

Semicontinuous PM_{2.5} Sulfate and Nitrate Measurements at an Urban and a Rural Location in New York: PMTACS-NY Summer 2001 and 2002 Campaigns

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ABSTRACT

Several collocated semicontinuous instruments measuring particulate matter with particle sizes $\leq 2.5 \mu\text{m}$ (PM_{2.5}) sulfate (SO₄²⁻) and nitrate (NO₃⁻) were intercompared during two intensive field campaigns as part of the PM_{2.5} Technology Assessment and Characterization Study. The summer 2001 urban campaign in Queens, NY, and the summer 2002 rural campaign in upstate New York (Whiteface Mountain) hosted an operation of an Aerosol Mass Spectrometer, Ambient Particulate Sulfate and

Nitrate Monitors, a Continuous Ambient Sulfate Monitor, and a Particle-Into-Liquid Sampler with Ion Chromatographs (PILS-IC). These instruments provided near real-time particulate SO₄²⁻ and NO₃⁻ mass concentration data, allowing the study of particulate SO₄²⁻/NO₃⁻ diurnal patterns and detection of short-term events. Typical particulate SO₄²⁻ concentrations were comparable at both sites (ranging from 0 to 20 $\mu\text{g}/\text{m}^3$), while ambient urban particulate NO₃⁻ concentrations ranged from 0 to 11 $\mu\text{g}/\text{m}^3$ and rural NO₃⁻ concentration was typically less than 1 $\mu\text{g}/\text{m}^3$.

Results of the intercomparisons of the semicontinuous measurements are presented, as are results of the comparisons between the semicontinuous and time-integrated filter-based measurements. The comparisons at both sites, in most cases, indicated similar performance characteristics. In addition, charge balance calculations, based on major soluble ionic components of atmospheric aerosol from the PILS-IC and the filter measurements, indicated slightly acidic aerosol at both locations.

IMPLICATIONS

Several continuous PM SO₄²⁻ and NO₃⁻ measurement techniques have been evaluated under urban and rural environmental conditions in New York. These time-resolved measurements provide the opportunity to better characterize and improve PM species exposure estimates for health effect assessments; advance process science governing aerosol formation, transport, and evolution in the atmosphere; and improve performance of source attribution models. Comparison of the continuous measurements with filter-based measurements, including U.S. Environmental Protection Agency Speciation Trends Network samples, indicate that continuous SO₄²⁻/NO₃⁻ concentrations are consistent with filter-based measurements. The reported instrument performance evaluations are essential in assessing the viability of these systems for routine field operation.

INTRODUCTION

In recent years, ambient particulate matter (PM) with particle sizes $\leq 2.5 \mu\text{m}$ (PM_{2.5}) has received significant attention from researchers and agencies as a result of implied environmental health risks.¹ Sulfate (SO₄²⁻) and nitrate (NO₃⁻) are among the major components of atmospheric aerosol, with SO₄²⁻ being a significant fraction

of the $PM_{2.5}$ mass in the eastern United States for all seasons, with NO_3^- playing a role in the cold seasons. Mass concentrations of ambient particulate SO_4^{2-} and NO_3^- are routinely measured by collecting integrated filter samples (usually over 24 hr) typically followed by analyses at a central laboratory using ion chromatographic techniques. The availability of time resolved PM SO_4^{2-} and NO_3^- measurements provides the opportunity to better characterize and improve exposure estimates for these species in health effect assessments as well as advancing process science governing aerosol formation, transport, and evolution in the atmosphere. In recent years, several semicontinuous instrumentation methods, capable of providing real-time SO_4^{2-} and NO_3^- measurements, have been developed.²

The $PM_{2.5}$ Technology Assessment and Characterization Study—New York (PMTACS-NY) is one of several U.S. Environmental Protection Agency (EPA) “Supersites” intended to provide enhanced measurement data on chemical and physical composition of PM and its associated precursors. Two intensive summer sampling campaigns, as a part of the PMTACS-NY, were conducted at an urban and a rural location in 2001 and 2002, respectively.

The summer 2001 intensive field study took place on the campus of Queens College in New York City, while the summer 2002 field study was conducted at Whiteface Mountain (Adirondack State Park) in the northeastern part of New York state. A variety of research-grade and commercial gas and aerosol instruments were deployed and operated side by side during the campaign. The aerosol instruments capable of measuring SO_4^{2-} and NO_3^- are an Aerosol Mass Spectrometer (AMS), developed and manufactured by Aerodyne Research, Inc.; a Particle-Into-Liquid Sampler with Ion Chromatographs (PILS-IC), developed by Brookhaven National Laboratory and Georgia Institute of Technology and built at the Georgia Institute of Technology; Rupperecht and Patashnick Co., Inc. (R&P) 8400N Ambient Particulate Nitrate and 8400S Ambient Particulate Sulfate Monitors; and a Continuous Ambient Sulfate Monitor (CASM) developed by Allen et al.³ at the Harvard School of Public Health. Several filter samplers were operated during the summer 2001 and summer 2002 campaigns. Those operated during both campaigns included a Sequential Cyclone Sampler (SCS), developed and built at Wadsworth Center, New York State Department of Health; an R&P Model 1400 Tapered Element Oscillating Microbalance (TEOM) monitor with an Automated Cartridge Collection Unit (ACCU); and an R&P Partisol Model 2300 Speciation Sampler.

As a result of the summer 2001 campaign, several semicontinuous SO_4^{2-} measurement technologies were evaluated and their potential for routine monitoring was assessed.⁴ Results of evaluation of semicontinuous NO_3^-

technologies from the summer 2001 campaign have not been published separately and will be briefly discussed in this paper. Performing a similar evaluation of the SO_4^{2-} - and NO_3^- -measuring instruments in a rural environment during the summer 2002 field campaign allowed the assessment of instrument performance under aged aerosol and significantly lower precursor concentration conditions.

DATA COLLECTION

Instruments Field Deployment

Urban Site—Queens College. The summer 2001 campaign took place on the Queens College campus, Queens, New York City. The site was located at 40° 44' N latitude, 73° 49' W longitude, and ~25 m above sea level. There are two busy highways nearby: less than 1 km to the north is the Long Island Expressway (I-495), and ~1 km to the west is the Van Wyck Expressway (I-678). The semicontinuous instruments were housed in air-conditioned trailers situated in a parking lot of Queens College. Approximate heights of inlets of the instruments measuring particulate SO_4^{2-} and NO_3^- are listed in Table 1. The 8400N, the 8400S, and the CASM inlets were located within 2 m of the AMS and the PILS-IC inlets. The inlets of the 6-hr filter sampler (SCS) and one of the 24-hr samplers (TEOM/ACCU) were located ~10 m from the inlets of the semicontinuous instruments. Although the height of the SCS and the TEOM/ACCU inlets of 2 m above ground level is lower than that suggested by the EPA siting guidance, the $PM_{2.5}$ concentrations at 2 m are not expected to differ greatly from those at 5–10 m because of the relatively low deposition velocity for $PM_{2.5}$. The inlet of the Partisol 2300 Speciation Sampler (24-hr sampler) was on the roof of Public School 219 (PS219), located 100 m to the west of the Queens College parking lot, and separated by an athletic field. Because of the difference in ground elevation between the two sites, the inlet of this filter sampler was approximately at the same elevation as the inlets of the semicontinuous instruments. Another TEOM/ACCU sampler was located on the roof of PS219 as well. The results from these filters will not be presented in this paper. They are very similar to those from the first ACCU and can be found in Drewnick et al.⁴

Rural Site—Whiteface Mountain. The summer 2002 campaign took place at the Whiteface Mountain field station operated by the Atmospheric Sciences Research Center (ASRC) of the University at Albany. The sampling site for the intensive campaign was located at the station main facility on the shoulder of the Whiteface Mountain (44° 21' N latitude, 73° 51' W longitude, and ~600 m above sea level), properly known as Marble Mountain. Whiteface Mountain is part of the Adirondack Mountains in

Table 1. Characteristics of the semicontinuous instruments and the filter samplers.

Instrument	Measured Species	Inlet Height (m)	Inlet Flow—Sample Flow (L/min)	Size Selector	Denuder	Aerosol Collection	Analysis Method
8400N	NO ₃	QC: 4.5 WfM: 5	5–1	Sharp-cut PM _{2.5} cyclone	Activated carbon	Impaction on a NiChrome flash strip	Pulsed chemiluminescence (NO, NO ₂)
8400S	SO ₄	QC: 4.5 WfM: 5	5–1	Sharp-cut PM _{2.5} cyclone	Activated carbon	Impaction on a platinum flash strip	Pulsed fluorescence (SO ₂)
AMS	SO ₄ , NO ₃ , NH ₄	QC: 5 WfM: 5	10–0.1	PM _{2.5} cyclone	None	Continuous impaction on a heater	Mass spectrometry
CASM	SO ₄	QC: 4.5 WfM: 5	5–0.5	Sharp-cut PM _{2.5} cyclone	NaCO ₃ and carbon	Continuous flow through heated coil	Pulsed fluorescence (SO ₂)
PILS-IC	SO ₄ , NO ₃ , NH ₄	QC: 5 WfM: 5	10–5	PM _{2.5} cyclone	NaCO ₃ and citric acid	Particle growth in water vapor, impaction on a plate, liquid flow formation	Ion chromatography
SCS	SO ₄	QC: 2 WfM: 3	42	PM _{3.5} cyclone operated at higher flow to get PM _{2.5}	None	Zefluor filter	Ion chromatography
ACCU	SO ₄	QC: 2 WfM: 4.5	16.7–13.67	PM _{2.5} cyclone	None	Zefluor filter	Ion chromatography
Partisol 2300 Speciation Sampler	SO ₄ , NO ₃ , NH ₄	QC: 6.5 WfM: 4.5	14	PM _{2.5} impactor	NaCO ₃	Nylon filter	Ion chromatography

Note: Column 'Measured Species' includes only species discussed in this paper; inlet height is given in meters above the ground; QC = Queens College, summer 2001; WfM = Whiteface Mountain, summer 2002.

northeastern New York. The site is located in a clearing surrounded by a mix of deciduous and evergreen trees, many of which have grown to the height of 20 m or higher. Approximate distances to principal highways are 2 km (to Route 86) and 10 km (to Route 9N). The Adirondack Northway (I-87) is ~25 km to the west of the sampling site, and there are no major cities within 20 km. The semicontinuous instruments were housed in air-conditioned shelters. Approximate heights of inlets of the instruments are listed in Table 1.

The inlets of the semicontinuous instruments were not more than 15 m apart. (Distance between some inlets was much shorter.) One of the 24-hr filter samplers (the SCS) was located within 5 m of the AMS shelter. Two other 24-hr filter samplers (a 2300 speciation sampler and a TEOM/ACCU) were located on the roof of a main shelter within a few meters of the AMS shelter. The shelters located at approximately the same elevation on the mountain slope housed the 8400N, the 8400S, the CASM, and PILS-IC instruments. The AMS shelter and the SCS platform were located ~1 m up the slope, and the ground elevation of the shelter which housed the 2300 Speciation Sampler and the TEOM/ACCU was ~0.5 m higher than that of the AMS shelter. Because of the difference in ground elevation between some instrument shelters, elevation of the sampling inlet of the AMS was ~1 m higher than those of other semicontinuous instruments

and the same as that of the 2300 Speciation Sampler and the TEOM/ACCU. Each instrument had a PM_{2.5} selective inlet—the AMS and the PILS-IC were equipped with URG 2000–30EN cyclones operated at 10 L/min, the 8400N, the 8400S, and the CASM inlets had BGI sharp cut cyclones operated at 5 L/min. The SCS was equipped with a 28 L/min PM_{3.5} cyclone (URG 2000–30EC), operated at 42 L/min to shift the cutoff of the cyclone to 2.5 μm. The ACCU shared an inlet with a TEOM, which was equipped with a 16.7 L/min URG 3000–30EH cyclone. The 2300 Speciation Sampler was equipped with a Harvard impactor (greased sharp cut PM_{2.5} impactor) operated at 10 L/min.

Instrument Operation

This section briefly describes the operation of the instruments measuring mass concentrations of particulate SO₄²⁻ and NO₃⁻ during both campaigns. A detailed description of design, operation, quality assurance procedures, data reduction and processing, and performance evaluation of the AMS, the 8400S, the CASM, and the PILS-IC during the Queens field study can be found elsewhere.⁴ For the most part, the semicontinuous instruments were operated in a similar manner during the Whiteface Mountain campaign. Some of the characteristics and operational parameters of the instruments are listed in this section and in Table 1. Important differences

in instrument operation during the Whiteface campaign compared with the Queens study (if any) are noted in this section as well.

