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Intercomparison of near real time monitors of PM2.5 nitrate and sulfate at the U.S. Environmental Protection Agency Atlanta Supersite

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[1] Five new instruments for semicontinuous measurements of fine particle (PM2.5) nitrate and sulfate were deployed in the Atlanta Supersite Experiment during an intensive study in August 1999. The instruments measured bulk aerosol chemical composition at rates ranging from every 5 min to once per hour. The techniques included a filter sampling system with automated water extraction and online ion chromatographic (IC) analysis, two systems that directly collected particles into water for IC analysis, and two techniques that converted aerosol nitrate or sulfate either catalytically or by flash vaporization to gaseous products that were measured with gas analyzers. During the one-month study, 15-min integrated nitrate concentrations were low, ranging from about 0.1 to 3.5 $\mu g\ m^{-3}$ with a mean value of 0.5 $\mu g\ m^{-3}$. Ten-minute integrated sulfate concentrations varied between 0.3 and 40 $\mu g\ m^{-3}$ with a mean of 14 $\mu g\ m^{-3}$. By the end of the one-month study most instruments were in close agreement, with r-squared values between instrument pairs typically ranging from 0.7 to 0.94. Based on comparison between individual semicontinuous devices and 24-hour integrated filter measurements, most instruments were within 20–30% for nitrate ($\sim$0.1–0.2 $\mu g\ m^{-3}$) and 10–15% for sulfate (1–2 $\mu g\ m^{-3}$). Within 95% confidence intervals, linear regression fits suggest that no biases existed between the semicontinuous techniques and the 24-hour integrated filter measurements of nitrate and sulfate;, however, for nitrate, the semicontinuous intercomparisons showed significantly less variability than intercomparisons amongst the 24-hour integrated filters. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS:* particulate matter, PM2.5, instrumentation, ionic aerosol components, sulfate, nitrate, online analysis, semicontinuous, Supersite

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1. Background

[2] The U.S. Environmental Protection Agency (EPA) selected Atlanta as one of the first EPA Supersites. The ongoing EPA Supersite program supports centers for intensive measurements of fine atmospheric particulate matter with aerodynamic diameters smaller than 2.5 μm (PM2.5). This effort is motivated by studies that suggest exposure to these particles may produce significant adverse health effects (for a review see *Pope* [2000, and references therein]) and has resulted in the promulgation of a new EPA PM2.5 standard [*U. S. Environmental Protection Agency* (*EPA*), 1997].

[3] The specific objectives of the Atlanta Supersite were to undertake an intensive study for comparing newly developed, or still emerging instrumentation, for measuring fine aerosol chemical properties, and secondly, to improve understanding of the processes affecting urban PM2.5 concentrations in the southeast United States. Operating from 3 August 1999 to 1 September 1999 the ground-based site was located in a mixed residential and industrial neighborhood approximately 4-km northwest of downtown Atlanta. A wide range of instrumentation for both aerosol and gas-phase measurements were deployed. Instrumentation for aerosol chemical composition measurements were

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divided into 3 broad groups: (1) Integrated measurements (i.e., integrating filter techniques), (2) semicontinuous measurements, which includes automated instruments for measurement of bulk aerosol composition, the focus of this paper, and (3) single particle instruments, which essentially includes all mass spectrometer-based systems. This paper focuses on comparisons between those semicontinuous instruments that measured particulate nitrate and sulfate. Additional investigators deployed semicontinuous instruments that measured other aerosol components, such as organic and elemental carbon. Intercomparison of these devices is discussed by *Lim et al.* [2002]. Along with the gaseous and aerosol chemical data, aerosol optical properties and a suite of meteorological measurements were made.

[4] The Atlanta Supersite study provided a unique opportunity for side-by-side comparisons of multiple instruments of widely varying design measuring real atmospheric aerosols. This produced unique insights and a degree of confidence into the operation of each instrument that would not be possible through individual instrument calibrations. Given that some of the instruments tested in the study are in various stages of commercialization, and moreover, that many are deployed at other EPA Supersites, the Atlanta study is especially pertinent. For a more complete description of the Atlanta Supersite experiment objectives, the site, and instrumentation deployed, see *Solomon et al.* [2002].

