign was 30 June until 31 July. Most of the instruments, however, were operated until 5 August.

All semi-continuous sulfate instruments, described in this paper, were housed in two trailers located next to each other. Every instrument had its own sampling inlet, equipped with a PM_{2.5} cyclone. The inlets were all located at a height of approximately 5 m above ground and not more than 2 m apart from each other.

A 6-h filter sampler and one of three 24-h filter samplers were located at the Queens College site. The inlets of these samplers were at a height of approximately 3 m above the parking level, located ca. 10 m from the inlets of the semi-continuous instruments. The other two 24-h filter samplers were located on the roof of Public School 219, ca. 100 m west of the Queens College site with a running track between the two locations. Due to a difference in ground elevation between the two sites, the inlets of these samplers were approximately at the same elevation (a.S.L) as the inlets of the semi-continuous instruments located at Queens College.

2.1. Aerosol mass spectrometer (AMS)

An instrument schematic of the AMS is shown in Fig. 1. A more detailed description of the apparatus and its operation is given in Jayne et al. (2000). The vacuum system consists of three differentially pumped chambers: an aerosol sampling chamber, a particle sizing chamber and an analysis chamber, divided by a skimmer and a channel aperture.

The ambient aerosol is introduced into the instrument through a aerodynamic particle beam-forming lens, similar to the one described by Liu et al. (1995a,b). Particles in the size range ca. 60–600 nm are focused with almost 100% efficiency (Jayne et al., 2000). The inlet flow is restricted to 0.11/min by a critical orifice.

In the vacuum the particle beam passes the skimmer, the particle sizing chamber and an aperture before it impacts on the heater surface at about 700°C. After flash vaporization of the volatile and semi-volatile particle components, the vapor is ionized by electron impact. The ions are analyzed with a quadrupole mass spectrometer (Balzers, QMG 422) and detected with an electron multiplier.

For particle sizing, a chopper wheel is moved into the particle beam right after the skimmer. This time-of-flight mode allows the measurement of the particle velocities, by setting the QMS on a single mass and measuring the time-resolved ion signal. The velocity distribution can be

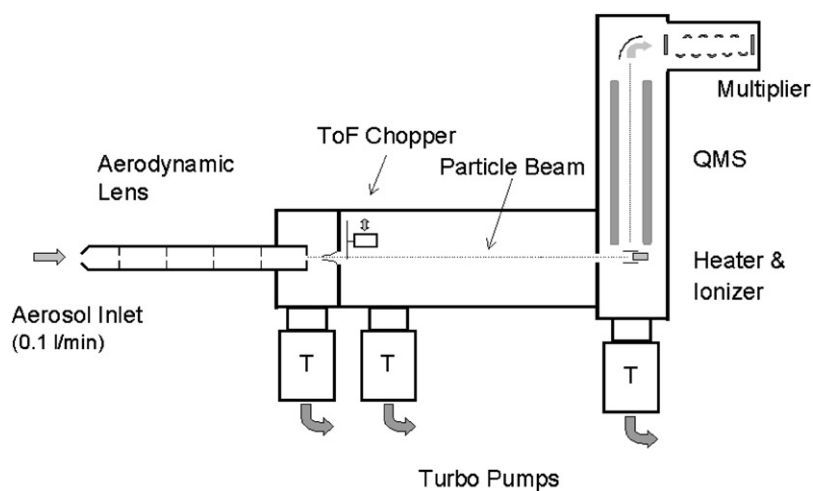


Fig. 1. Schematic of the AMS. Ambient aerosol is sampled and focused through the aerodynamic lens into the vacuum. The fine particle beam, formed by the lens, passes a skimmer and a chopper and impacts onto a heater, followed by flash vaporization and electron impact ionization. The ions are analyzed by the QMS.

transformed into a particle size distribution for the species represented by the selected mass.

In a second mode of operation, the ‘mass spec’ mode, the chopper wheel is completely removed from the particle beam to maximize the amount of particles hitting the heater. No size information is obtained in this mode. The mass spectrometer is scanned over a mass range from 1 to 300 amu at a frequency of 3 Hz, measuring the bulk composition of the non-refractory aerosol components. For measurement of the background signal, the chopper wheel is moved into the particle beam to completely block it.

For field operation, the AMS was set to an ‘alternate mode’, to periodically switch between time-of-flight mode and Mass Spec mode every 20 s. For the sulfate mass concentration measurement only the Mass Spec mode was used. Every 10 min the mass spectrum and size distribution averages were saved to disc. The AMS was operated almost continuously from 30 June until 5 August.

The aerosol mass concentrations were calculated from the mass spectrum signal at masses 48 (SO^+), 64 (SO_2^+) and 80 (SO_3^+) amu. Other fractions that also belong to sulfate have not been used due to interferences by fractions of organic species. A more detailed description of the operation parameters and the data processing of the AMS data are given in Drewnick et al. (2003).

For calculation of the aerosol mass concentrations from the mass spectrum data, the inlet flow and the multiplier gain were monitored continuously using a differential pressure flow meter at the AMS inlet and the air signal in the mass spectra, respectively. Daily

calibrations of the multiplier gain as well as frequent calibrations of the ionization and transmission efficiency (IE) of the mass spectrometer, using 350 nm ammonium nitrate particles, were performed for quality assurance.

For pure ammonium nitrate particles, the probability of impaction on the heater is 100% (this is why these particles are used for calibration) and the evaporation and IE is known due to the IE calibration. However, a constant fraction of the ambient sulfate particles is lost due to incomplete focusing in the aerodynamic lens. In addition, sulfate has a different IE than nitrate, and not all the sulfate fragments produced during the evaporation and ionization process are used to determine the sulfate mass concentrations. This has to be accounted for by multiplication of the sulfate data with a correction factor, which was determined by comparison of the AMS with the PILS (focusing loss) and laboratory studies (IE, fragmentation pattern). The PILS was used for determination of the AMS correction factor for focusing loss because it has the longest track record of the semi-continuous instruments used in this study.