Aerosol Mass Spectrometer (AMS). A comprehensive description of the Aerosol Mass Spectrometer (AMS) and its principles of operation can be found in Jayne et al.⁵ Aerosol particles are focused by an aerodynamic lens: the lens used in Queens focused 60–600 nm spherical particles with almost 100% efficiency; for the lens used at the Whiteface, this range was wider: 40–600 nm. After being focused, the particles impact on a 500–700 °C heater surface, where volatile and semi-volatile particle components evaporate. The vapor is ionized by electron impact, and ions are analyzed with a quadrupole mass spectrometer. The AMS can be operated in two modes: the mass spectrometer mode (MS mode) and the time-of-flight mode (TOF mode). In the MS mode, the bulk composition of nonrefractory aerosol components is measured. In the TOF mode, the particle velocity distribution after the gas expansion into the vacuum (which can be transformed into a particle size distribution) is measured for the species represented by a selected mass. A detailed description of the AMS operation during the Queens campaign is given in Drewnick et al.^{6,7}

Operation parameters and maintenance procedures of the AMS during the Whiteface campaign were the same as those during the Queens campaign. During both campaigns, the AMS was switching between the TOF mode and the MS mode every 20 sec. Every 10 min, mass spectra, accounting for the AMS background signal, were saved on disk. Data processing, which takes into account various operational parameters and calibration factors, yielded concentrations of select PM chemical species, such as NO_3^- , SO_4^{2-} , ammonia (NH_3), and “organics.” The latter is the sum of all mass peaks that cannot be attributed to inorganic or gas-phase species. Therefore, particulate organics measured by the AMS may differ from mass concentration of “organics” measured by (or inferred from) other methods.

A correction factor had to be applied to the raw data to account for incomplete particle collection by the AMS, as a result of incomplete focusing of particles by the aerodynamic lens onto the heater. While pure ammonium nitrate (NH_4NO_3) particles are collected on the heater with 100% efficiency (as defined by laboratory and field calibrations), ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$] particles, as well as internally mixed $\text{NH}_4\text{NO}_3/(\text{NH}_4)_2\text{SO}_4$ particles are collected with significantly lower efficiencies.^{6,8} During both campaigns, the AMS particle size distribution measurements indicated that SO_4^{2-} and NO_3^- were internally mixed, validating the use of the correction factor, which was determined empirically. An average value of

the correction factor was calculated during the first week of the campaign by comparing the AMS and PILS-IC SO_4^{2-} data and then was applied to the AMS measurements throughout the entire campaign. The value of the factor was checked during other time periods of the same campaign, and no change was found.

The PILS-IC was used for determination of the AMS correction factor, because it has the longest track record among the semicontinuous instruments used in these two studies. It should be noted that there are indications that the correction factor value may change as a function of the NO_3^- to SO_4^{2-} ratio in the PM and the relative humidity and, therefore, could be a source of error in the AMS measurements for situations of extremely low or extremely high NO_3^- to SO_4^{2-} ratios. For the Queens campaign, the average correction factor was 2.34, while for the Whiteface campaign it was 1.48. This difference may be related to a different composition of the aerosol particles in the urban and rural environments. A difference in the ambient aerosol composition may lead to a difference in the particle shape, thus leading to a difference in focusing efficiency. More spherical particles are focused better, resulting in a smaller correction factor. In addition, the AMS had a different aerodynamic lens during the Whiteface campaign. This new and improved lens was used to increase the transmission efficiency for smaller particles. It is possible that using this aerodynamic lens also resulted in a different focusing efficiency of the aerosol particles.

Ambient Particulate Nitrate Monitor (8400N). The 8400N (manufactured by Rupprecht and Patashnick Co., Inc.) is the commercialized version of a prototype NO_3^- monitor described in Stolzenburg and Hering.⁹ A full operational cycle (10 min long during both campaigns) consists of a sampling and an analysis period. During the sampling part of the cycle (515 sec), aerosol is collected by impaction onto a NiChrome strip. Before collection, the sample passes through a honeycomb activated carbon denuder to remove potential gaseous interferents (nitric acid [HNO_3] and sulfur dioxide [SO_2] among other gases) and followed by a humidifier, where hydrophilic particles deliquesce, thus increasing their collection efficiency on the strip. Particles with diameters higher than 100 nm are collected with >95% efficiency.^{9,10} During the analysis period, the collection cell is purged with nitrogen and the strip is heated by electric current (~100 amp) from a battery to flash-volatilize the collected material. The heating time depends on the strip type. Originally, the instrument employed flat strips (used during the Queens campaign) and typical heating times were 65–90 msec. For formed strips (used during the Whiteface campaign), typical heating times were 90–120 msec. Formed strips have a kink at

each edge, which makes them more flexible. Consequently, they experience less stress during flash heating and are characterized by a longer lifetime compared with the flat strips. As a result of flash-volatilization, collected particulate NO_3^- is reduced to oxides of nitrogen (NO_x) ($\text{NO} + \text{NO}_2$). The evolved gases pass through a molybdenum converter of a NO_x gas analyzer, where an NO_2 fraction of NO_x is converted to NO . The gas analyzer measures total NO_x concentration from the light intensity of the chemiluminescent reaction of NO with ozone. The NO_x signal from the gas analyzer is converted to the mass concentration of particulate NO_3^- using the pressure, temperature, sample time, sample flow, conversion factors, and the baseline signal. Data post-processing includes corrections for the NO_x analyzer cell pressure, for analyzer audit results, and for dynamic blank readings. (The latter were measured every two weeks during the Queens study and every week during the Whiteface study.)

Ambient Particulate Sulfate Monitor (8400S). Design and operation principles of the 8400S (manufactured by Rupprecht and Patashnick Co., Inc.) are very similar to those of the 8400N. The main differences are that PM is collected on a platinum strip (typical heating times are 10–14 msec), a higher flash temperature is employed to reduce SO_4^{2-} to SO_2 (approximate current is 400 amp), the sampling cycle length is slightly shorter (485 sec), purge gas is air, evolved SO_2 (product of SO_4^{2-} reduction) is quantified by pulsed fluorescence.

Continuous Ambient Sulfate Monitor (CASM). The CASM was licensed from the Harvard School of Public Health and built in the field during the Queens study by one of the authors. Design and operation of the CASM is described in detail in Drewnick et al.,⁴ where it is referred to as the HSPH instrument. Ambient air passes through two denuders: an annular carbonate denuder and a honeycomb carbon denuder, to remove potential gaseous interferents (HNO_3 and SO_2 , among other gases). After passing through a Nafion dryer, the air flows through a 2.4-m-long stainless steel coil, which is located in a tube furnace heated to 900 °C. Particulate SO_4^{2-} evaporates and is reduced to SO_2 , which is continuously quantified by pulsed fluorescence in a gas analyzer. During both campaigns, measured SO_2 concentrations were recorded every minute and were used to calculate SO_4 concentrations, which were reported as 10-min averages. The first 10 min of every hour were used for an auto-zero cycle, which yielded the background signal (produced by the heated stainless steel coil and potential gaseous interferents not removed by the denuders). During this auto-zero cycle, the gas analyzer measured the concentration of SO_2 in

particle-free air, which was used for the baseline correction.

Particle-Into-Liquid Sampler with Ion Chromatographs (PILS-IC). The PILS-IC measures water-soluble ionic components of PM. Comprehensive descriptions of the instrument are given in Weber et al.¹¹ and Orsini et al.¹² Ambient air passes through two URG 2000 annular glass denuders (one coated with citric acid, another coated with sodium carbonate) to remove gaseous NH_3 , HNO_3 , and SO_2 . The air sample is then turbulently mixed with steam and passes into a small chamber at ambient temperature, creating a saturated environment. Particles down to ~25 nm are activated and grow to sizes between 1 and 5 μm diameter. These droplets are collected with a vertical impactor plate into a flow of purified water spiked with a known concentration of lithium bromide. The liquid flow is split and directed into two ion chromatographs, where the collected aerosol samples are analyzed for anions and cations simultaneously every 15 min. The PILS-IC provided 6-min (Queens study) and 10-min averages (Whiteface study) of the aerosol concentration every 15 min. Liquid concentrations of the ions were calculated from the peak areas of chromatograms, using multi-point calibration curves (separate calibrations were done for each ion several times during the campaigns). The liquid ion concentrations then were converted into the ambient aerosol concentrations, using the liquid lithium dilution factor and the aerosol sample flow. The background signal was checked approximately twice a week.

Sequential Cyclone Sampler (6-hr or 24-hr SCS). The 6-hr filter samples (Queens) and 24-hr filter samples (Whiteface) were collected using the SCS. In this instrument, no denuder was used to remove gaseous interferents. The aerosol is collected on 47-mm Zefluor filters. The filters were analyzed for SO_4^{2-} by ion chromatography in the laboratories of the New York State Department of Health (NYSDOH) at Wadsworth Center, Albany.

R&P Model 1400 TEOM Monitor with an Automated Cartridge Collection Unit (24-hr ACCU). 24-hr filter samplers were collected using the ACCU. The sampler shares the inlet with an R&P TEOM and uses its 13.67-L/min bypass flow. No denuder was used to remove gaseous interferents. The ACCU has an aluminum manifold that feeds to eight filter channels, each equipped with a 47-mm Zefluor filter. The filters are analyzed for SO_4^{2-} by ion chromatography in the NYSDOH laboratories at Wadsworth Center.

R&P Partisol Model 2300 Speciation Sampler (24-hr STN). These samplers are operated by the New York State Department of Environmental Conservation (NYSDEC). The

24-hr filter samples were collected every third day on 47-mm Nylon filters as part of the EPA Speciation Trends Network (STN). A glass honeycomb denuder coated with sodium carbonate was placed before the filter. The denuder was washed and re-coated after each sample day. After sampling, the filters were stored in a refrigerator and shipped in a cooler maintained at or below 4 °C. The filters were sent to the Research Triangle Institute to be analyzed by ion chromatography for NO_3^- , SO_4^{2-} , ammonium (NH_4^+), potassium, and sodium.

Data: Processing and Completeness

During the Queens summer 2001 campaign, most of the semicontinuous SO_4^{2-} and NO_3^- measurements, as well as the SCS and the ACCU filter measurements, started June 29–July 1 and continued until August 4–5. The only exception was the CASM. It was built in the field during the summer 2001 campaign and had a much shorter operation period compared to other instruments. During the Whiteface Mountain summer 2002 campaign, the semicontinuous and the SCS filter SO_4^{2-} and NO_3^- measurements started on July 9–13 and ended on August 5–7. The ACCU filter measurements at Whiteface are ongoing measurements performed by the ASRC, University at Albany, and the NYSDOH. The STN filter measurements in Queens and at Whiteface are ongoing measurements performed by the NYSDEC as part of the PMTACS-NY Supersite program. For the purpose of data comparison, filter data covering the periods of June 30–August 5, 2001, and July 13–August 6, 2002, were used. Periods of operation of each instrument are listed in Table 2.

As mentioned in the previous sections, the semicontinuous data used for analysis were adjusted based on instrument calibrations, various audits (e.g., flow checks for all instruments, gas analyzer performance checks for 8400N and 8400S monitors), and blank tests (where applicable). The filter data were adjusted for blanks. For statistical intercomparison of the semicontinuous SO_4^{2-} and NO_3^- instruments, hourly averages of mass concentration data from each instrument were calculated. Different sampling frequencies (also listed in Table 2) and collection and analysis schemes of

Table 2. Sampling information for the semicontinuous instruments and the filter samplers.

Instrument	Sampling Period	Sampling Frequency	Data Completeness
8400N	06/29–08/04 (QC)	10 min	86% (QC)
	07/09–08/07 (WfM)		88% (WfM)
8400S	06/29–08/05 (QC)	10 min	93% (QC)
	07/09–08/07 (WfM)		89% (WfM)
AMS	06/30–08/05 (QC)	10 min	94% (QC)
	07/09–08/07 (WfM)		98% (WfM)
CASM	07/22–08/05 (QC)	Continuous (10-min averages)	98% (QC)
	07/13–08/05 (WfM)		81% (WfM)
PILS-IC	07/01–08/05 (QC)	15 min	70% (QC)
	07/10–08/05 (WfM)		65% (WfM)
SCS	06/29–08/06 (QC)	4/day (QC), 1/day (WfM)	94% (QC)
	07/10–08/06 (WfM)		96% (WfM)
ACCU	07/07–08/03 (QC)	1/day	89% (QC)
	Ongoing measurements (WfM)		86% (WfM)
Partisol 2300 Speciation Sampler	Ongoing measurements (QC and WfM)	1 every 3rd day	85% (QC) 90% (WfM)

Note: 'Data Completeness' for each instrument is calculated for the whole sampling period; for semicontinuous instrument the calculation is based on 1-hr data; QC = Queens College, 2001, WfM = Whiteface Mountain, 2002.

the semicontinuous instruments were taken into account when averaging the data. Averaging intervals that had less than 75% valid values were removed from the data set. A similar averaging scheme was used to calculate 6- and 24-hr averages (used for statistical comparison of the semicontinuous and filter measurements).

Table 2 reports the "data completeness," which is calculated as the ratio of valid data points over the maximum possible data points. "Invalid" points include data missed because of scheduled maintenance or unexpected instrument stops, data removed by instrument operators (e.g., when the operational parameters of the instruments were outside the acceptable range), and data points removed during data processing, when averaging intervals are covered by less than 75%, when an instrument was malfunctioning, or when it is obvious before detailed analysis that data are faulty. Almost all data sets are 85–98% complete. The PILS-IC data sets are 65% (Queens) and 70% (Whiteface Mountain) complete because of various operational problems (e.g., operational errors, tubing failure, presence of air in the system, parts corrosion, necessity for nonroutine maintenance procedures, and down-times for the daily IC filter analysis). It should be noted that the completeness parameter is the first estimate. Data sets used for further analysis may be even less complete as a result of disqualification of outliers.