2. Experiment: Measurement Techniques

[5] Six research groups fielded instrumentation for near real-time measurements of fine aerosol nitrate or sulfate during the Atlanta Supersite experiment. Of this group, five reported a sufficient quantity of data to make reasonable intercomparisons possible. The institutions, abbreviations used in this paper to identify the measurements, the principle investigators, and brief details of the measurements are summarized in Table 1. Three groups, GT/BL, ECN, and TT, measured both sulfate and nitrate (among other aerosol ionic species) using ion chromatographic detection techniques. Two groups, ADI and ARA, used gas phase analytical techniques. In the following analysis, we compare these indirect measurements of nitrate and sulfate to those of the IC under the assumption that these instruments are primarily measuring nitrate and sulfate.

[6] In all cases, fine aerosol concentrations were measured by employing cyclones or impactors to sample particles smaller than 2.5 μm aerodynamic diameter. All instruments provide bulk aerosol measurements with no particle size-resolution below 2.5 μm. In addition, all the semicontinuous techniques used some type of gas denuders up-stream of the instrument to remove gaseous species that could interfere with the aerosol measurement. There was no common denuder type used by the various groups. The denuders employed ranged from activated carbon honeycomb structures (ADI), URG annular glass denuders (GT/BL), and continuously washed denuders of parallel plate (TT) and cylindrical (ECN) designs. The various instruments were housed in several temporary buildings, and inlets (except ARA) were all within approximately 5 m from each other. The ARA inlet was located about 15 m from the others. This separation is not considered important for the hourly or longer averaging periods that are discussed herein. Each building had its own air conditioning system. Differing heat loads and size of air conditioning units resulted in considerable variability in indoor temperatures amongst the various building. However, during daylight hours, indoor temperatures were generally lower than outdoor temperatures. Care was also taken not to excessively cool the trailers to avoid condensation forming within indoor sample lines. Each instrument also used individual sampling lines of various size and length to conduct ambient air from about 3 m above the buildings to the instruments. With the exception of ADI, investigators did not take extra precautions to maintain the sample at ambient temperatures during transport to the instrument. For the environmental conditions experienced during this experiment, the fact that the instruments generally agreed well suggest that measurements of fine aerosol nitrate and sulfate were fairly insensitive to the type of size selector (cyclone versus impactor) or denuders employed, and slight alteration of the ambient temperature of the sample, (if it is cooled prior to sampling).

[7] Various instrument sample integration and cycle times are also shown in Table 1. Sample integration times varied from 5 to 15 min (the ARA instrument has a very small integration time). Duty cycles varied from once every 30 seconds to once per hour. Because the instruments were not synchronized for simultaneous measurements, and many did not make continuous measurements, natural variability in ambient nitrate and sulfate concentrations add uncertainty to the comparisons and also required that the data be merged onto a common time base. A 1-hour mean was chosen as the basis for the intercomparisons since this was the longest cycle time of all the measurements. Tests with shorter averaging times (15 min) were found to give similar results as the 1-hour means, however, differences in averaging times could have an impact in cases when ambient concentrations change rapidly. A brief description of each measurement approach is given below.

2.1. Instrument Descriptions

2.1.1. Aerosol Dynamics Inc. (ADI), Nitrate, and Sulfur Measurements

[8] In this instrument particles are collect by a humidified impaction process, vaporized and the evolved gases measured with commercial detectors. A detailed description of the integrated collection and vaporization cell (ICVC) is given by *Stolzenburg and Hering* [2000]. The instrument is fully automated and can operate unattended for extended periods. One instrument was used for nitrate and a separate system for sulfur.