2.2. Particle into liquid sampler (PILS)

An instrument schematic of the PILS-IC is shown in Fig. 2. A comprehensive description of the instrument is given in Weber et al. (2001). It consists of three main parts: (1) A set of diffusion denuders upstream of the PILS to remove gaseous species that could interfere with the aerosol measurement (e.g., HNO_3 , SO_2 , and NH_3). (2) The PILS, which collects particles into a small flow

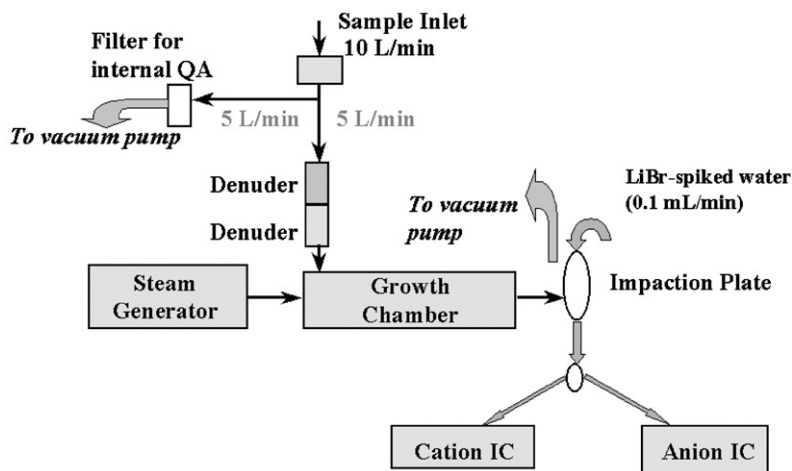


Fig. 2. Schematic of the PILS, consisting of denuders, growth and impaction chamber (PILS) and ICs.

of LiBr solution. (3) A set of two ICs for quantitative mass analysis of the ionic species dissolved in the water generated by the PILS.

For removal of gas-phase interferences, two concentric cylinder glass denuders (*URG*) are coupled in series. One denuder is coated with a sodium carbonate solution for removal of acidic gases; the other is coated with citric acid for removing basic gases. The denuders and the PILS are in close proximity so that the aerosol does not evolve due to the removal of the gases before being analyzed with the PILS.

The PILS itself consists of a steam generator and mixer, a growth chamber and a droplet collector. The saturated water vapor is turbulently mixed with the ambient sample air coming from the denuders at a flow rate of 5 l/min. Particles down to ca. 25 nm are activated and grown in the growth chamber to sizes between 3 and 7 μm diameter. These droplets, which contain the soluble aerosol components, are collected with an impactor into a flow of 0.1 ml/min of purified water, spiked with a known concentration of LiBr. A peristaltic pump at the bottom of the vertical impactor plate draws off the collected solution. Air in the flow stream is removed with a debubbler and the flow is then split and directed to the sample loops of the two ICs.

Each IC is equipped with a 150- μl sample loop. The liquid is continually drawn through these loops. The time to fill a loop determines the period over which the ambient measurement is integrated. The concentrations of the major ionic components of the collected aerosol samples are analyzed using computer-controlled ICs (*Metrohm Inc.*) for both the anions and cations simultaneously. Each instrument is equipped with a dual piston pump, an analytical separation column (*Metro-Sep 1–2*, for cations; *Phenomenex Star Ion A-300*, for anions), a suppressor (anion system only), and a

conductivity meter. The analysis is performed with isocratic elution using an eluent of 1 mM of dipicolinic acid and 4 mM of tartaric acid for the cations and of 2.5 mM sodium carbonate and 6 mM sodium bicarbonate for the anions. The cation IC operates at a flow rate of 1.0 ml/min, the anion system at 0.8 ml/min.

The PILS-IC was operated starting 1 July until 5 August with some minor interruptions. The cycle length of the instrument was determined by the duration of the IC analysis to 15 min. At the given flow rate of the liquids it took 6 min to fill the sample loops of the ICs. Therefore, the PILS provides 6-min averages of the aerosol concentration every 15 min.

For quality assurance, the ICs were calibrated several times during the campaign with a multi-point calibration using nine NIST traceable standard solutions. In addition, the air flow rates at the PILS inlet were measured every week using a Drycal flowmeter. The LiBr water flow was measured gravimetrically every week. The denuders were exchanged every 4–5 days.

For calculation of the ambient aerosol mass concentrations from the IC data (ion concentration in the liquid), the dilution of the sample solution by water from the steam generator was calculated using the measured LiBr concentrations. A more detailed description of the operation and data analysis is given in [Peters \(2002\)](#) and [Diamond \(2002\)](#).

2.3. R&P 8400S sulfate monitor (R&P 8400S)

A schematic of the *Rupprecht & Patashnick* Particulate Sulfate Monitor Model 8400S is provided in [Fig. 3](#). A more detailed description of the very similar nitrate monitor R&P 8400N can be found in [Stolzenburg et al. \(2000\)](#). The instrument consists of two main parts: The pulse generator that collects the particles on a strip and

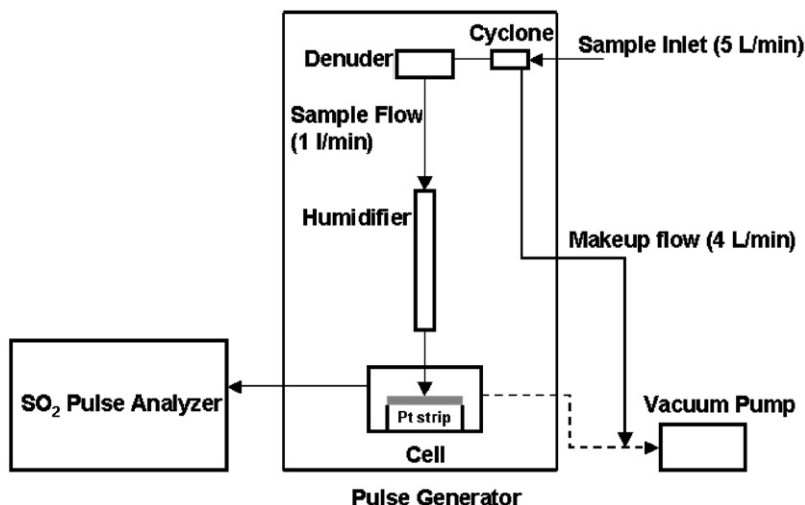


Fig. 3. Schematic of R&P 8400S Monitor with the pulse generator and pulse analyzer. Some flow lines, as well as SO₂ and air gas tanks, are not shown on the schematic.

flash-evaporates them; and the pulse analyzer, that determines the amount of SO₂, produced during vaporization of the particles.

Ambient aerosol samples are pulled through a sharp cut cyclone at a flow rate of 5 l/min to remove particles above 2.5 μm. From this flow a 1 l/min sub-flow is used for sulfate analysis. After passing through a carbon honeycomb denuder to remove potential gaseous interferences, it is directed through a humidifier to wet the particles. The wetted particles are collected by impaction onto a platinum strip mounted in a collection and vaporization cell. The collection efficiency of this impactor is >95% for particles in the range 0.1–0.8 μm (Stolzenburg et al., 2000). Typical sample period is 8.5 min. After sample collection the system switches from collection mode to analysis mode.

During analysis, the sampling flow bypasses the collection cell while this is flushed with clean air from a tank. The air flows through the cell and into a sulfur dioxide analyzer (pulse analyzer). The collection substrate is then flash heated by a current from a battery until reaching an infrared cutoff. Typical heating times are 10–14 ms. Evolved sulfur oxides are carried with the airflow to the analyzer, where they are detected by UV fluorescence. The analyzer output is integrated over the signal read time, then converted using the ambient pressure, temperature and calibration factors to yield the sulfate concentration. Additionally, the analyzer baseline is read prior to each analysis flash while flushing cell and analyzer with clean air. Following this analysis step, the instrument returns to sample collection, starts the next sampling interval and submits the sulfate concentration and the system operation parameters to the data acquisition computer.