RESULTS AND DISCUSSION

SO₄²⁻ Measurements

Time series of the semicontinuous particulate SO₄²⁻ mass concentrations are shown in Figures 1a (Queens, summer 2001) and 2a (Whiteface Mountain, summer 2002). Observed concentration values ranged from 0 to 53 μg/m³ (Queens, summer 2001) and from 0 to 20 μg/m³ (Whiteface, summer 2002; as measured by the AMS). Particulate SO₄²⁻ concentrations are comparable at both sites. Several “SO₄²⁻ events” were detected during the campaigns. Most of those events were associated with long-range transport, while some of those events (e.g., July 16–17, 2001) can be attributed to local SO₄²⁻ formation at the urban site.

All four semicontinuous instruments provided particulate SO₄²⁻ data of high time resolution. Figures 1a and 2a show that the SO₄²⁻ measurements from the AMS, the 8400S, the CASM, and the PILS-IC generally tracked each other well during both campaigns (some discrepancies in measured SO₄²⁻ concentrations will be discussed later in this section). Good correlation between the instruments was observed during clean periods as well as during SO₄²⁻ events. However, Figure 2a shows that, while for the period of July 9–16, 2002, the CASM agreed well with the other semicontinuous instruments, after July 17, 2002, the CASM systematically over-measured SO₄²⁻. This could be explained by the fact that during a part of the summer 2002 campaign, the CASM has experienced several operational problems. The environmental conditions in the shelter significantly contributed to those problems.

Specifically, on July 17, as a result of excessive air conditioning, condensation was observed in zero cycle gas lines for the first time. The presence of liquid water in the line resulted in unreliable measurements of a baseline, leading to unreliable measurements of particulate SO₄²⁻. After July 17, there were short periods of time when disagreement between the CASM and other semicontinuous instruments was very small. Nevertheless, it was decided not to consider any CASM data collected after July 17 for further analysis.

Average diurnal patterns of particulate SO₄²⁻ calculated using different semicontinuous instruments look similar. In this paper, only average diurnal patterns of particulate SO₄²⁻ calculated from the AMS data are presented (see Figure 3). During both campaigns, the AMS proved to be a reliable instrument, which generated the most complete particulate component mass concentration data set. In addition, the AMS SO₄²⁻ data compared very well with the data from other semicontinuous instruments during the Queens campaign.⁴ The average diurnal pattern data are presented as boxplots, with the means, medians, and 5%, 25%, 75%, and 95% percentiles of the mass concentrations shown for every hour of the day. Although the mean diurnal concentrations from both studies appear to have maxima (see Figures 3a and 3b), they were caused by several high concentration events. The median diurnal SO₄²⁻ concentrations from both urban and rural sites did not follow a pronounced pattern, which is a characteristic feature of the dominating long-range transport of the particulate SO₄²⁻ into the eastern

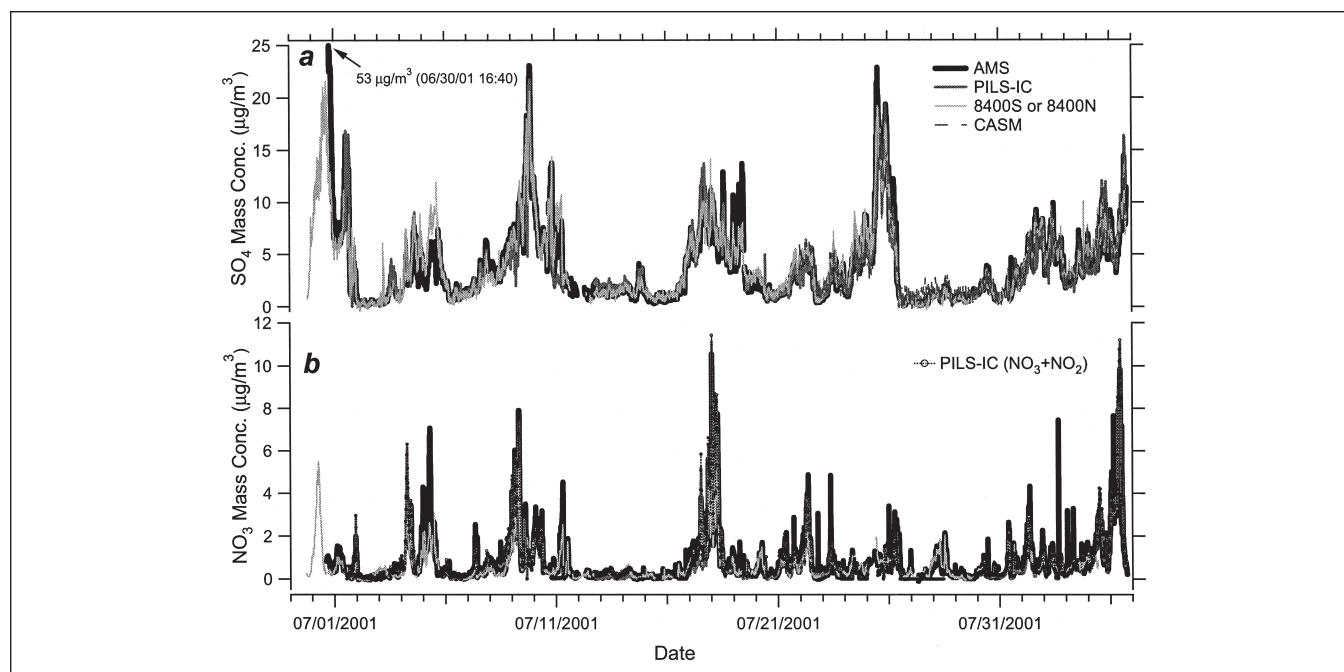


Figure 1. Time series of semicontinuous particulate (a) SO₄²⁻ and (b) NO₃⁻ mass concentrations measured during the summer 2001 campaign (Queens).

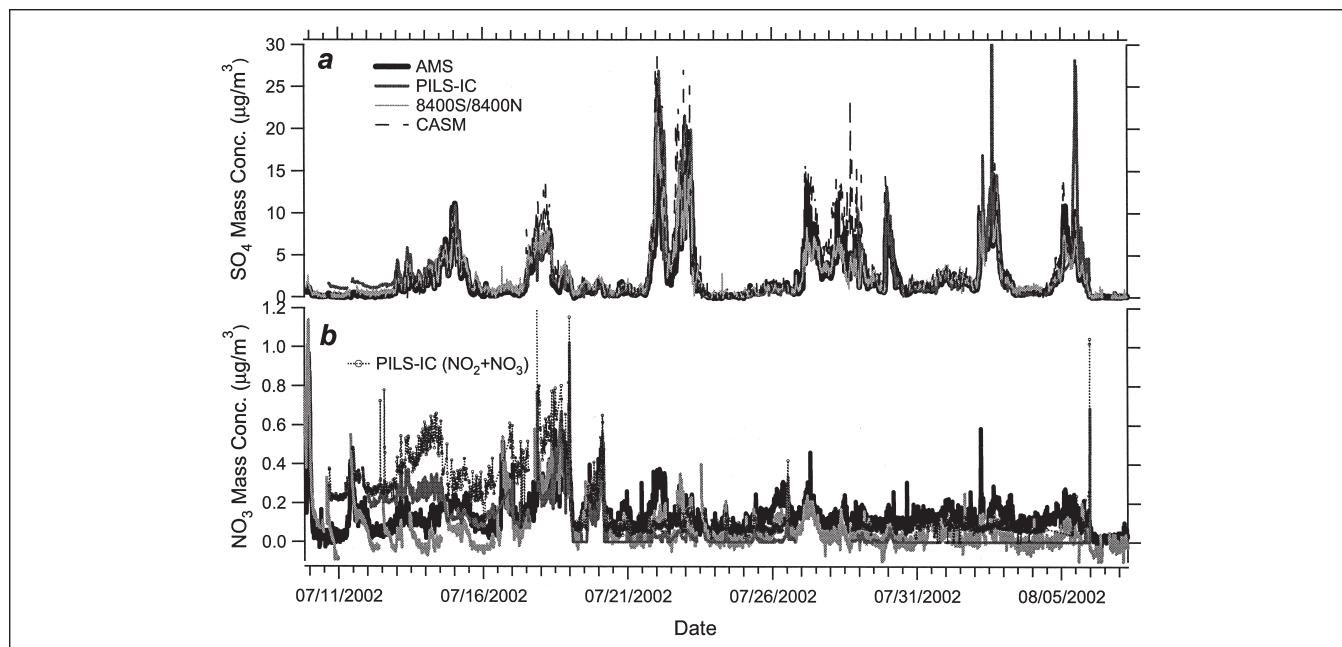


Figure 2. Time series of semicontinuous particulate (a) SO_4^{2-} and (b) NO_3^- mass concentrations measured during the summer 2002 campaign (Whiteface Mountain).

New York area. It should be noted that while it is not expected to observe a diurnal pattern of particulate SO_4^{2-} in a rural area, where the concentration of precursors is low, in the urban area, local sources contribute to the total concentration of particulate SO_4^{2-} (although this local contribution of the local sources is not apparent from the observed diurnal patterns).

Particulate SO_4^{2-} measurements from the AMS, the 8400S, the CASM, and the PILS-IC were intercompared using a linear regression analysis of the mass concentrations, averaged on a common 1-hr time basis. For details see Drewnick et al.⁴ Only the data that were above the instruments limit of detection (LOD) and data points that satisfy the 75% time completeness criterion were used for the analysis. The 75% time completeness criterion means that if less than 75% of valid data are available for the averaging period, the data for this period were removed from the data set used for analysis.

An example of the intercomparison of the semicontinuous instruments (the 8400S versus the AMS) for both campaigns is shown in Figure 4. A more complete set of the intercomparison results is given in Table 3. The table lists the slopes and the intercepts for the linear fits, as well as the number of points used for analysis, the concentration ranges over which the comparison was performed, R^2 (the correlation coefficient squared) values for each correlation, and the slopes of the direct linear correlations when the intercept is set to 0. (This slope is referred to as the recovery.) The recovery is used for direct comparison of the instrument responses. The semicontinuous SO_4^{2-}

data were first compared with the AMS, because it has the most complete data sets for both campaigns. The SO_4^{2-} measurements also were compared with the PILS-IC, because it has the longest field record. However, the PILS-IC data set is the least complete one for both campaigns (see Table 2). In fact, completeness of a data set used for analysis is even lower than the value shown in Table 2: during the Whiteface Mountain study, although the PILS-IC was operating from July 10 to August 5, the data from August 2 to August 5 are not usable because of a significant malfunctioning of the instrument peristaltic pump, which has resulted in an erratic impactor flow.

The semicontinuous SO_4^{2-} data from the four instruments from the Queens study are in excellent agreement: R^2 are 0.87–0.94, and the recoveries are 0.98–1.06. Correlating the data with the AMS and the PILS-IC produces similar results. On the other hand, a greater discrepancy exists between the various semicontinuous SO_4^{2-} data sets from the Whiteface study. The recoveries are 1.05 (8400S) and 1.3 (PILS-IC) with R^2 values of ~ 0.9 , when comparing the data to the AMS. As was discussed earlier in this section, after July 17, 2002, the CASM systematically over-measured SO_4^{2-} . Correlating the CASM data from July 9 to July 16 only with those from the AMS yielded the recovery of 0.96 and R^2 of 0.73. These results might not be representative of the whole summer 2002 intensive campaign, and, although shown in the Table 3, they will not be used in further discussion.