[9] In these instruments the sample flow is drawn through a 2.5 μm cut impactor followed by a 300-channel activated carbon denuder (MAST Carbon). The flow is split below the denuder, with 1.0 l min^{-1} flow directed to the nitrate system, and 2.7 l min^{-1} flow for sulfate. Each sample flow passes through a Nafion humidifier (PermaPure Model 110H) operated with a water jacket sheath. This results in relative humidity values of 94 ± 4% for the nitrate system and 85 ± 5% for sulfate. Humidification is done to minimize particle losses due to bounce during collection via impaction. The flow enters the collection cell where the humidified particles are impacted onto a metal strip using a single-jet nozzle operating under sonic conditions. Jet diameters are 0.37 mm

Table 1. Participants and Methods Employed for Semicontinuous Measurements of PM2.5 Nitrate or Sulfate During the Atlanta Supersite Experiment

Institution	Abbreviation	PI	Sample Integration/ Cycle Time	Analytical Technique	Species Measurement
Aerosol Dynamics Inc.	ADI	S. Hering	8 min/10 min	gases	NO_3/SO_4[a]
Atmospheric Research and Analysis	ARA	E. Edgerton	none/30 s	gases	NO_3[a]
Georgia Institute of Technology/Brookhaven Lab	GT/BL	R. Weber/Y. Lee	5 min/7 min	IC	NO_3/SO_4
Netherlands Energy Research Foundation	ECN	J. Slanina	15 min/1 hour	IC	NO_3/SO_4
Texas Institute of Technology	TT	P. Dasgupta	15 min/30 min	IC	NO_3/SO_4

[a]These instruments actually measure nitrogen and/or sulfur but are calibrated with nitrate and sulfate standards (ADI) or with NO (ARA).

(0.0145 in) for nitrate and 0.61 mm (0.024 in) for sulfate. Tests show that particles down to 0.1 μm are collected with near 100% efficiency with the smaller jet used on the nitrate system. Collection efficiency is 90% at 0.1um and above 99% for particles larger than 0.3 μm for the larger jet used on the sulfate system. The collection cells and upstream components are housed in a box that is ventilated with outdoor air to maintain near-ambient temperature.

[10] The sampling procedure involves collection of particles followed by a 2-min analysis period. A measurement cycle is completed every 10 min. For analysis, the sample flow is bypassed around the cell. Collected particles are flash-vaporized into a carrier gas that flows through the cell, across the metal collection strip and into a commercial gas phase analyzer. For nitrate measurement, particles are collected on a stainless steel substrate and analyzed using a nitrogen carrier gas and a ThermoEnvironmental 42C-chemiluminscence analyzer equipped with a molybdenum catalyst. For sulfate measurement, particles were collected on a nichrome substrate until 25 August 1600 EST when the nichrome was replaced with 0.05-mm thick platinum. The substrate is flash-heated in dry air, and the evolved SO_2 is detected by UV-fluorescence using an Advanced Pollution Instruments Model 100AH, or, (for the latter portion of the study), a ThermoEnvironmental 43C-TR. On both systems the analyzer baselines are read for 10 s immediately prior to each flash, and the concentration peaks are integrated over a period of 20 s for nitrate and 40 s for SO_2.

[11] The systems are calibrated weekly using aqueous standards of sodium nitrate, ammonium nitrate, and oxalic acid mixed with ammonium sulfate. These are applied directly to the collection strip using a microliter syringe, and flash analyzed. Each calibration consisted of duplicate measurements at each of three levels plus water blank. For nitrate the regression slopes for the calibrations differed by less than 5% over the course of the study, and thus a single calibration factor was applied to the entire data set. For sulfate, three calibration constants were used, corresponding to the three configurations employed (API analyzer with nichrome substrate, the TEI analyzer with nichrome, and the TEI analyzer with the platinum substrate).

[12] Data are corrected for the average field blank, which in Atlanta were 0.02 ± 0.04 μg m^{-3} for nitrate and 0.3 ± 0.2 μg m^{-3} for sulfate. At three times the blank standard deviation, this corresponds to lower detection limits of 0.1 and 0.4 μg m^{-3} for nitrate and sulfate, respectively.

2.1.2. Atmospheric Research and Analysis (ARA) Nitrogen Measurements

[13] The ARA instrument is a variation on the denuder difference technique. Sample air is drawn through a cyclone at 3 liters per minute then through a roof penetration into the instrument shelter. Inside the shelter, air passes through a KI denuder, to remove HNO_3 and NO_2, then through dual sodium chlorite denuders to remove some or all NO. The sample is then split into three separate streams, of which only the first two are of relevance here. One stream goes directly into a 350°C molybdenum (Mo) mesh converter, which reduces odd nitrogen species to NO. It is assumed that there is 100% collection, vaporization, and transmission efficiency in the Mo converter. The second stream passes through a Teflon filter and KCl denuder, for removal of particulate nitrogen, than into a 350°C Mo converter.