The R&P 8400S was operated almost continuously from 29 June until 5 August. It was set to a 10-min cycle length, including a 495 s sampling interval, followed by 30 s purging of the flash cell, a 10 s baseline read and ca. 40 s flash and analysis time.

For quality assurance the instrument performs an internal audit every other day, using a 1 ppm standard gas (*Scott-Marrin*) from a cylinder. In addition, the complete system is calibrated manually with aqueous standards applied directly to the collection strip every second week. Field blanks are measured every second week by placing a Teflon filter between the cyclone and the denuder. Daily checks include cylinder pressure, make-up and orifice flows and other operational parameters. Flash cell pressure, sample flow rate and strip flash time are recorded at every cycle and used for calculation of sulfate mass concentration.

The sulfate mass concentration is automatically calculated from the SO₂ analyzer reading, using the sample flow rate and sampling time as well as the conversion efficiency, determined during aqueous standard calibration. Manually, these data are corrected for variations in the automatic analyzer calibrations and the manual liquid standards calibrations, as well as for the field blank readings. (Note: the R&P algorithm for conversion of integrated SO₂ gas measurements to aerosol SO₄ mass concentrations had an error during this campaign. All data presented here have been recalculated to remove this error.)

2.4. HSPH continuous sulfate monitor (HSPH)

An instrument schematic of the continuous sulfate monitor is provided in Fig. 4. The instrument was

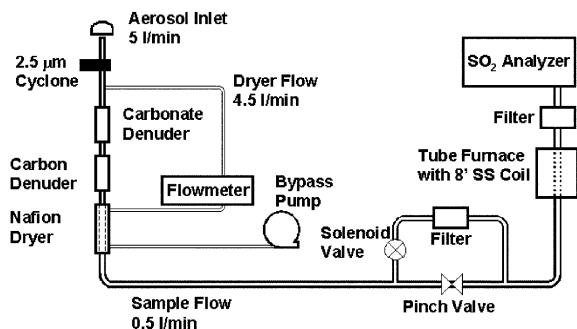


Fig. 4. HSPH continuous sulfate monitor with inlet assembly, tube furnace and SO₂ analyzer.

developed by Allen et al. (2001) at HSPH. It consists of three main parts: An inlet assembly to remove unwanted gas or particle components from the sample air, a stainless-steel coil in a tube furnace to convert aerosol sulfate into SO₂, and a high-sensitivity SO₂ analyzer to detect the particulate-originated sulfur dioxide.

The ambient aerosol is sampled through a weather cap and a 2.5 µm sharp-cut cyclone (both BGI) at a flow rate of 5 l/min. After the cyclone, the air flow is split into a 4.5 l/min dryer flow and a 0.5 l/min sample flow. The sample flow passes an annular carbonate denuder (URG 2000-30 × 150-3CSS) and a honeycomb carbon denuder (MAST) to remove possible gas-phase interferences. Finally in a nafion dryer moisture is removed from the sample flow. The dryer is purged by the dryer flow at low pressure. To maintain the low pressure, the dryer flow is drawn through an adjustable flowmeter with the bypass pump.

During sampling intervals, the sample flow passes a pinch valve and flows through a stainless-steel coil (SS-316) of 2.4 m length, OD = 0.318 cm, ID = 0.159 cm, which is located in a tube furnace (LINDBERG/BLUE M TF55030A-1), heated to 900°C. At this temperature, the sulfate particles evaporate and the vapor is converted to SO₂, thought to be promoted by the carbon and trace metals in the stainless steel.

The SO₂-laden air passes a 47 mm PTFE filter (5–6 µm pore size) and is introduced into a hi-sensitivity pulsed-fluorescence SO₂ analyzer (Thermo Environmental Instruments Inc., Model 43S). The sulfur dioxide reading of the analyzer was continuously logged by a datalogger. The first 10 min of every hour were used for an 'auto-zero' cycle.

The 'auto-zero' cycle is used to continuously monitor the background signal coming from the heated SS coil or from other potential interferences that are not removed by the denuders. During this cycle the pinch valve is closed and the solenoid valve opens to guide the sample flow through a small Ballston filter. The SO₂ analyzer then only reads the sulfur dioxide concentration of the particle-free air.

The continuous sulfate monitor was licensed from HSPH and built in the field by one of the authors (J.J.S.). The instrument was almost continuously operated from 22 July until 5 August.

The sulfate mass concentrations were calculated from the SO₂ concentrations and the sample flow rate, assuming quantitative conversion of sulfate to SO₂. The conversion of ammonium sulfate to SO₂ varies from 80–85% at 800°C to effectively 100% at 1000°C (George Allen, private communication). We did not measure the conversion efficiency at the operating temperature of 90°C, but assumed it to be greater than 95% based on the work of Allen. The 'auto-zero' cycle was used for baseline correction. The data were reported as 1 h averages.

2.5. 6-h filters (DOH 6 h QC)

The 6-h filter samples were collected at the Queens College site ca. 10 m apart from the inlets of the semi-continuous instruments using a Sequential Cyclone Sampler. The airflow first passes through a nylon screen to eliminate bugs, then a 28 l/min PM_{3.5} cyclone (URG 2000-30EC), operated at 42 l/min to shift the cut-off of the cyclone to 2.5 µm. The aerosol is collected on 47 mm teflon filters in four filter holders, controlled by a timer and solenoid valves. Mass flow controllers automatically compensate for temperature variations.

The filters are analyzed by IC in the labs of New York State Department of Health (DOH) at Wadsworth Center, Albany Dutkiewicz et al. (2003).

The DOH 6 h filters were collected from 29 June until 6 August almost continuously for 6 h per filter, starting at midnight, 6:00, noon and 18:00. Every fifth day the schedule changed to obtain one blank filter, one 12-h sample, and two 6-h samples. In this instrument no denuder was used to remove gaseous interferences.

2.6. 24-h filters (DOH 24 h QC)

These 24-h filter samples were collected at the Queens College site, next to the 6-h filter samples, using a Rupprecht & Patashnick automated cartridge collector unit (ACCU) sampler. The ACCU sampler shares the inlet with an R&P TEOM and uses the bypass flow of this instrument. The TEOM/ACCU sampler inlet is equipped with a 16.7 l/min PM_{2.5} cyclone (URG 3000-30EH). The ACCU contains an aluminum manifold that feeds to eight filter channels each equipped with a 47 mm Zeffluor filter (PALL Gelman). The filter collection is automatically timed for 24 h from midnight till midnight. A blank filter is collected by placing an ACCU cartridge loaded with a filter inside the sampler during collection. No denuder is used with the ACCU sampler to remove gaseous interferences.

The DOH 24 h QC ACCU sampler was operated from 7 July until 3 August, sampling one filter every day. The filters were analyzed by IC in the labs of New York State DOH at Wadsworth Center, Albany.