The AMS, the 8400S, and the PILS-IC SO_4^{2-} data also were correlated with data from the filter samples. For

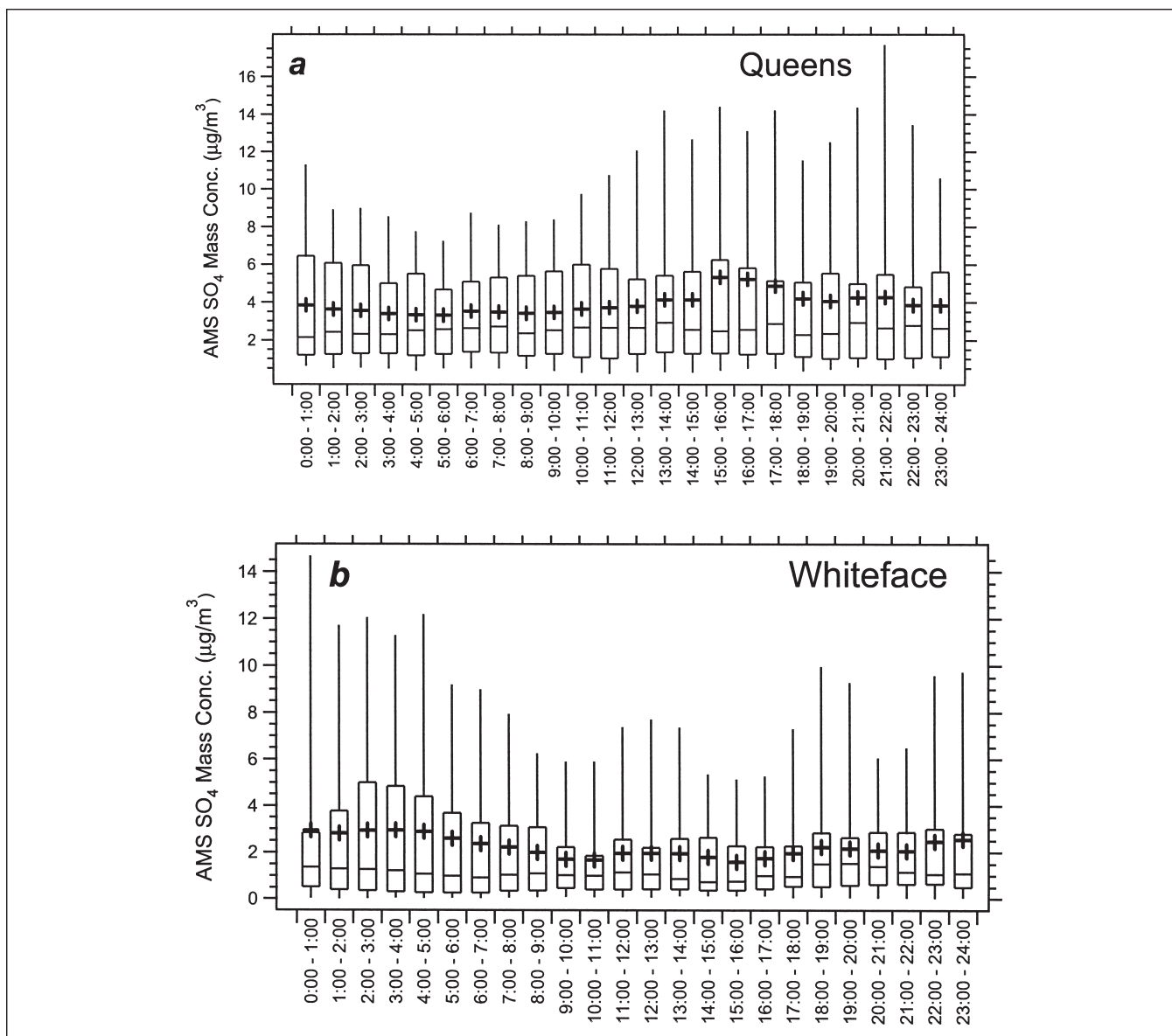


Figure 3. Average diurnal patterns for SO_4^{2-} mass concentrations, as measured by the AMS during (a) summer 2001 (Queens) and (b) summer 2002 (Whiteface Mountain). Boxes = 25% percentiles, the medians, and the 75% percentiles; whiskers = 5% and 95% percentiles; crosses = the means.

these comparisons, the semicontinuous data have been averaged over the filter collection time intervals: 6 hr (the SCS filters in Queens) and 24 hr (the SCS filters at Whiteface, the TEOM/ACCU sampler, and the STN filter sampler for both campaigns). Examples of such correlations are shown in Figure 5: the AMS and the 8400S data plotted versus the ACCU filter data and the corresponding linear fit lines. Complete results of correlations of the semicontinuous SO_4^{2-} measurements with those from integrated measurements, as well as of the filter measurements intercomparisons, are listed in Table 3.

Correlations between the semicontinuous instruments and the SCS filter data in Queens and at Whiteface are highly linear, with the R^2 ranging from 0.91 to 0.97.

For the Queens data, the slopes of linear correlations are between 0.71 and 0.73, with intercepts of the linear fits ranging from 0.09 to $0.34 \mu\text{g}/\text{m}^3$. The recoveries range from 0.72 to 0.77. For the Whiteface data, the slopes of the linear correlations span a much wider range from 0.74 (AMS and 8400S) to 1.15 (PILS-IC), and the intercepts range from -0.46 to $0.43 \mu\text{g}/\text{m}^3$. Correspondingly, there is a large difference in recoveries for different instruments (0.77 [AMS]–1.07 [PILS-IC]). The recovery values suggest that only $\sim 75\%$ of the SCS-measured SO_4^{2-} was detected by the semicontinuous instruments in Queens. At Whiteface the 8400S and the AMS under-measured SO_4^{2-} by 15–23% compared with the SCS filters, while the PILS-IC at Whiteface over-measured SO_4^{2-} by 7% compared with

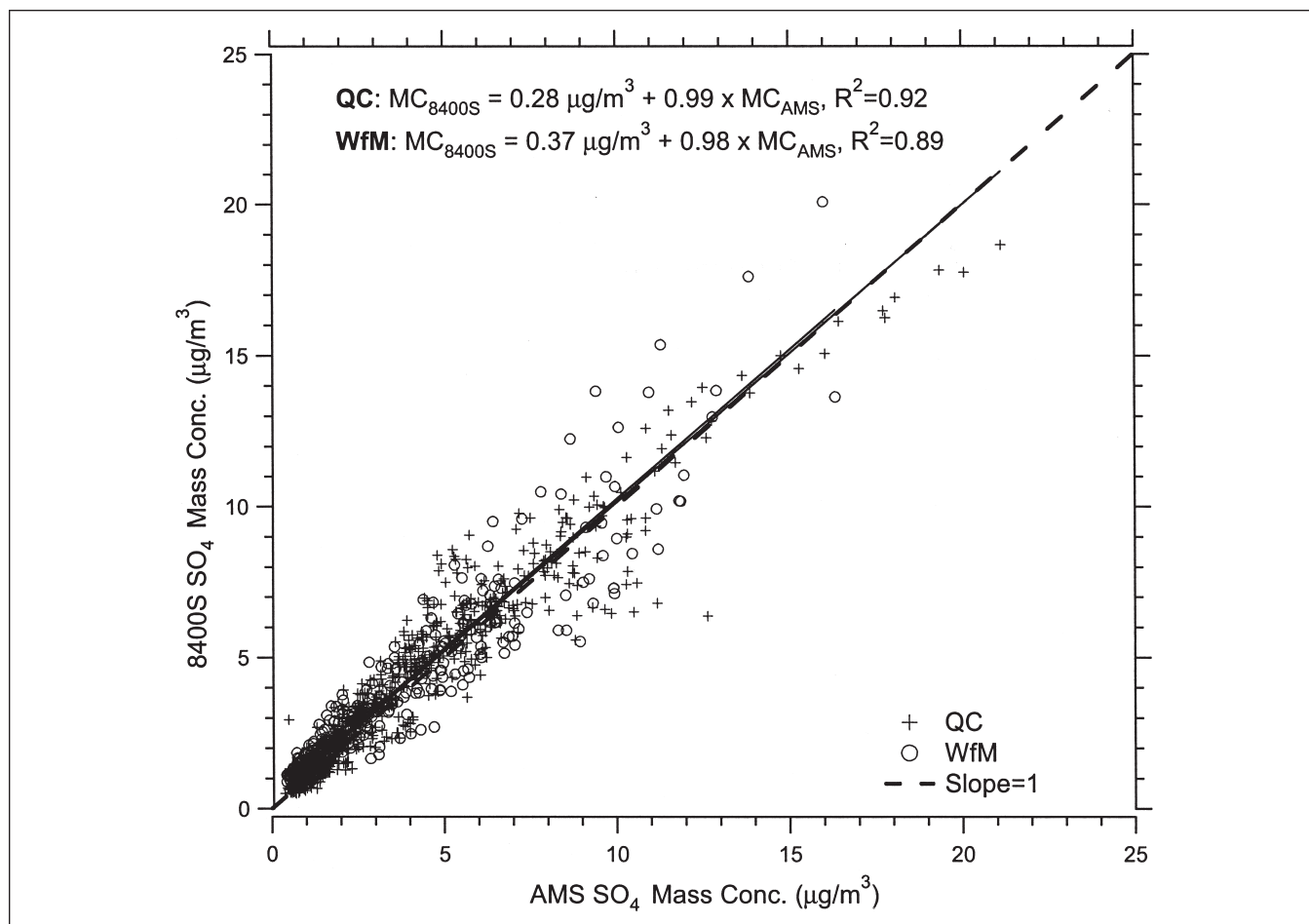


Figure 4. Queens (QC) and Whiteface Mountain (WfM) 8400S SO_4^{2-} mass concentration data (averaged over 1 hr) plotted vs. AMS data. Data points corresponding to the mass concentration measurements below the instrument LODs are not plotted.

the SCS filters. Similar trends were observed for the correlations of the semicontinuous SO_4^{2-} measurements with those from the ACCU filters— R^2 for both campaigns range from 0.92 to 0.98, the recoveries range from 0.8 to 0.87 in Queens and from 0.76 to 1.11 at Whiteface, with the PILS-IC being biased high compared with the ACCU filters.

Highly linear correlations were found between the semicontinuous instruments and the STN filter samples during both campaigns (R^2 0.97–0.99). The recoveries range from 0.83 to 0.91 for the Queens data. For the Whiteface data, the 8400S and the AMS SO_4^{2-} recoveries are 0.7 and 0.73 respectively. Correlating the PILS-IC measurements with those from the STN filters yielded the recovery of 1.29 and an R^2 of 0.65. This result is questionable. Only three data points were available to perform a comparison between the PILS-IC and the STN 24-hr filter samples.

Possible reasons for discrepancies between the semicontinuous instruments and the filter samples observed

during the Queens campaign are discussed elsewhere.⁴ Briefly, the discrepancies can be attributed to inlet transport losses, $\text{PM}_{2.5}$ selector cutoff issues, incomplete sampling of $\text{PM}_{2.5}$ by the semicontinuous instruments, SO_4 -to- SO_2 conversion losses of particles in the CASM, and positive filter artifacts. The incomplete sampling of the semicontinuous instruments is caused by inlet losses; <100% transmission efficiency of the AMS aerodynamic lens for particles with $D_{ae} < 60$ nm and $D_{ae} > 600$ nm; <95% strip collection efficiency of the 8400S for particles $D_{ae} < 100$ nm; <100% activation efficiency of the smaller particles; and losses of particles with $D_{ae} > 2$ μm because of impaction in the PILS-IC. Although during summer 2001, inlet losses caused by diffusion of smaller particles and impaction of larger particles were on the order of few percent, during the summer 2002 campaign, improved inlets were used to reduce these losses even more. In addition, using a different aerodynamic lens increased the AMS transmission efficiency of smaller particles.

Table 3. Parameters for the linear regression between the particulate SO_4^{2-} concentrations measured by four semi-continuous instruments and between the particulate SO_4^{2-} concentrations measured by the semicontinuous instruments and the 24-hr filters. For semicontinuous instruments intercomparisons, 1-hr averages were used. Only valid averaging intervals have been used for analysis; the recovery is the slope of the linear fit with the intercept forced to zero, R^2 is the correlation coefficient squared, N is the number of points, and MC is the mass concentration measured by the reference instrument.