[14] After the converters, NO in each stream is measured via NO-O_3 chemiluminescence using a commercial NO_x analyzer (Thermo-Environmental Model 43ctl). Sample flow through the analyzer is monitored with mass flow controllers (one per stream). A bypass switch is used to maintain constant flow through converters at all times. The NO_x analyzer is calibrated with NO four times per day using method of additions. Converter efficiency is also tested once per day using n-propyl nitrate as a surrogate for particulate nitrate. The n-propyl nitrate is introduced near the inlet in the gas phase via method of additions. This test is merely a check on converter efficiency for an organic nitrate. It does not check inlet losses or volatilization. Conversion efficiency was above 95 percent throughout the study.

[15] Sample measurements for each channel are acquired by the data system every 30 seconds, then combined into 1-min and longer averages during postprocessing. Fine particulate nitrate is thus defined as the difference between the first and second sample streams. This definition assumes that nitrate is the only particulate odd-nitrogen species that is: (1) reduced to NO by the Mo converter, and (2) removed from the sample stream by a Teflon filter in the Teflon filter/KCl denuder leg. Results of tests conducted in Bakersfield, CA during January 1999 suggest these assumptions are valid when particulate nitrate concentrations are high (i.e., $>2-5$ μg m^{-3}).

[16] As with all differencing techniques, measurement precision is dictated largely by ambient NO_x (background) and the NO_x removal efficiency of the KI and $NaClO_2$ denuders. At high NO_x concentrations, or low removal efficiencies, it becomes difficult to measure the difference between the first and second sample streams. Variability in ambient NO_x also affects measurements because 30-second averages for the first and second streams are not fully synchronized.

2.1.3. Georgia Institute of Technology/Brookhaven National Laboratory (GT/BL): Nitrate and Sulfate

[17] The instrument fielded by GT/BL was developed just prior to this study and was based on the original work of *Simon and Dasgupta* [1995]. The approach is to expose

atmospheric particles to a saturated vapor in order to grow the particles to large drops which are than easily collected by inertial techniques. The resulting liquid flow containing the dissolved aerosol components is merged with a liquid transport flow and analyzed with a dual channel ion chromatograph. GT/BL tested two methods for growing the ambient particles to drops. The first employed a modified commercially available condensation particle counter (TSI 3010 CPC, St. Paul MN) which used butanol as the working fluid. Once mixed with a water transport flow the resulting solution contained at most ~1% butanol. The second approach used a modified form of the mixing condensation particle counter of *Okuyama et al.* [1984] to grow the droplets via water condensation. In this case water vapor supersaturations were achieved by turbulently mixing of ambient air with steam. The large drops were collected with a newly designed impactor developed to minimize the wetted area and thus provide fast response times. The impactor also employed a means for continually washing the impacted liquid with the transport flow. A more detailed instrument description is given by *Weber et al.* [2001].

[18] Quantitative analysis of the liquid stream was done with a dual channel ion chromatograph (Dionex, Model 300DX). This permitted continuous online determination of the cations and anions, however, here we focus only on the measured anions, nitrate and sulfate. Each analysis channel consisted of a 150 μL sample loop, an analytical separation column (IonPac CS12A, 4 × 250 mm, for cations; IonPac AS11, 4 × 250 mm, for anions, both from Dionex), a membrane suppressor, and conductivity meter. The analysis was performed with isocratic elution using a 20-mM H_2SO_4 eluent for the cations and a 7.0-mM NaOH eluent for the anions, both at a flow rate of 1.0-mL min^{-1}. IC calibrations were done approximately every 3 days throughout the study using four different standard solutions.