2.7. 24-h filters (DOH 24h PS)

These 24-h filters were collected at the PS219 site, located ca. 100 m west of the QC site using an identical sampler as for the DOH 24 h QC filter samples. These filters also were analyzed by IC in the DOH labs in Albany. Sampling started at this location on 30 June 2001 and is ongoing. Results reported for the present study consider data from the period 30 June to 5 August 2001.

2.8. 24-h filters (DEC 24h PS)

This 24-h filter set was collected at the PS219 site, ca. 100 m west of the QC site, using a Rupprecht & Patashnick Partisol Sequential Speciation Sampler Model 2300. The Partisol sampler has an inlet flow of 10 l/min. The inlet is equipped with a PM_{2.5} impactor. The 47 mm nylon filters are contained in ChemComb speciation sampling cartridges together with a sodium carbonate denuder. The whole cartridge is exchanged with every filter change, providing a fresh denuder for every filter.

These filter samples are part of the EPA Speciation Trends Network and are collected for 24 h from midnight till midnight, every third day. These measurements are also ongoing and the data reported are from samples collected between 30 June and 5 August. The filters were analyzed by IC in the labs of Research Triangle Institute, the EPA contractor for the Speciation Trends Network.

An overview of the most important instrument characteristics of all four semi-continuous instruments as well as all four filter samplers is given in Table 1.

3. Results

3.1. Intercomparison of the semi-continuous instruments

During the time of deployment, all the four semi-continuous particulate sulfate instruments showed very reliable performance with a high percentage of up-time (see Table 1) and only few instrument problems that caused interruption of the measurement. Therefore, semi-continuous sulfate concentration data are provided for virtually the whole period of the campaign from the AMS and the R&P 8400S instruments. The PILS instrument provided semi-continuous sulfate concentration data for the whole period of the campaign with some larger interruptions. Since the HSPH continuous

Table 1
Instrument characteristics and sampling information for all instruments discussed in this comparison

	AMS	PILS	R&P 8400S	HSPH	DOH 6h QC	DOH 24h QC	DOH 24h PS	DEC 24h PS
Sampling site	QC	QC	QC	QC	QC	QC	PS	PS
Analysis	Mass spectrometry	Direct IC	Pulsed fluorescence	Pulsed fluorescence	Filter/IC	Filter/IC	Filter/IC	Filter/IC
Inlet flow (l/min)	10	10	5	5	42	16.7	16.7	10
Sample flow (l/min)	0.1	5	1		13.67	13.67		
PM inlet	PM _{2.5} cyclone	PM _{2.5} cyclone	PM _{2.5} sharp cut cyclone	PM _{2.5} sharp cut cyclone	PM _{3.5} cyclone operated at higher flow to get PM _{2.5}	PM _{2.5} cyclone	PM _{2.5} cyclone	PM _{2.5} impactor
Denuder	No	Sodium carbonate, citric acid	Carbon denuder	Sodium carbonate, carbon denuder	No	No	No	Sodium carbonate
Sampling period	30 June–5 August	1 July–5 August	29 June–5 August	22 July–5 August	29 June–6 August	7 July–3 August	30 June–6 August	30 June–5 August
Sampling frequency	10 min	15 min	10 min	Continuous, 1-h averages	4/day	1/day	1/day	1 every 3rd day
Data completeness (%)	93	69	95	80	98	89	97	85

Sampling site: QC: Queens College site, PS: PS219 site.

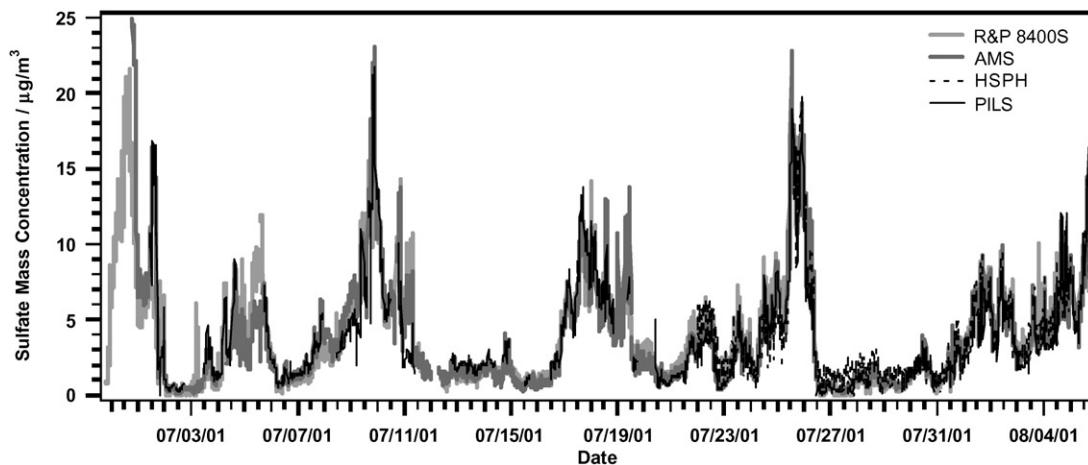


Fig. 5. Particulate sulfate mass concentration time series of the AMS, the PILS, the R&P 8400S and the HSPH continuous sulfate monitor for the whole PMTACS-NY 2001 campaign.

sulfate monitor was built in the field, its data cover only the period starting from 22 July. In Fig. 5, the sulfate mass concentration time series of the four instruments are shown for the whole campaign.

As shown in Fig. 5, all four semi-continuous sulfate instruments track each other very well, during periods of low sulfate concentration as well as during pollution events.

For statistical intercomparison of the sulfate concentration data for the four instruments, the data have been averaged to a common time base of 1 h. Since the different instruments have different sample collection and analysis schemes, special attention was paid on exact assignment of sampling times and reporting intervals. For this purpose all data first have been copied and filled in 1-min time intervals using the instruments sampling scheme. The 1-min data have been averaged for common 1 h intervals for comparison. Only averaging intervals that have been covered by 75% or more of the possible sampling time and containing data that are above detection limit for a certain instrument have been used for intercomparison.

Statistical intercomparison was done by linear regression analysis. For every pair of instruments and pair of instrument and filter, a scatter plot was generated and a linear fit of the data was calculated. Since regular linear regression algorithms neglect the errors of the y -data set and simply minimize the horizontal distance of the data points to the fit line, leading to different fits depending on the order of the compared data sets, a more general correlation algorithm was programmed in IGOR Pro (*Wavemetrics*) that takes the errors of both data sets into account. Using this algorithm, linear correlations for every pair of data as well as their inverse combination were calculated and are given as slope and intercept of the correlation line. In addition, the multiple- R^2 values

provided for each correlation is indicative of the fraction of the variance explained by the linear model. For a direct comparison of the magnitude of the instrument responses, the recovery was calculated by performing a linear fit with intercept constrained to zero.