Correlated Data	Site	Slope	Intercept $\mu\text{g}/\text{m}^3$	R^2	Recovery	N	MC Range $\mu\text{g}/\text{m}^3$
8400S vs. AMS	QC	0.99	0.28	0.92	1.03	695	0.4–21.1
8400S vs. AMS	WfM	0.99	0.37	0.89	1.05	407	0.4–16.3
PILS-IC vs. AMS	QC	0.99	-0.06	0.91	0.98	549	0.2–21.1
PILS-IC vs. AMS	WfM	1.32	-0.14	0.91	1.3	369	0.1–16.3
CASM vs. AMS	QC	0.97	0.39	0.94	1.04	316	0.2–17.8
CASM vs. AMS	WfM	0.84	0.52	0.73	0.96	64 ^a	0.4–10.5
8400S vs. PILS-IC	QC	0.99	0.36	0.87	1.04	526	0.5–20.4
8400S vs. PILS-IC ^b	WfM	0.82	0.59	0.94	0.89	228	0.3–23.8
AMS vs. PILS-IC	QC	1.01	0.06	0.91	1.02	549	0.1–20.4
AMS vs. PILS-IC ^b	WfM	0.76	0.11	0.91	0.77	369	0.1–24.4
CASM vs. PILS-IC	QC	0.99	0.48	0.93	1.06	280	0.1–17.5
CASM vs. PILS-IC ^b	WfM	0.95	-0.66	0.73	0.81	56 ^a	0.9–9.4
AMS vs. Filters (6-hr SCS)	QC	0.73	0.09	0.93	0.75	124	0.3–26
AMS vs. Filters (24-hr SCS)	WfM	0.74	0.16	0.96	0.77	27	0.1–11.9
8400S vs. Filters (6-hr SCS)	QC	0.73	0.34	0.95	0.77	114	0.4–21.6
8400S vs. Filters (24-hr SCS)	WfM	0.74	0.43	0.96	0.83	25	0.2–11.9
PILS-IC vs. Filters (6-hr SCS)	QC	0.71	0.13	0.91	0.72	85	0.3–21.6
PILS-IC vs. Filters (24-hr SCS)	WfM	1.15	-0.46	0.97	1.07	11	0.7–11.9
AMS vs. Filters (24-hr ACCU)	QC	0.85	-0.09	0.97	0.84	22	0.9–10.8
AMS vs. Filters (24-hr ACCU)	WfM	0.71	0.3	0.93	0.76	24	0.1–11.8
8400S vs. Filters (24-hr ACCU)	QC	0.85	0.1	0.96	0.87	23	0.9–14.3
8400S vs. Filters (24-hr ACCU)	WfM	0.74	0.52	0.92	0.84	22	0.1–11.8
PILS-IC vs. Filters (24-hr ACCU)	QC	0.81	-0.07	0.98	0.8	16	0.6–14.3
PILS-IC vs. Filters (24-hr ACCU)	WfM	1.11	0.01	0.96	1.11	11	0.3–11.8
AMS vs. Filters (24-hr STN)	QC	0.89	-0.37	0.97	0.84	8	1.3–11.2
AMS vs. Filters (24-hr STN)	WfM	0.68	0.21	0.99	0.73	9	0.1–7.7
8400S vs. Filters (24-hr STN)	QC	0.94	-0.21	0.97	0.91	7	1.3–11.2
8400S vs. Filters (24-hr STN)	WfM	0.53	0.16	0.97	0.7	7	0.2–7.7
PILS-IC vs. Filters (24-hr STN)	QC	0.85	-0.16	0.98	0.83	8	0.6–11.2
PILS-IC vs. Filters (24-hr STN)	WfM	2.37	-1.8	0.65	1.29	3	1–1.9
Filters: 6-hr SCS vs. 24-hr STN	QC	1.04	-0.04	0.99	1.04	11	0.6–25.8
Filters: 24-hr SCS vs. 24-hr STN	WfM	0.95	0.17	1	0.99	9	0.1–7.7
Filters: 24-hr ACCU vs. 24-hr STN	QC	0.98	-0.1	1	0.97	7	0.6–11.2
Filters: 24-hr ACCU vs. 24-hr STN	WfM	0.82	0.24	0.97	0.87	9	0.1–7.7

Note: QC = Queens College, summer 2001; WfM = Whiteface Mountain, summer 2002; ^aData from July 9–16, 2002, only; ^bThe original Whiteface PILS-IC data set is only 65% complete. In addition, data from August 2 to August 5 were removed from the data set used for the analysis.

Formation of additional SO_4^{2-} on the filters through oxidation SO_2 or condensation of H_2SO_4 on the filters may occur in a basic environment if filter samplers are not equipped with denuders (the case with SCS and the ACCU). The data from the undenuded SCS and ACCU filter samples were compared with those from the denuded STN filters (the results are shown in Table 3). For both campaigns, the filter correlations were highly linear (R^2 0.97–1), with the recoveries ranging from 0.87 to 1.04. Therefore, it is unlikely that positive filter artifacts

are responsible for the discrepancies between the semicontinuous SO_4^{2-} measurements and those from the SCS and the ACCU filters during both campaigns, as well as for larger discrepancies between the semicontinuous SO_4^{2-} measurements and those from the SCS filters, compared with the STN filters in Queens.

Also, while the other instruments used $\text{PM}_{2.5}$ cyclones or a $\text{PM}_{2.5}$ impactor, the SCS sampler was operated with a $\text{PM}_{3.5}$ cyclone at an elevated flow rate to get a $\text{PM}_{2.5}$ cutoff. This could cause a slight shift in sampling

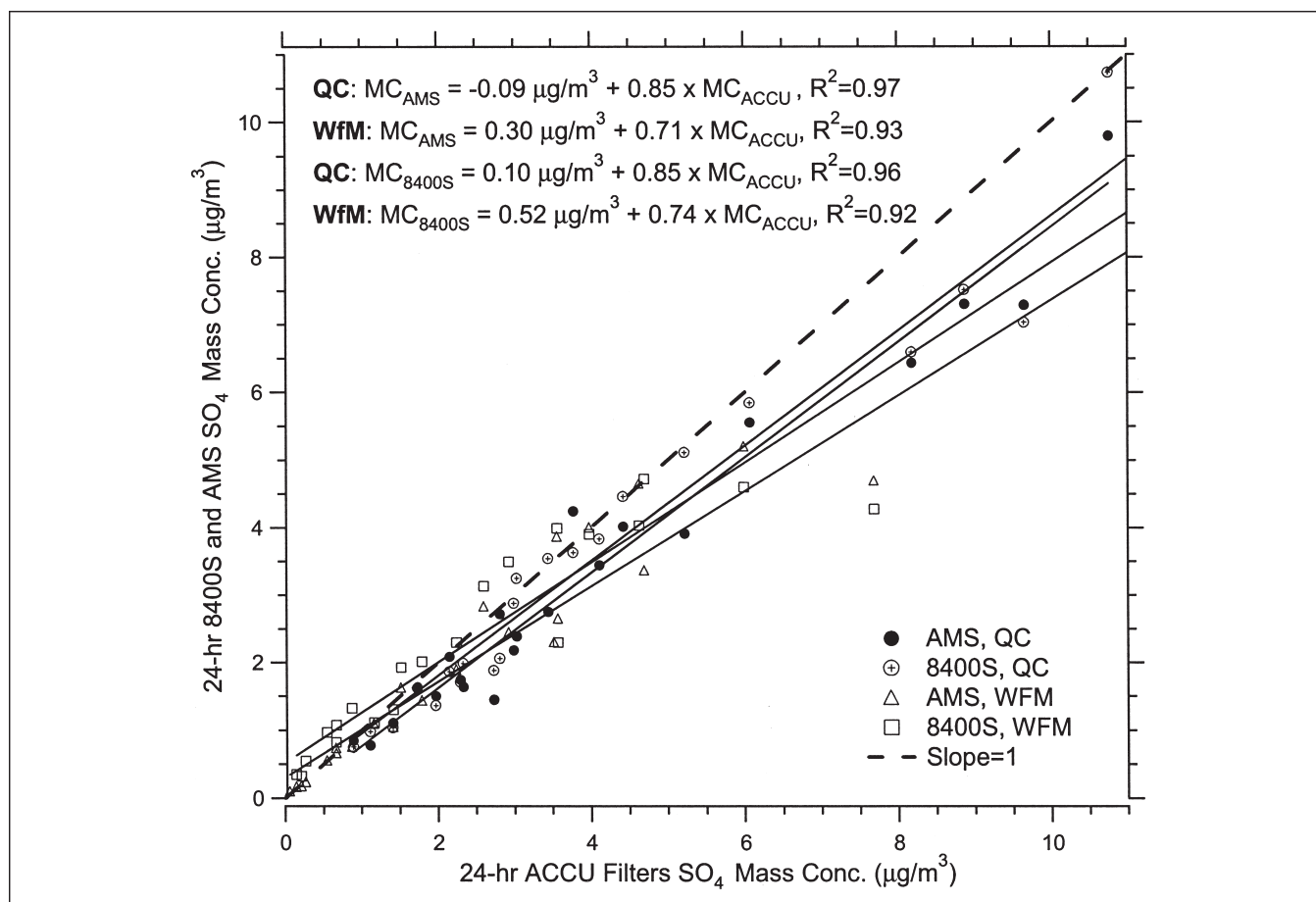


Figure 5. 8400S and AMS SO_4^{2-} mass concentration data plotted vs. 24-hr TEOM/ACCU filter data. The semicontinuous data are averaged over 24 hr.

cutoff and a less steep cutoff curve, possibly causing the observed higher SO_4^{2-} mass concentrations. However, while the recoveries of “the semicontinuous instruments versus SCS filters” regressions are 5–10% higher than “the semicontinuous instruments versus ACCU filters” regressions in Queens, the recoveries of the linear regressions agree within 4% for the comparisons with the SCS and the ACCU filters at Whiteface. Therefore, over-measuring of particulate SO_4^{2-} by the SCS filters at Whiteface cannot be attributed to cutoff characteristics of the $\text{PM}_{3.5}$ cyclone on the SCS.

The other factors associated with the semicontinuous instruments, which were listed previously, can explain some of the discrepancies between the semicontinuous instruments and the filter samples during the Queens campaign. However, recovery values of the AMS and the 8400S versus the STN filters regressions during the Whiteface campaign cannot be explained by those factors alone. The recoveries of the AMS versus STN filters regressions were 0.84 in Queens and 0.73 at Whiteface. A similar trend was observed for the 8400S: 0.91 recovery

in Queens and 0.7 recovery at Whiteface. Incomplete sampling of larger particles ($D > 0.6 \mu\text{m}$) can be an issue for the AMS. The size distribution data from an SMPS (TSI Model 3936) and an APS (TSI Model 3322), operated during both campaigns, were used to calculate the total aerosol mass from particles with $D < 0.6 \mu\text{m}$ ($M_{D<0.6 \mu\text{m}}$) and particles with $D < 2.5 \mu\text{m}$ ($M_{D<2.5 \mu\text{m}}$). The average ratio of $M_{D<0.6 \mu\text{m}}$ to $M_{D<2.5 \mu\text{m}}$ was 0.82 in Queens and 0.78 at Whiteface. Therefore, the incomplete sampling of the larger particles by the AMS is not the only reason for the lower recovery of the AMS at Whiteface (compared with that at Queens). The difference in the recovery values (Queens versus Whiteface) is even larger for the 8400S than for the AMS. No explanation for this discrepancy was found. It should be noted that, while in the Queens data set the SO_4^{2-} mass concentrations from the STN filters were distributed relatively evenly between 1.3 and $11.2 \mu\text{g}/\text{m}^3$, in the Whiteface STN data set, most data points were in the range of 0.1– $2.7 \mu\text{g}/\text{m}^3$, and only one data point was $7.7 \mu\text{g}/\text{m}^3$. Removal of the latter from the Whiteface STN filter data set would result in significant

changes in calculated recoveries: 0.89 for the AMS and 1.18 for the 8400S (instead of 0.73 and 0.7, respectively).

It was also shown that, while in Queens the SO_4^{2-} recoveries of all semicontinuous instruments (compared with all filter samples) were less than unity, at Whiteface, this was not the case for the correlations of the PILS-IC versus the SCS (1.07) and the ACCU (1.11) filters. The reason for these greater than unity recovery values is not clear.

NO_3^- Measurements

Time series of the particulate NO_3^- mass concentration for the semicontinuous instruments are shown in Figures 1b (Queens, summer 2001) and 2b (Whiteface Mountain, summer 2002). The observed particulate NO_3^- mass concentrations ranged from 0 to $11 \mu\text{g}/\text{m}^3$ (Queens, summer 2001) and from 0 to $1 \mu\text{g}/\text{m}^3$ (Whiteface, summer 2002; as measured by the AMS). Generally, during the Queens study, the AMS, the 8400N, and the PILS-IC NO_3^- measurements tracked each other well. However, during certain time periods, the 8400N under-measured the particulate NO_3^- mass concentration. The Whiteface semicontinuous NO_3^- measurements appeared to show less correlation with each other than with those from Queens. At the rural site, the AMS measured more NO_3^- than did the 8400N for the most part; however, in some instances, the opposite was observed. Most of the 8400N measurements at the rural site were below the LOD of the instrument, and the variations in those concentrations largely reflect instrumental noise. The AMS, on the other hand, appeared to have captured the fine time structure of particulate NO_3^- . This is the result of the average value of the AMS LOD being much lower than the 8400N LOD (0.03 versus $0.15 \mu\text{g}/\text{m}^3$).

For the first week of the Whiteface campaign, the PILS-IC measured more NO_3^- than did the AMS and the 8400N, then, up to July 20, the PILS-IC seemed to agree with the other two instruments, whereas for the remainder of the campaign, the PILS-IC under-measured NO_3^- compared with the AMS and the 8400N. The agreement between the three semicontinuous instruments improves when the sum of nitrate and nitrite as measured by the PILS-IC is used (see Figure 2b; the AMS and the 8400N do not distinguish between these two particulate species, while the PILS-IC does). It is clear that, for data up to July 19, the PILS-IC had a systematic positive error in measuring nitrite. This was because of an unnecessarily large aqueous flow through the PILS impactor (caused by wider tubing used in a peristaltic pump) resulting in greater dilution of the soluble aerosol components delivered to the ion chromatographs during the beginning of the campaign. The generally low ambient loading of nitrite observed during this period, combined with the excessive

dilution, resulted in the aqueous concentrations of nitrite to be very close to the IC LOD (thus increasing the uncertainty of IC measurements). On July 18, the aqueous impactor flow was reduced, effectively reducing the volume into which the ambient aerosol was diluted, and resulted in nearly a factor of 4 improvement of in the LOD. The inconsistent quality of distilled water also may have contributed to the over-measuring of nitrite. Larger aqueous impactor flow and inconsistent water quality did not seem to have a pronounced effect on the measured SO_4^{2-} concentrations (see Figure 2a); however, they did affect the measured NO_3^- concentrations significantly. Starting July 19, the PILS-IC ($\text{NO}_3^- + \text{NO}_2^-$) data seem to correlate better with the NO_3^- data from the AMS and the 8400N. It was decided not to use PILS-IC measurements from the beginning of the campaign to July 19 for data comparisons. As was discussed in the previous section, the data from August 2 to August 5 were not used for the comparisons either. It is worth noting that, while combining the nitrite and NO_3^- concentrations significantly changed the PILS-IC correlation with the other semicontinuous instruments at Whiteface, doing so for the Queens data did not lead to any significant changes. This is likely caused by the significantly lower ambient NO_3^- observed at the rural site compared with the urban site.