[19] The butanol-based system failed to function due to severe interferences with the IC analysis. Thus, no data is reported for the GT/BL group for the first half of the Supersite experiment. The water-based system did function and this data is used in the following intercomparisons. Detection limits and measurement uncertainty for nitrate and sulfate are estimated at 0.1 μg m^{-3} and 15%, respectively.

2.1.4. Netherlands Energy Research Foundation (ECN): Nitrate and Sulfate

[20] Online measurement of nitrate and sulfate was also made by the ECN group using an integrated system that was capable of measuring a wide range of gaseous and aerosol species. Interfering gases are removed by a rotating wet-annular denuder system. The aerosol measurement system continuously collected particles into water using the steam jet aerosol collector [*Khlystov et al.*, 1995; *Slanina et al.*, 2001]. Similar to the GT/BL method, saturated water vapor (steam) is rapidly mixed with ambient air producing supersaturated conditions and condensational growth of the ambient particles to large drops. In this instrument, the drops are collected using a cyclone and the combined flow from collected droplets containing dissolved aerosol components and wall steam condensate is directed to an anion IC for analysis (Pump, Sykam, Germany, Dionex concentrator column, TAC-LD1, separator column AS12A, membrane suppressor ASR-2 and conductivity detector CD-20 Dionex). The system employs an online calibration system by means of an internal bromide standard, maintains a sampling volume between 1 and 7 ml depending on the ambient concentrations, and employs automated systems for measuring liquid flow rates.

2.1.5. Texas Tech University (TT): Nitrate and Sulfate

[21] The TT instrument was also developed just prior to this study. The approach does not use steam because of concerns that NO_x not removed by upstream denuders can produce small amounts of nitrate and nitrite upon reaction with steam. It is also based on IC-analysis of the soluble fraction of collected particles and permits the quantification of a large variety of analytes. Operationally, this instrument closely resembles standard filter-based techniques used to measure atmospheric aerosol ionic species. In this approach, particles in the sample stream (5l min^{-1}), after being processed through a cyclone and a parallel plate wet denuder [*Simon and Dasgupta*, 1993] are collected on one of two 2.5 cm prewashed glass fiber filters for a period of 15 min. After this time, the sampling switches over to the other filter. The particles on the freshly sampled filter are automatically extracted for 6.5 min by elutriation of the filter with water. The resulting liquid flow containing the dissolved aerosol components is preconcentrated on an anion exchange column (TAC LP1). For the remaining 8.5 min of the 15 min cycle the extracted filter is dried by clean hot air in preparation for sampling at the end of the cycle. Chromatography was conducted on a Dionex model DX120 instrument, using AG11HC and AS11HC guard and separator columns, using 22.5 mM NaOH isocratically at 1-ml min^{-1}. Electrodialytic suppression was used with a drive current of 50 mA. Calibration was conducted with aqueous standards placed on the filters. The front end of the system is identical to that recently described for an aerosol Cr(VI) analyzer [*Samanta et al.*, 2001]. The two-channel system permits continuous measurement by alternating between collection and analysis. However, during the initial days of the study, water inadvertently penetrated into a sampling flow controller and there are reasons to believe that subsequently the sample flow rate was not maintained at a constant value in this channel, resulting in uncertainties in measured aerosol concentrations. Because of this, the data from only one channel are reported and compared.

3. Results: Intercomparisons of Semicontinuous Nitrate and Sulfate

[22] The general approach in the following intercomparison is to first present the time series traces for each instrument over the one-month sample period. This unmerged data provides insights into the range in nitrate and sulfate during the study, the amount of data available for each measurement, and a simple first comparison between the instruments. Because the agreement between instruments was much better during the second half of the study, the intercomparison period is divided into first and second halves. The first half covers 3 August to the end of 16 August, and the second half, 17 August to the end of 31 August. To show the correlation between instruments, r^2 values between all instrument pairs are presented. Each instrument is then compared with the average of all the semicontinuous instruments. The average is used as the