In Fig. 6, the correlation between AMS and PILS is shown in a scatter plot. This correlation plot confirms the very good correlation of the instruments, already indicated in the graph of the time series in Fig. 5.

In Fig. 6 only the valid 1 h averages are plotted, i.e. only the averages for which the measuring time of the instruments has been 75% or more of the possible time (45 min or more) and the data were above detection limit of AMS and PILS, respectively. The slope of the correlation is close to one and the intercept close to zero, with a multiple $R^2 = 0.91$. Using all available data (also the averages with less than 75% coverage of the sampling time and data below detection limit) almost does not change the slope and intercept of the correlation.

Some of the data points in Fig. 6 deviate significantly from this linear relationship between these two instruments, lying well above the 'bulk' of the data. These points represent a period from 8 July until 11 July, during which the AMS has measured significantly higher sulfate concentrations than the PILS (Fig. 7).

During this period, several routine checks and calibrations have been performed with the AMS, but no incidents have been observed that could cause a temporary increase in measured sulfate. The PILS had some problems with its denuder. It was changed on 9 July at 13:00. During this time also some problems with corrosion in one of the ICs and some issues with the debubbler occurred, but of these problems show a good coincidence with the periods of large difference and no

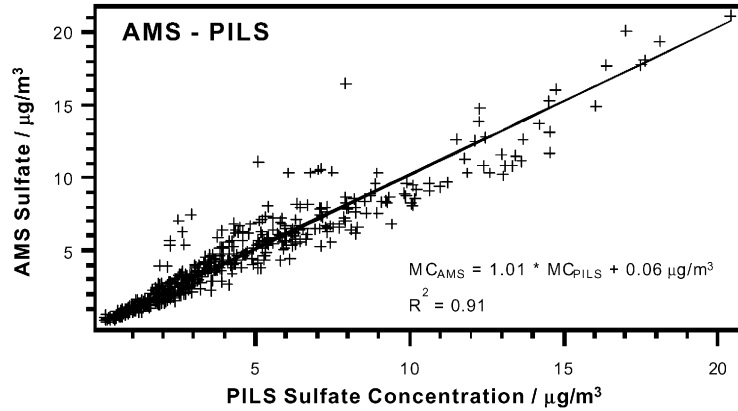


Fig. 6. AMS sulfate 1 h data plotted versus PILS sulfate 1 h mass concentration data. Only valid averaging periods are plotted (see text).

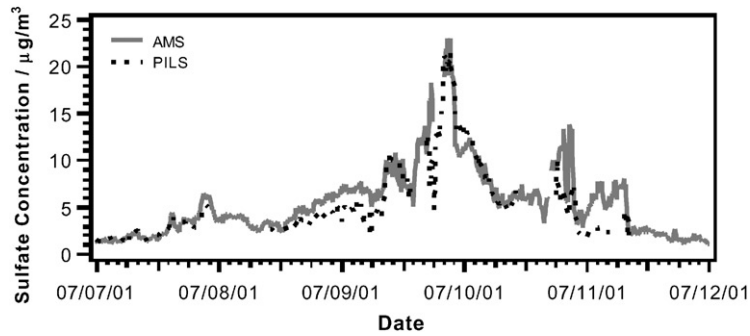


Fig. 7. AMS and PILS sulfate concentration data for the period of disagreement between these two instruments.

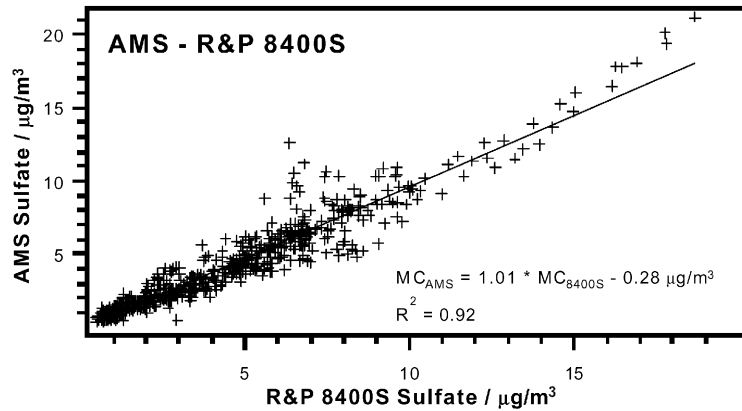


Fig. 8. AMS sulfate 1 h data plotted versus R&P 8400S sulfate 1 h mass concentration data. Only valid averaging periods are plotted (see text).

causal relationship was found for a possible under-measurement of sulfate with the PILS.

Another correlation, the one between the AMS and the R&P 8400S Sulfate Monitor, is shown in Fig. 8.

Also, a linear relationship between these two instruments is found with a slope of 1.01 and an intercept of $-0.28 \mu\text{g}/\text{m}^3$, with a multiple- $R^2 = 0.92$ these instruments track each other also very well. Again, there is no

Table 2
Summary of all correlations between the semi-continuous sulfate instruments

Combination	Slope	Intercept ($\mu\text{g}/\text{m}^3$)	Squared correlation coeff. R^2	Recovery	Number of points
AMS–PILS	1.014	0.064	0.913	1.023	549
PILS–AMS	0.987	–0.063	0.913	0.977	
AMS–8400S	1.015	–0.280	0.922	0.972	695
8400S–AMS	0.986	0.276	0.922	1.029	
AMS–HSPH	1.029	–0.403	0.940	0.965	316
HSPH–AMS	0.972	0.391	0.940	1.036	
PILS–8400S	0.988	–0.363	0.870	0.960	526
8400S–PILS	1.012	0.359	0.870	1.042	
PILS–HSPH	1.013	–0.490	0.930	0.940	280
HSPH–PILS	0.987	0.483	0.930	1.064	
8400S–HSPH	1.020	0.061	0.908	1.029	293
HSPH–8400S	0.981	–0.059	0.908	0.972	

Only valid averaging intervals have been used for calculation; for calculation of the ‘recovery’ the intercept is forced to zero.

significant change in the parameters of the correlation when using all available averaging periods instead of only the valid ones.

A summary of all correlations between the semi-continuous sulfate instruments is provided in Table 2. The correlations for Table 2 are calculated for only the valid averaging intervals. Using all available data does not result in a significant change of the slope or intercept of the correlation function. Just the correlation coefficient decreases slightly when using all data.

As already indicated in Fig. 5 of the mass concentration time series, all the semi-continuous sulfate instruments show excellent correlations with slopes between 0.97 and 1.03 and the intercepts in a range –0.49–0.48 $\mu\text{g}/\text{m}^3$. With the exception of one combination (PILS–R&P 8400S), all multiple- R^2 are above 0.9 with an average of 0.91. The ‘recovery’ values found for these correlations are in the range 0.94–1.03, indicating that the responses of the four instruments agree within 5% or less.