Figure 6 shows average diurnal patterns of particulate NO_3^- calculated using the AMS data. The average diurnal patterns data are presented as boxplots, with the means, medians, and 5%, 25%, 75%, and 95% percentiles of the mass concentrations shown for each hour of the day.

The average particulate NO_3^- concentrations measured in Queens exhibited a clear diurnal pattern (see Figure 6a) with a maximum NO_3^- concentration observed in the morning hours, peaking between 6:00 a.m. and 8:00 a.m. local time. A minimum NO_3^- concentration was observed in the afternoon around 2:00–4:00 p.m. During the night, NO_3^- levels increased again, resulting in a second smaller maximum around midnight. The observed NO_3^- diurnal pattern is qualitatively consistent with the gaseous precursor sources for NH_4NO_3 and the observed summertime diurnal temperature pattern for the measurement period.⁶ Similar diurnal trends in particulate NO_3^- have been observed in previous studies.⁹ At Whiteface, the average diurnal NO_3^- concentrations did not follow a pronounced pattern (see Figure 6b). This is likely caused by the very low levels of particulate NO_3^- precursors present in the rural area. Only one NO_3^- "event" (maximum observed NO_3^- concentration was $\sim 1 \mu\text{g}/\text{m}^3$) was observed at Whiteface, while in Queens, several NO_3^- events were detected with measured mass concentrations as high as $12 \mu\text{g}/\text{m}^3$. All NO_3^- events

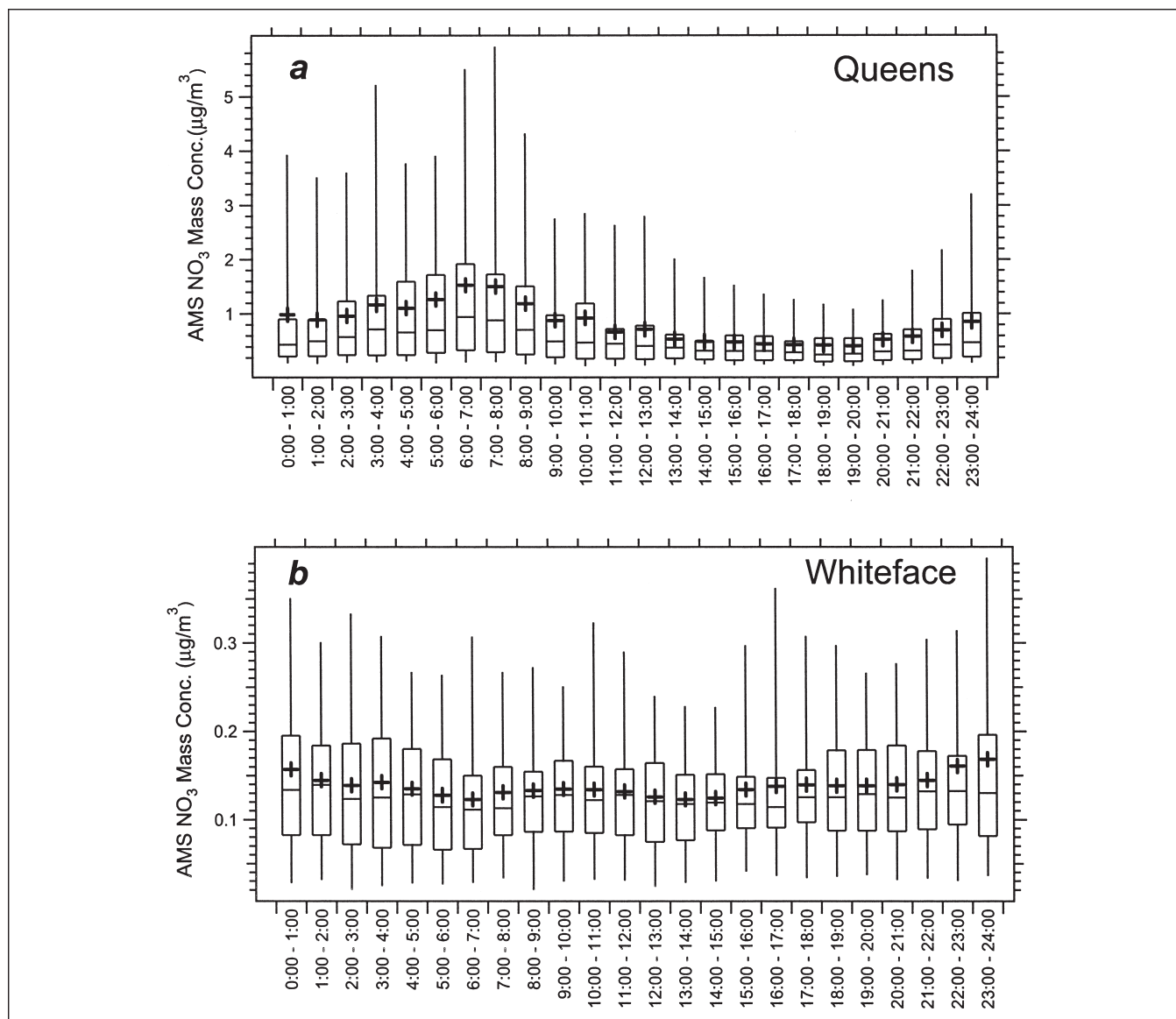


Figure 6. Average diurnal patterns for NO_3^- mass concentrations, as measured by the AMS during (a) summer 2001 (Queens) and (b) summer 2002 (Whiteface Mountain). Boxes = 25% percentiles, the medians, and the 75% percentiles; whiskers = 5% and 95% percentiles; crosses = the means.

coincided in time with SO_4^{2-} events (see Figures 1b and 2b). Particulate NO_3^- observed during those events could be either transported together with SO_4^{2-} from distant locations to the measurement sites or formed locally when the ambient concentration of OH radicals increased, leading to local formation of both NO_3^- and SO_4^{2-} . The AMS size distribution measurements suggest that the SO_4^{2-} and NO_3^- were internally mixed and can support both source possibilities.

The particulate NO_3^- measurements from the AMS, the 8400N, and the PILS-IC were intercompared. The intercomparison was performed by linear regression analysis of the mass concentrations, using the same technique as described in the previous section for SO_4^{2-} . Only data

that were above the detection limits of the corresponding semicontinuous instruments were included in the analysis. This resulted in fewer points being available for the intercomparison at Whiteface, compared with Queens. The PILS-IC data used for this intercomparison were the sum of NO_3^- and NO_2^- mass concentrations. If at least one of the NO_3^- and NO_2^- measurements was above the corresponding LOD value ($0.05 \mu\text{g}/\text{m}^3$ for NO_3 and $0.14 \mu\text{g}/\text{m}^3$ for NO_2), the corresponding ($\text{NO}_3^- + \text{NO}_2^-$) data point was used for the intercomparison of the PILS-IC with other semicontinuous instruments. All hourly data used for the analysis satisfy the 75% time completeness criterion. An example of semicontinuous NO_3^- data intercomparison (the 8400N versus the AMS) is shown in

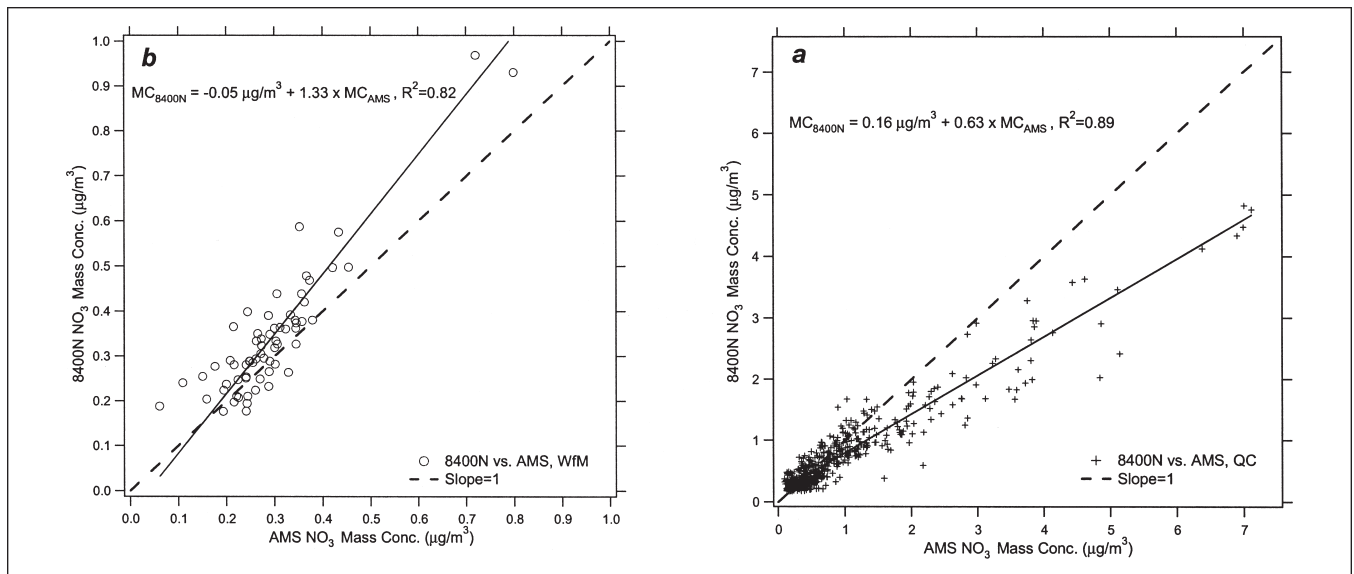


Figure 7. 8400N NO₃⁻ mass concentration data (averaged over 1 hr) plotted vs. AMS data for (a) Queens (QC) and (b) Whiteface Mountain (WfM) campaigns. Data points corresponding to the mass concentration measurements below the instrument LODs are not plotted.

Figure 7a for the Queens campaign and in Figure 7b for the Whiteface Mountain campaign. The results of all intercomparisons are shown in Table 4. The AMS and the PILS-IC were both used as reference instruments for the intercomparisons. The table lists the slope, the intercept, and the recovery for each linear correlation, along with the number of points and the concentration range used for the analysis.

Correlations between the semicontinuous NO₃⁻ measurements in Queens are highly linear: R² ranges from 0.89 to 0.95. Corresponding values of R² at Whiteface are lower: 0.61–0.82. During the Queens campaign, the AMS measured 12% less NO₃⁻ than did the PILS-IC. During the Whiteface campaign, the recovery of the AMS versus PILS-IC correlation was 1.02. Much better agreement of the 8400N measurements with those from the PILS-IC

Table 4. Parameters for the linear regression between the particulate NO₃⁻ concentrations measured by three semi-continuous instruments and between the particulate NO₃⁻ concentrations measured by the semicontinuous instruments and the 24-hr filters. For semicontinuous instruments intercomparisons, 1-hr averages were used. Only valid averaging intervals have been used for analysis; the recovery is the slope of the linear fit with the intercept forced to zero, R² is the correlation coefficient squared, *N* is the number of points, and MC is the mass concentration measured by the reference instrument.

Correlated Data	Site	Slope	Intercept µg/m ³	R ²	Recovery	<i>N</i>	MC Range µg/m ³
8400N vs. AMS	QC	0.63	0.16	0.89	0.72	533	0.1–7.1
8400N vs. AMS	WfM	1.33	-0.05	0.82	1.18	65	0.1–0.8
PILS-IC vs. AMS	QC	1.15	-0.03	0.95	1.14	363	0.1–7.5
PILS-IC vs. AMS	WfM	1.81	-0.19	0.61	0.98	45	0.1–0.4
AMS vs. PILS-IC	QC	0.87	0.03	0.95	0.88	363	0.2–10
AMS vs. PILS-IC ^a	WfM	0.55	0.1	0.61	1.02	45	0.1–0.5
8400N vs. PILS-IC	QC	0.57	0.18	0.9	0.63	285	0.2–8.4
8400N vs. PILS-IC ^a	WfM	0.49	0.13	0.66	0.91	16	0.1–0.5
AMS vs. Filters (24-hr STN)	QC	0.92	-0.06	0.99	0.9	7	0.2–3.9
AMS vs. Filters (24-hr STN)	WfM	0.51	0.06	0.46	0.93	9	0–0.2
8400N vs. Filters (24-hr STN)	QC	0.65	0.05	0.99	0.67	8	0.2–2.8
8400N vs. Filters (24-hr STN)	WfM	0.73	-0.01	0.83	0.65	7	0–0.2
PILS-IC vs. Filters (24-hr STN)	QC	1.05	-0.29	0.98	0.92	7	0.2–2.8
PILS-IC vs. Filters (24-hr STN)	WfM	—	—	—	—	2	0.1–0.2

Note: QC = Queens College, summer 2001; WfM = Whiteface Mountain, summer 2002; ^aThe original Whiteface PILS-IC data set is only 65% complete. In addition, data from July 10 to July 18 and August 2 to August 5 were removed from the data set used for the analysis.

was observed during the Whiteface campaign (0.63 versus 0.91 recovery values). Results shown in Table 4 also indicate that the 8400N under-measured NO_3^- by 28% compared with the AMS in Queens, but over-measured it by 18% at Whiteface. However, much of the 8400N NO_3^- data at Whiteface is at or below the instrument LOD (see Figure 2b). Correlating the 8400N with the AMS measurements from the Whiteface site using all data points yields the recovery of 0.8 (not shown in the table), but lower R^2 value (0.74 versus 0.82 when only data above the LODs are used). It should be noted that including the NO_3^- mass concentrations below the LOD in the linear regressions analyses resulted in almost no change in the slopes and the intercepts of the 8400N versus the AMS fit for Queens data. This was not the case for the Whiteface data, because there was a much larger fraction of the NO_3^- mass concentrations below the 8400N LOD.