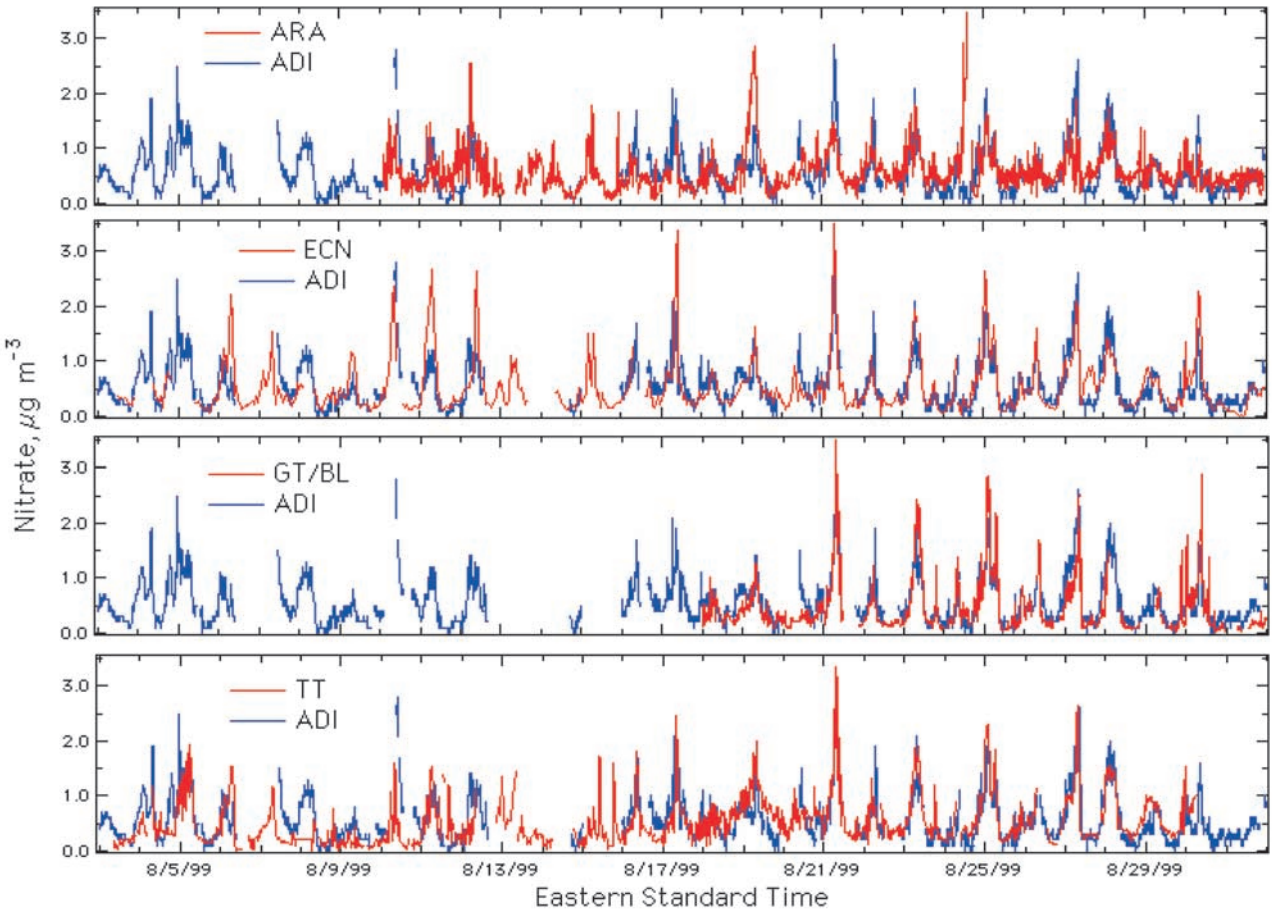

Figure 1. Time series traces of PM2.5 nitrate recorded by all semicontinuous instruments deployed at the EPA Atlanta Supersite from 3 to 31 August 1999. To permit comparisons between graphs the ADI nitrate measurement is included in each plot. Acronyms for various measurements are given in Table 1.

reference for the comparison since there is no a priori standard by which the instruments can be judged. Finally, the semicontinuous data is merged onto the 24-hour filter measurement periods and compared to the filters for data collected throughout the 1-month study.