3.2. Comparison of the semi-continuous instruments with filter samples

In addition to the intercomparison of the semi-continuous instruments with each other, the instruments were also evaluated based on comparisons with analyzed filter sample data.

For comparison, the semi-continuous sulfate data have been averaged for the filter collection time intervals. Again, these data first have been copied and filled into 1-min time intervals to take the different

sampling schemes of the instruments into account. Derived sulfate mass concentration averages from the semi-continuous instruments for comparison with the respective filter collection intervals must contain 75% or more of the possible data within the averaging interval and must be above the instrument detection limit. The number of filter samples potentially available for comparison is 139 for the 6-h filters and a total of 72 for all three sets of 24-h filters. The number of samples used for comparison with the individual instruments is given in Table 3.

The correlations between all four semi-continuous sulfate instruments and the 6-h sulfate filter data (DOH 6 h QC) are plotted in Fig. 9.

Also in this comparison, highly linear correlations have been found between the semi-continuous instruments and the 6-h filter data with a multiple- R^2 between 0.91 and 0.95. As indicated by the intercomparison of the different instruments, the linear fits for this comparison are very close to each other. Slopes of the correlations are between 0.68 and 0.73, intercepts of the linear fits between 0.10 and 0.63 $\mu\text{g}/\text{m}^3$. As indicated by the recovery values between 0.72 and 0.77, it suggests that 75% on average of the 6-h filter sulfate mass concentration is observed by the semi-continuous sulfate instruments. A summary of all correlations between the instruments and the filter data is given in Table 3.

Also, consideration of all data (i.e. data not meeting averaging criteria) showed no significant difference in the reported correlation results.

A group of PILS data points in Fig. 9 (circle ‘1’) located significantly under the correlation line were

Table 3
Correlations between semi-continuous sulfate mass concentrations and sulfate filter data

Combination	Slope	Intercept ($\mu\text{g}/\text{m}^3$)	Squared correlation coeff. R^2	Recovery	Number of points
AMS–DOH 6 h QC	0.734	0.095	0.931	0.745	124
DOH 6 h QC–AMS1.362	1.362	−0.129	0.931	1.342	
PILS–DOH 6 h QC	0.708	0.128	0.907	0.723	85
DOH 6 h QC–PILS	1.413	−0.181	0.907	1.384	
8400S–DOH 6 h QC	0.727	0.336	0.953	0.768	114
DOH 6 h QC–8400S	1.375	−0.462	0.953	1.302	
HSPH–DOH 6 h QC	0.679	0.634	0.922	0.759	54
DOH 6 h QC–HSPH	1.473	−0.934	0.922	1.318	
AMS–DOH 24 h QC	0.853	−0.086	0.965	0.839	22
DOH 24 h QC–AMS	1.172	0.100	0.965	1.192	
PILS–DOH 24 h QC	0.813	−0.072	0.977	0.804	16
DOH 24 h QC–PILS	1.230	0.088	0.977	1.244	
8400S–DOH 24 h QC	0.851	0.103	0.963	0.865	23
DOH 24 h QC–8400S	1.176	−0.121	0.963	1.156	
HSPH–DOH 24 h QC	0.760	0.559	0.891	0.904	11
DOH 24 h QC–HSPH	1.316	−0.735	0.891	1.106	
AMS–DOH 24 h PS	0.784	0.240	0.935	0.821	31
DOH 24 h PS–AMS	1.276	−0.307	0.935	1.218	
PILS–DOH 24 h PS	0.790	0.237	0.968	0.821	18
DOH 24 h PS–PILS	1.266	−0.300	0.968	1.217	
8400S–DOH 24 h PS	0.844	0.307	0.950	0.889	29
DOH 24 h PS–8400S	1.185	−0.364	0.950	1.125	
HSPH–DOH 24 h PS	0.794	0.725	0.862	0.960	13
DOH 24 h PS–HSPH	1.260	−0.913	0.862	1.042	
AMS–DEC 24 h PS	0.892	−0.354	0.971	0.845	8
DEC 24 h PS–AMS	1.121	0.397	0.971	1.184	
PILS–DEC 24 h PS	0.852	−0.15	0.9801	0.831	8
DEC 24 h PS–PILS*	1.174	0.177	0.980	1.203	
8400S–DEC 24 h PS	0.935	−0.208	0.974	0.907	7
DEC 24 h PS–8400S	1.069	0.223	0.974	1.102	
HSPH–DEC 24 h PS	0.681	0.561	0.914	0.798	4
DEC 24 h PS–HSPH	1.469	−0.824	0.914	1.253	

Only valid averaging intervals have been used for calculation; for calculation of the ‘recovery’ the intercept is forced to zero.

reviewed and found to be associated with a 2-day period of 10 and 11 July, where the PILS had some issues with the denuders as already discussed above. Another set of data points (circle ‘2’) where all four instruments are close to each other and all are well below the linear fits are all from comparison with the same filter sample (24 July 12:00). The close proximity of these points indicates that there is a contamination on this filter.

The correlations between all four semi-continuous sulfate instruments and the 24-h sulfate filter data sampled at the Queens College site (DOH 24 h QC) are plotted in Fig. 10, with their associated correlation parameters reported in Table 3.

Also with this set of filters the correlations are highly linear with a multiple- R^2 between 0.89 and 0.98. The

slopes of the correlations are in the range 0.76–0.85; the intercepts are between -0.09 and $0.56 \mu\text{g}/\text{m}^3$. Recovery values between 0.80 and 0.90 indicate, that on average, about 85% of the filter sulfate mass concentrations of this set of filters are measured by the semi-continuous instruments.

A very similar picture is found in the comparisons of the semi-continuous instrument data with the two other 24-h filter data (DOH 24 h PS and DEC 24 h PS, see Table 3). For these filter samples, the correlations are also highly linear with an average multiple- R^2 of 0.93 and 0.91, respectively. The average recovery of the filter mass concentration by the semi-continuous instruments is also about 87% and 85%, respectively. As with previous comparisons, no significant change

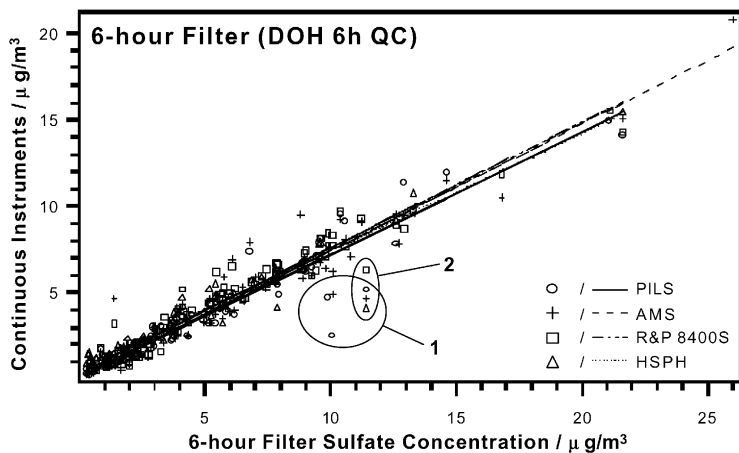


Fig. 9. Correlations between the semi-continuous sulfate concentrations and the 6-h filter data. Only valid averaging intervals have been used (see text).