The semicontinuous NO_3^- data from the AMS and the 8400N were also compared with data from the STN filter samples. Because there were only two data points for the PILS-IC versus the Whiteface STN filters correlation, these data are not presented. Figures 8a and 8b show examples of the correlations: the AMS and the 8400N data plotted versus the filter data and the corresponding linear fit lines for the Queens campaign and the Whiteface campaign, respectively. Table 4 also presents results of the comparison of all semicontinuous NO_3^- measurements with those from the STN filter samples. Correlations between the semicontinuous instruments and the filter data in Queens are highly linear, with the 0.98–0.99 R^2 . During the Queens campaign, the AMS and the PILS-IC agree

with the filters within 10%. The 8400N, however, under-measures NO_3^- by 33% compared with the filters. Possible reasons for the 10% discrepancy between the semicontinuous NO_3^- measurements and those from the filters during the Queens campaign include $\text{PM}_{2.5}$ inlet cutoff issues, incomplete sampling of $\text{PM}_{2.5}$ by the semicontinuous instruments, and inlet transport losses. They are likely to be the same for the Whiteface campaign. The reason for the larger disagreement between the 8400N and the filters (as well as between the 8400N and other semicontinuous instruments in Queens) is unknown. Recoveries of the AMS and the 8400N compared with the filters are almost the same for two campaigns: 0.9 (AMS, Queens) versus 0.93 (AMS, Whiteface), and 0.67 (8400N, Queens) versus 0.65 (8400N, Whiteface). The 8400N appears to systematically under-measure particulate NO_3^- compared with filters at both the rural and the urban location with an approximate difference of 35%. The 8400N measurements continued at Whiteface after the intensive campaign in cooperation with the NYSDEC as a part of the PMTACS-NY Supersite program. Correlating the 8400N data with the STN filter data for the period of August–December 2002 yielded the recovery of 0.69, which is consistent with the results from the intensive studies. For comparison, correlating the 8400N data from another PMTACS-NY monitoring site in New York City (School 52, Bronx) for the same time interval yielded the recovery value of 0.51 (the slope was 0.47 and the intercept was 0.15, with an R^2 of 0.94). The recovery for the Bronx August–December 2002 data is only slightly lower than the recovery obtained during the summer 2001 campaign.

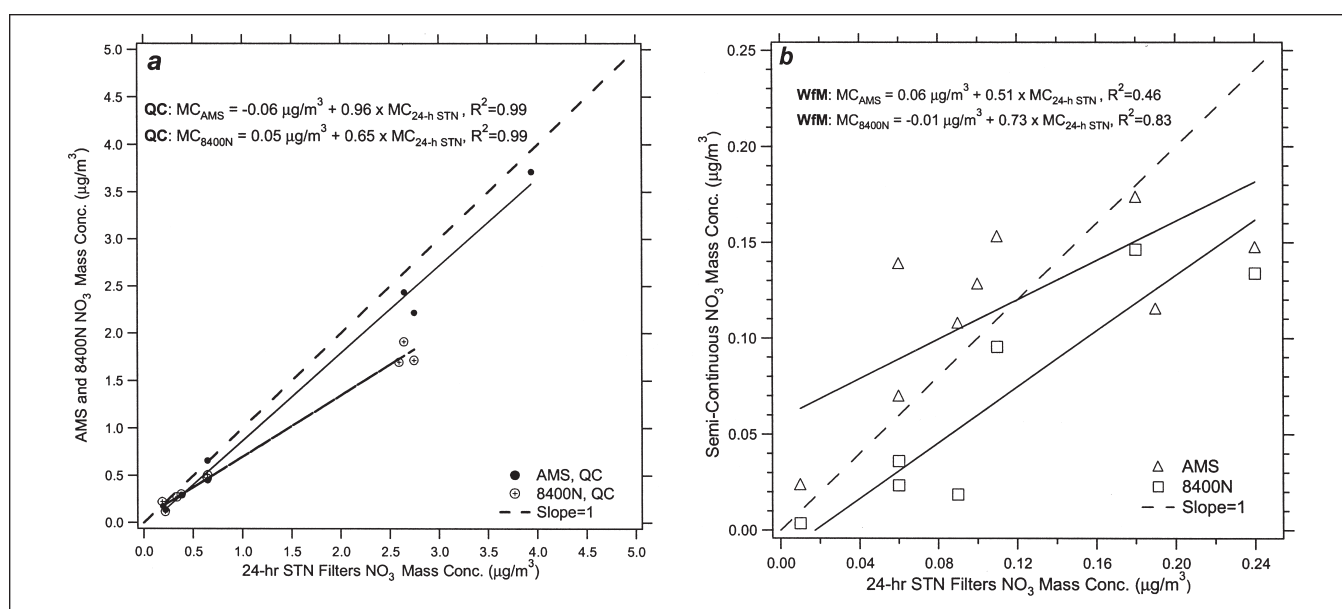


Figure 8. 8400N and AMS SO_4^{2-} mass concentration data plotted vs. 24-hr STN filter data for (a) Queens (QC) and (b) Whiteface Mountain (WfM) campaigns.

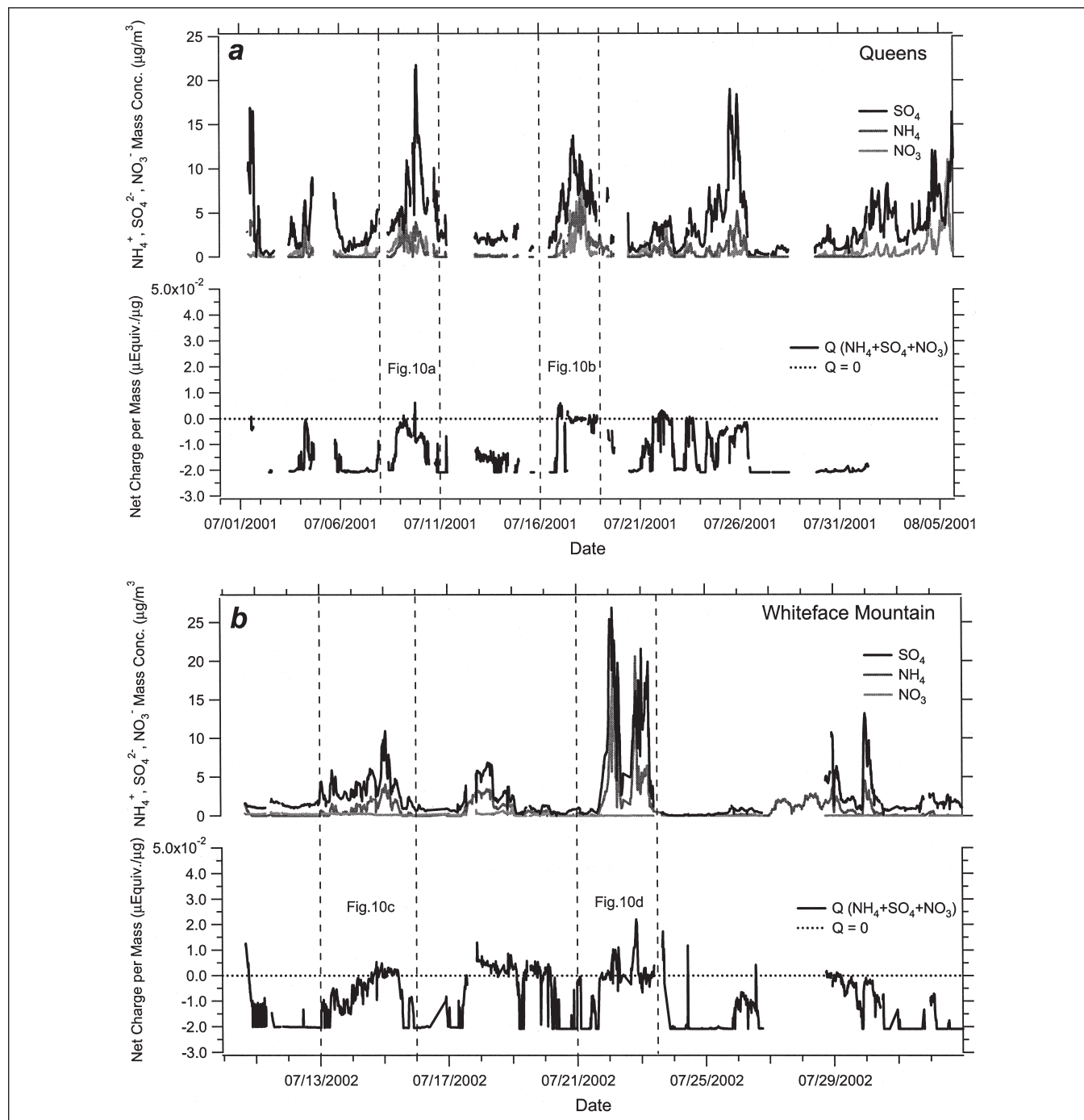


Figure 9. Time series of 15-min PILS-IC mass concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , and the aerosol net charge per unit mass of aerosol Q . Only contributions from $\text{NH}_4^+ + \text{SO}_4^{2-} + \text{NO}_3^-$ are shown for (a) Queens study and (b) Whiteface Mountain study. The lower limit of Q of $-0.02 \mu\text{Equivalent}/\mu\text{g}$ corresponds to a SO_4^{2-} -dominated aerosol. The upper limit of $0.029 \mu\text{Equivalent}/\mu\text{g}$ (which was not observed during the campaigns) corresponds to an NH_4^+ -dominated aerosol. Aerosol episodes marked by vertical dashed lines are shown in more details in Figure 10.

Ion Charge Balances

The charge balance of the main ionic components of the sampled aerosol was calculated for both campaigns, using the PILS-IC and the 24-hr STN filter data. The ionic species considered were SO_4^{2-} , NO_3^- , and NH_4^+ . The mass concentrations of major ionic species were

used to calculate corresponding microequivalent ion concentrations and, subsequently, the net charge of the soluble fraction of the aerosol per microgram of total aerosol mass.

The analysis using PILS-IC measurements showed an average contribution from non- NH_4^+ cationic components

to the total positive charge measured in Queens was 10%, while at Whiteface, their contribution was ~2%. Contribution of anionic components other than SO_4^{2-} and NO_3^- to the negative aerosol charge was 5% in Queens and 8% at Whiteface. It should be mentioned that fewer ionic species were measured at Whiteface than in Queens. While potassium, sodium, calcium, and chloride were measured during both campaigns, magnesium, phosphate, formate, acetate, and oxalate were measured in Queens only. Adding minor cations and anions to the ion balance does not change observed net differences and, therefore, they will not be considered in this discussion. It should be noted that the lower levels of particulate NO_3^- observed at Whiteface had an insignificant effect on the net charge balance, while the urban site had noticeable contributions from NO_3^- .

Time series of the aerosol net charge per aerosol mass from $\text{NH}_4^+ + \text{SO}_4^{2-} + \text{NO}_3^-$ are shown in Figures 9a and 9b for the Queens campaign and the Whiteface campaign, respectively. Time series of the mass concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- measured by the PILS-IC are presented in Figures 9a and 9b as well, to show the contribution of each ionic component to the ion balance. In addition, the net charge per aerosol unit mass was calculated considering a measurement error of the PILS-IC of 10%.¹¹ Figures 10a-d illustrate the estimated measurement error for two episodes from each campaign. The upper error bound trace is calculated by adding 10% to

the NH_4^+ concentration and subtracting 10% from the SO_4^{2-} and NO_3^- concentrations. The lower error bound is calculated by subtracting from the NH_4^+ concentration and adding to the SO_4^{2-} and NO_3^- concentrations. The charge balance presented in this paper, although approximate, gives a good indication of the net charge of the aerosol. For purposes of further discussion, the net charge of aerosol per unit mass will be referred to as the net charge.