3.1. Nitrate and Sulfate Trends

[23] Time series traces for nitrate and sulfate for the various semicontinuous techniques are plotted in Figures 1 and 2. Data for comparison span from 6 am 3 August to midnight 31 August. To simplify these graphs, measurements from individual samplers is plotted on separate graphs. The ADI nitrate and ECN sulfate measurements are included in each plot to serve as a reference when comparing instruments. No judgment on the quality of these data is intended by including these two measurements, they were chosen because they tended to have the most continuous data record throughout the study.

[24] The time series graphs of nitrate in Figure 1 show that during the study period nitrate concentrations ranged from levels below the detection limits of most instruments (typically about 0.1 μg m^{-3} for most instruments and 10 ng m^{-3} for the TT instrument) to maximum values of about 3.5 μg m^{-3} (ECN data, 15-min integrals). The average nitrate concentration throughout the study was ~0.5 μg m^{-3}. Nitrate concentrations also showed a fairly regular pattern, with minimum values occurring at mid to late afternoon during periods of highest temperature and lowest relative humidity (RH), and maximum values in the early morning hours during times of lowest temperatures and highest daily RH. The pattern is most pronounced during the latter part of August and can be seen in Figure 1. This diurnal variation is discussed in more detail by *Weber et al.* [2001].

[25] Sulfate concentrations were much higher than nitrate, ranging from 0.3 to 40 μg m^{-3} (ADI data, 8 min integrals) with an average value of ~14 μg m^{-3}. Sulfate did not exhibit a periodic variation, but instead showed short- and long-term features that may reflect local and regional conditions, respectively. Analysis has suggested that during high sulfate events the aerosol tended to be acidic whereas at other times the aerosol tended to be neutral [*Weber et al.*, 2001]. The lowest sulfate concentrations were observed during periods of precipitation. For example, sulfate concentrations below 1 μg m^{-3} in Figure 2, observed near noon on 24 August, occurred during a precipitation event. Following this period, the sulfate concentrations ramped back to more typical study values of 15–20 μg m^{-3}.

[26] Two relevant points can be deduced from the time series plots: (1) As the study progressed the instruments