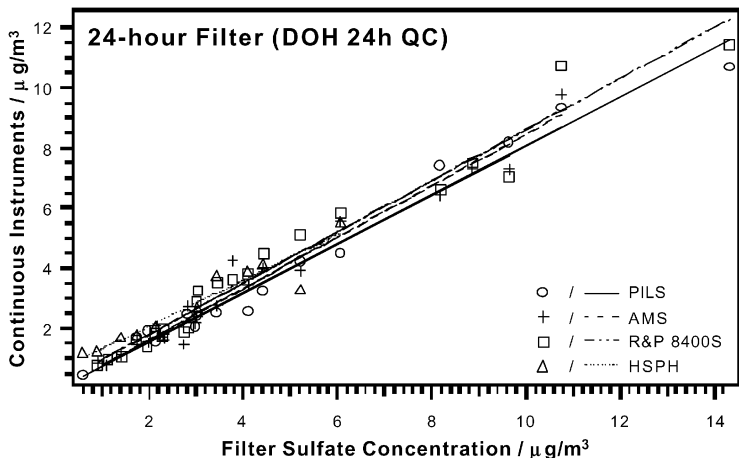


Fig. 10. Correlations between the semi-continuous sulfate concentrations and the 24-h filter data, collected at the Queens College site (DOH 24h QC). Only valid averaging intervals have been used (see text).

in the correlations is found when all available data (i.e. data not meeting averaging criteria are used in the calculations).

3.3. Intercomparison of the filter data sets

For intercomparison of the four sets of filter data, the 6-h filter data were averaged on a 24-h time base. A summary of all filter comparisons is provided in Table 4.

All correlations are highly linear with a multiple- R^2 of 0.975 and higher. While the 24-h DOH filter data sets show excellent agreement within less than 1% (recovery 1.007), small differences in the range 3–7% are found between the DOH and the DEC filter data. The 6-h filter data seem to have a positive offset of about 4–5% compared to the 24-h filter data.

4. Discussion

The four semi-continuous sulfate instruments, the AMS, PILS, the R&P 8400S and the HSPH continuous sulfate monitor, show excellent correlations with an average multiple- $R^2=0.91$. According to the recovery data, determined for these instruments, their responses agree within ca. 4%, which is within the uncertainties of the instruments. No significant intercept trends were found in the correlations, indicating that none of these instruments had serious contamination problems.

There are some outliers in the correlation plots of this instrument intercomparison, which mostly can be explained by instrument malfunctions. These data remind us of the importance of careful maintenance and operation of these instruments. Under these

Table 4
Correlations between the different sets of sulfate filter data

Combination	Slope	Intercept ($\mu\text{g}/\text{m}^3$)	Squared correlation coeff. R^2	Recovery	Number of points
DOH 6 h QC–DOH 24 h QC	1.048	–0.014	0.982	1.050	25
DOH 24 h QC–DOH 6 h QC	0.954	0.982	0.952		
DOH 6 h QC–DOH 24 h PS	0.970	0.545	0.975	1.024	36
DOH 24 h PS–DOH 6 h QC	1.031	–0.562	0.975	0.977	
DOH 6 h QC–DEC 24 h PS	1.040	–0.045	0.991	1.037	11
DEC 24 h PS–DOH 6 h QC	0.961	0.043	0.991	0.964	
DOH 24 h QC–DOH 24 h PS	0.978	0.201	0.983	1.007	25
DOH 24 h PS–DOH 24 h QC	1.022	–0.206	0.983	0.993	
DOH 24 h QC–DEC 24 h PS	0.978	–0.093	0.995	0.966	7
DEC 24 h PS–DOH 24 h QC	1.022	0.095	0.995	1.035	
DOH 24 h PS–DEC 24 h PS	1.150	–1.036	0.994	1.077	10
DEC 24 h PS–DOH 24 h PS	0.870	0.901	0.994	0.928	

For calculation of the ‘recovery’ the intercept is forced to zero.

circumstances, these instruments are capable of providing reliable measurements of particulate sulfate concentrations.

Also, the intercomparison of the filter data sets indicates that the mass concentrations obtained with these measurements are highly reliable and that the distance in sampling location of about 100 m between the two ‘Queens College’ site filter data and the two ‘PS 219’ site filter data sets does not result in significant or systematic differences in determined mass concentrations. The generation of aerosol sulfate, which occurs mainly through secondary reactions involving SO_2 and its significant lifetime in the atmosphere, is consistent with the observed spatial homogeneity of these measurements. The four filter data sets agree within a few percent and show highly linear correlations with a multiple- R^2 of 0.98 or higher. Just the 6-h filter data set shows a consistently higher mass concentration of about 4–5% higher than the other filter data. Since no systematic intercept in the correlations of the 6-h filters with the 24-h filters is found, contamination of the filters can be excluded as reason of this difference. A possible explanation of the high-mass concentrations on the 6-h filter could be related to inlet issues of the filter sampler used for this set of filter data. While the other filter samplers used $\text{PM}_{2.5}$ cyclones or a $\text{PM}_{2.5}$ impactor, this filter sampler was operated with a $\text{PM}_{3.5}$ cyclone at elevated flow rate to get a $\text{PM}_{2.5}$ cut-off. This could cause a slight shift in sampling cut-off and a softer cut-off curve, causing the observed higher sulfate mass concentrations.

While there is an almost one-to-one agreement within the four semi-continuous sulfate instruments as well as

within the filter data, the on-line instruments give systematically lower sulfate mass concentrations than the filters, indicated by average recovery values of 0.85 in comparison with the 24-h filters and of 0.75 in comparison with the 6-h filters. The absence of a systematic intercept in the correlations assures us that the observed difference between the semi-continuous instruments and the filter-based measurements is not due to contamination of the filters. This is the first time that this type of systematic difference has been observed so clearly between these on-line instruments and filter samples. A comparison of the PILS, a sulfate instrument similar to the R&P 8400S and three other semi-continuous sulfate instruments with filter samples during the Atlanta Supersite campaign 1999 showed good agreement between these techniques and the filters (Weber et al., 2001, 2003). Even though no systematic difference between the semi-continuous instruments and the filters was observed within the range of uncertainty of the measurements, in this study the semi-continuous measurements tend to measure several percent more sulfate than the filters (Weber et al., 2003).

It is unlikely that differences in meteorological conditions between Atlanta and New York City could explain the observed differences in instrument performance. The reported mean temperature during the New York City field campaign (30 June–5 August 2001) was 24.2°C with mean max and min temperatures of 30.2°C and 21.6°C , respectively, and a mean relative humidity of 61%. In contrast, although somewhat warmer, the mean temperature and humidity during the Atlanta 1999 field campaign was 26.8°C and 63.4%, respectively, with mean max and min temperatures of 34.1°C and 19.6°C .