It should be noted that laboratory experiments conducted after the summer 2001 campaign showed that there were losses of NH_4^+ from liquid samples of the PILS-IC. These losses were related to the tubing material (Teflon) used for the PILS-IC transport lines.¹³ During the Whiteface campaign, a different tubing material (polyetheretherketone) was used for PILS-IC liquid transport lines, which eliminated the problem. The summer 2001 data shown in Figure 9a were corrected for those losses using the suggested value of $0.56 \mu\text{g}/\text{m}^3$.¹³

Time series of the net charge of aerosol measured during the Queens study calculated from the PILS-IC data indicates that during most of the time the aerosol was slightly acidic. Although actual concentrations of hydrogen were not measured, but it is assumed that the negative net charge is balanced by hydrogen. The aerosol with calculated negative net charge is, therefore, referred to as "acidic." The time series of the net charge of the rural

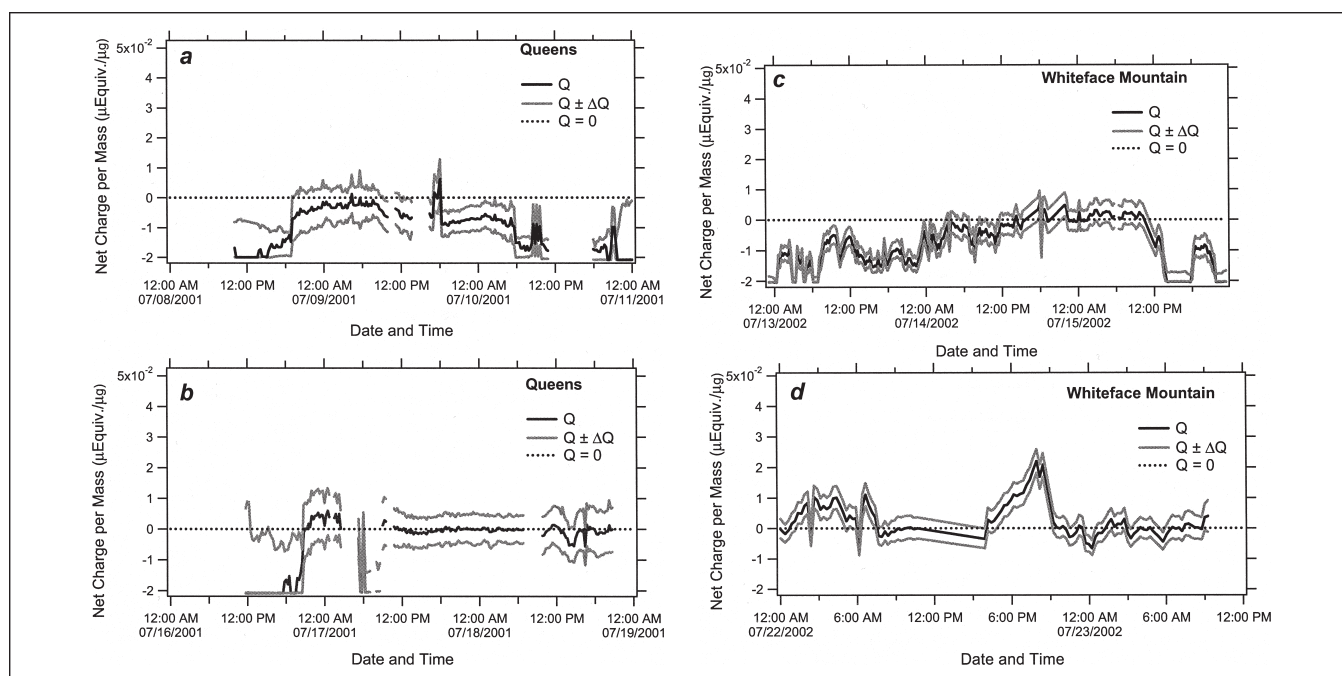


Figure 10. Time series of the aerosol net charge per unit mass of aerosol Q for aerosol events on (a) 07/08/01–07/08/01, (b) 07/16/01–07/18/01, (c) 07/13/01–07/15/02, and (d) 07/21/01–07/23/02. Q is calculated using concentrations of SO_4^{2-} , NO_3^- , and NH_4^+ only. The error bounds (gray lines) correspond to the aerosol net charge per unit mass calculated, taking into account a 10% measurement error of the PILS-IC.

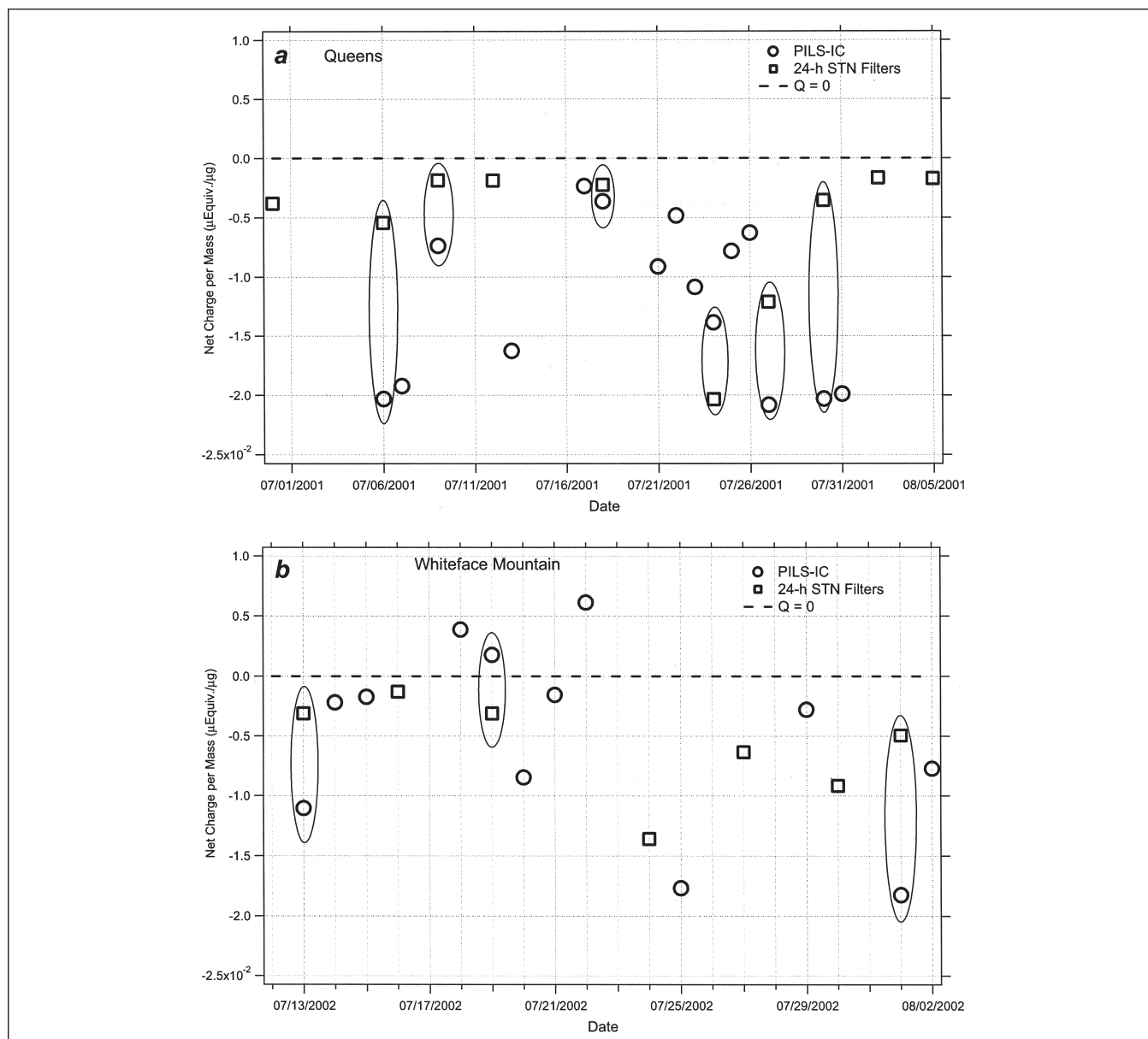


Figure 11. Time series of 24-hr STN filter and PILS-IC mass concentrations of the aerosol net charge per unit mass of aerosol Q . Only contributions from $\text{NH}_4^+ + \text{SO}_4^{2-} + \text{NO}_3^-$ are shown for (a) the Queens study and (b) the Whiteface Mountain study. Circled data correspond to days for which filter data and data from the PILS-IC are available.

aerosol (calculated using the Whiteface PILS-IC data) indicates that the aerosol was slightly acidic during certain periods, while the net charge changed sign during several higher aerosol concentration episodes.

Figure 11a and 11b show the 24-hr time series of the aerosol net charge calculated using the 24-hr STN filter data from Queens and Whiteface, respectively, as well as the corresponding averaged PILS-IC data. The filter data indicate acidity of the aerosol at the urban and the rural location: the average values of the net charge calculated from available 24-hr filter data are -0.005 and -0.008 $\mu\text{Equivalent}/\mu\text{g}$ for Queens and for

Whiteface, respectively. The net aerosol charge calculated using the 24-hr PILS-IC data from Queens is often more negative than that calculated from the corresponding STN filter data. This could, perhaps, be explained by the fact that HNO_3 dissolved in the aerosol liquid shell is likely to be lost from the filters over the sampling period, while the NO_3^- from the dissolved HNO_3 will be quantified by the PILS-IC.

SUMMARY

As a part of the PMTACS-NY study, two intensive summer field campaigns were conducted. The summer 2001

campaign took place in an urban area (Queens); the summer 2002 campaign was conducted at a rural site in upstate New York (Whiteface Mountain area). Various semicontinuous instruments, which measured ambient concentrations of $\text{PM}_{2.5}$, SO_4^{2-} and NO_3^- , were deployed side-by-side during the campaigns. The instruments were the Aerodyne Research, Inc. AMS; the PILS-IC developed at Georgia Institute of Technology; the CASM developed at Harvard School of Public Health and built in the field during the summer 2001 campaign; and the Rupprecht and Patashnick ambient particulate Sulfate and Nitrate Monitors (8400S and 8400N). The AMS and the PILS-IC measure both SO_4^{2-} and NO_3^- , while the other three instruments measure only one species.

The semicontinuous instruments, operating with 10–15 min cycles, provided real-time particulate SO_4^{2-} and NO_3^- mass concentration data throughout both field campaigns, which allowed for the study of diurnal patterns of particulate SO_4^{2-} and NO_3^- , as well as for the detection of short-term SO_4^{2-} and NO_3^- events. The particulate SO_4^{2-} concentrations are comparable at both sites (0–20 $\mu\text{g}/\text{m}^3$), as is the frequency with which high concentration events occurred. The particulate NO_3^- concentrations were significantly higher at the urban site (0–11 $\mu\text{g}/\text{m}^3$), while the rural site was characterized by less than 1 $\mu\text{g}/\text{m}^3$ concentrations of NO_3^- and by the absence of high concentration NO_3^- events. Out of the three instruments providing the semicontinuous NO_3^- measurements, the AMS was the only one capable of capturing a fine temporal structure of NO_3^- concentration at Whiteface. Generally, the intercomparison of the semicontinuous SO_4^{2-} measurements in Queens showed better agreement (in terms of recoveries and R^2) than at Whiteface. The 8400S and the AMS showed similar correlation at both sites. The intercomparison of the semicontinuous NO_3^- measurements from different instruments showed that, while the R^2 values are higher for the Queens data, the recoveries of the AMS versus the PILS-IC correlation for both sites differ by 0.14. It was also shown that, generally, the 8400N under-measured NO_3^- compared with the AMS and the PILS-IC at both sites.

Comparisons of the semicontinuous SO_4^{2-} and NO_3^- measurements with integrated filter measurements were performed. During both campaigns, the 8400S and the AMS under-measured SO_4^{2-} by 15–25% compared with the SCS filters. During the Queens campaign, the PILS-IC under-measured SO_4^{2-} by 28% compared with the SCS filters. However, during the Whiteface campaign, the PILS-IC over-measured SO_4^{2-} by 7% compared with the SCS filters. No explanation for this discrepancy was found. Similar trends were observed for the comparisons

between the semicontinuous SO_4^{2-} measurements and those from the ACCU filter samples (with recoveries being slightly higher during Queens study). The AMS and the 8400S under-measured SO_4^{2-} compared with the STN filters during both campaigns. The difference between the AMS SO_4^{2-} measurements and those from the STN filters was 16% in Queens and 27% at Whiteface. The 8400S measurements in Queens were 9% lower than those from the STN filters and, at Whiteface, they were 30% lower. Correlating the 8400N and the STN filters NO_3^- data showed that during both campaigns, the 8400N measurements were ~35% lower. The AMS NO_3^- measurements during both campaigns were within 10% of the STN filter measurements.

The net charge from the main soluble ionic components of atmospheric aerosol (SO_4^{2-} , NO_3^- , and NH_4^+) was calculated for both campaigns using the PILS-IC and the 24-hr STN filter data. It was shown that at both the urban and the rural locations, the ambient aerosol was slightly acidic.

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