Both sites reported minimal precipitation during their respective study periods.

Possible explanations for the systematic differences observed were investigated and discussed as follows.

4.1. Incomplete sampling of $PM_{2.5}$ by the on-line instruments

In the R&P 8400S sulfate monitor, the humidified aerosol impacts onto a metal strip. Collection in the impactor has lower efficiency for small particles below ca. 100 nm.

The inlet transmission efficiency of the AMS aerodynamic lens falls off sharply for particles with diameter below ca. 50 and above 600 nm, resulting in a loss of small and large particles.

The efficiency of activation of small particles by the steam in the PILS gradually decreases with decreasing particle diameter, for large particles ($D_{ac} > 2 \mu\text{m}$) the collection efficiency decreases significantly due to impaction losses in the growth chamber (Weber, 2002).

According to particle transmission measurements through membrane filters (Liu, 1976), the collection efficiency of the filters used in this study should be larger than 85% for particles in the size range below 100 nm, relevant for particulate mass measurements.

Using the average sulfate particle size distribution measured during this campaign with the AMS (Drewnick et al., 2003), corrected for the inlet transmission efficiency of the AMS, the losses due to this mechanism can be estimated for the AMS to be around 2–3%, for the PILS they are slightly less and the R&P 8400S could lose about 5–10% of the total sulfate mass concentration. The HSPH instrument does not exhibit this loss mechanism for small particles.

4.2. HSPH sulfate-to- SO_2 conversion issues

In the original version of this instrument (Allen, 2001), the stainless-steel conversion tube is heated to ca. 850°C. During this campaign the furnace was set to 900°C. This higher temperature of the tube should give better conversion of SO_4 to SO_2 than the 80–85% reported by Allen et al. (2001), but it is likely that conversion is below 100%. The magnitude of this systematic error is not known exactly to date, but we estimate it to be on the order of 5%.

4.3. Inlet transport losses

Small particles are lost in the inlet tubing by diffusion to the walls, large particles are lost due to impaction in curvatures of the inlet line and settling in horizontal parts of the inlet line. The AMS inlet was optimized to minimize these inlet losses. They were calculated to be below ca. 10% for 2.5 μm particles and about 10% for

20 nm particles. In between these extreme diameters, they were lower with a minimum of about 0.8% for 300 nm particles. Taking the average size distribution of the sulfate particles into account, these inlet losses could account for 25% loss of the total sulfate mass concentration.

The PILS had a very similar inlet with comparable losses (Peters, 2002), resulting in inlet transport losses of the same order of magnitude. The inlet losses of the R&P 8400S and HSPH instruments were not calculated. Since their inlet setups were not extremely different from the AMS and PILS inlets, the losses for these instruments due to this mechanism could be estimated to be in the same range.

The filter samplers also have inlet losses due to the above-mentioned mechanisms. The inlet losses of the filter samplers are assumed to be significantly lower than the losses of the semi-continuous instruments due to significantly shorter inlet lines in these samplers compared to the on-line instruments, which had to be housed in the trailers.

4.4. $PM_{2.5}$ selector cut-off issues

Three of the filter samplers are equipped with regular cyclones, the fourth with an impactor as $PM_{2.5}$ selector. While we have no information about the transmission curve of the $PM_{2.5}$ impactor, the cyclones are known to have a very broad transition from 100% to 0% penetration. At 4.5 μm particle diameter, the transmission of these cyclones is still in the range of 10% (Kenny, 1998).

In the set of semi-continuous instruments, the HSPH instrument and the R&P 8400S are equipped with sharp-cut cyclones, providing a much sharper cut-off at 2.5 μm . The two other semi-continuous instruments were also equipped with regular cyclones, but contrary to the filter samplers they have large intrinsic losses for large particles: The AMS has almost zero transmission efficiency through the aerodynamic lens for particles larger than about 2 μm . In the PILS, the particles have to make a 90° turn during mixture with the steam. The larger the particles, the larger the losses due to impaction onto the PILS tube walls during this turn.

Using literature data of urban sulfate size distributions (Wall, 1988), the contribution of sulfate particles larger than $PM_{2.5}$ to the total sulfate mass concentration was determined. This leads to an estimate of over-sampling by the filters of 2–5% due to this mechanism.

4.5. Filter artifacts

Gases and vapors, in this case SO_2 and sulfuric acid, could undergo oxidation or condensation processes on filters or in instruments, resulting in additional sulfate. Three of the on-line instruments (PILS, HSPH, R&P

8400S) were equipped with denuders to remove these potential gaseous interferents. The AMS removes gas-phase interferents internally by focusing the particles into a narrow beam and skimming off the gas around the particle beam.

Only one of the filter samplers (DEC 24 h PS) was equipped with a denuder. This gives the other filter samples the potential of positive artifacts on the filter due to the above-mentioned mechanisms. Since inter-comparison of the filter data sets does not show a significant difference between the DEC 24 h PS data and the other filter data, this artifact has to be small.

On the other hand, the DEC 24 h PS filters were not corrected for filter blanks. The reported laboratory sulfate filter blanks are in the range 1–2% of the measured sulfate mass concentrations.

This leads to an estimated potential over-measurement of sulfate by the filter samples of 1–2% due to these two filter artifact mechanisms.

5. Summary

Four different semi-continuous particulate sulfate instruments have been deployed during the PMTACS-NY in July and August 2001 in Queens, New York. The four instruments were an AMS, a PILS-IC, a Rupprecht & Patashnick Sulfate Monitor model 8400S and a continuous sulfate monitor designed by HSPH. In addition to these on-line instruments, four sets of filter data were collected at the same site or at a site located ca. 100 m apart from this site.

Intercomparison of $PM_{2.5}$ sulfate concentration measurements from these four instruments, that use very different collection and analysis techniques, showed excellent agreement with multiple- R^2 ranging from 0.87 to 0.94 (average: multiple- $R^2 = 0.91$) and with slopes of the correlation functions close to one and intercepts close to zero $\mu\text{g}/\text{m}^3$. Some outliers from these linear relationships have been found, but almost all of them could be explained by malfunctions of one of the instruments, indicating that the four instruments are capable of providing reliable high-frequency measurements of particulate sulfate concentrations with a time resolution of several minutes.

Comparisons of these semi-continuous sulfate data with 6- and 24-h filter data provide also highly linear relationships with a multiple- $R^2 = 0.86$ and above (average: multiple- $R^2 = 0.93$). However, these correlations show that only about 85% of the filter sulfate concentrations are found with the semi-continuous instruments. There is no single explanation for this difference. Most likely it is caused by a combination of over-measurement by the filters due to $PM_{2.5}$ selector issues as well as filter artifacts and under-measurement by the on-line instruments due to inlet transport losses,

cut-off of small particles and conversion efficiency in one of the instruments.

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