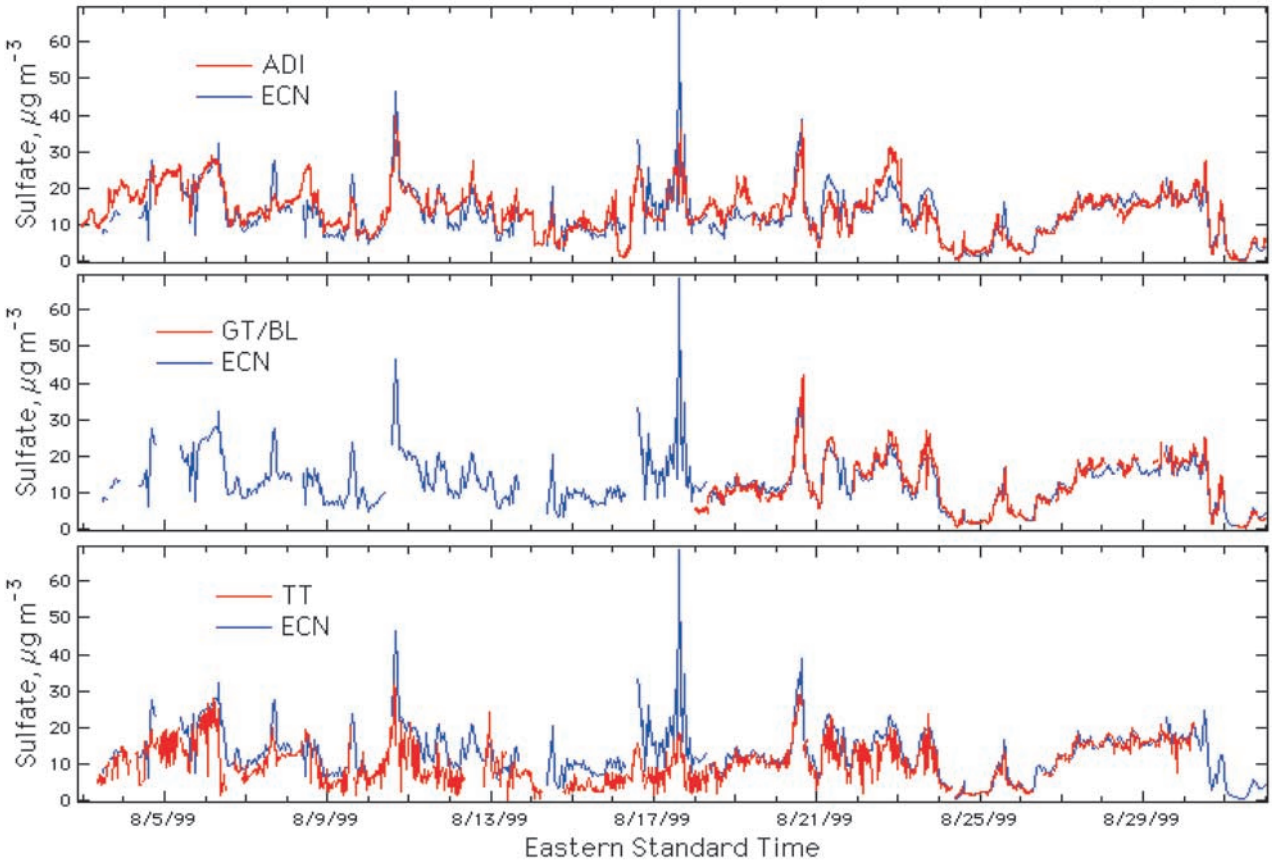

Figure 2. Time series traces of PM2.5 sulfate recorded by all semicontinuous instruments deployed at the EPA Atlanta Supersite from 3 to 31 August 1999. The ECN nitrate measurement is included in each plot for comparison.

tended to run more reliably, and (2) the agreement between measurements improved with time.

3.2. Nitrate Semicontinuous Intercomparison

[27] Five techniques for online measurements of nitrate are compared; ARA, ADI, ECN, GT/BL, and TT. Because GT/BL report no data for the first half of the study, only four measurements are compared during this period.

[28] Intercomparisons between individual devices compared poorly during the first half of the Atlanta study. Table 1 shows that the correlation (r^2 values) between instrument pairs ranged from only 0.012 (ARA and TT) to at best 0.342 (ECN and TT). Correlations improved considerably during the second half. During this period instrument paired r^2 - values ranged from 0.259 (ARA and ECN or GT/BL) to 0.900 (GT/BL and ECN). Note that the r^2 among the IC-detection techniques (ECN, GT/BL, and TT) ranged from 0.76 to 0.9, whereas when compared to the ADI technique (which measures volatilized NO_x to infer particle nitrate) the r^2 was lower, 0.70–0.74 (see Tables 2a and 2b). The higher correlation between the IC-based instruments may in part be due to the similarities between their analytical approaches.

[29] Because there is no "gold" standard by which the various instruments can be compared, comparisons are made between each instrument and the mean of the group. This approach tends to favor the group of most similar instruments in the majority (e.g., ECN, GT/BL, TT, all IC-based detectors,) however, it does provide some insight into the performance of individual instruments.

Table 2a. Nitrate Correlation Coefficients (r^2) for the First Half (3–16 August) and the Second Half (17–31 August) of the Atlanta Supersite Experiment[a]

	ARA		ADI		ECN		GT/BL	
	First	Second	First	Second	First	Second	First	Second
ADI	0.162	0.259						
ECN	0.284	0.261	0.318	0.695				
GT/BL	–	0.259	–	0.739	–	0.900		
TT	0.012	0.297	0.132	0.697	0.342	0.764	–	0.821

[a]Instrument acronyms are defined in Table 1.

Table 2b. Nitrate Number of Comparisons for the First Half (3–16 August) and the Second Half (17–31 August) of the Atlanta Supersite Experiment[a]

	ARA		ADI		ECN		GT/BL	
	First	Second	First	Second	First	Second	First	Second
ADI	77	322						
ECN	131	346	168	320				
GT/BL	0	289	0	271	0	286		
TT	122	304	112	280	153	302	0	249

[a]Instrument acronyms are defined in Table 1.

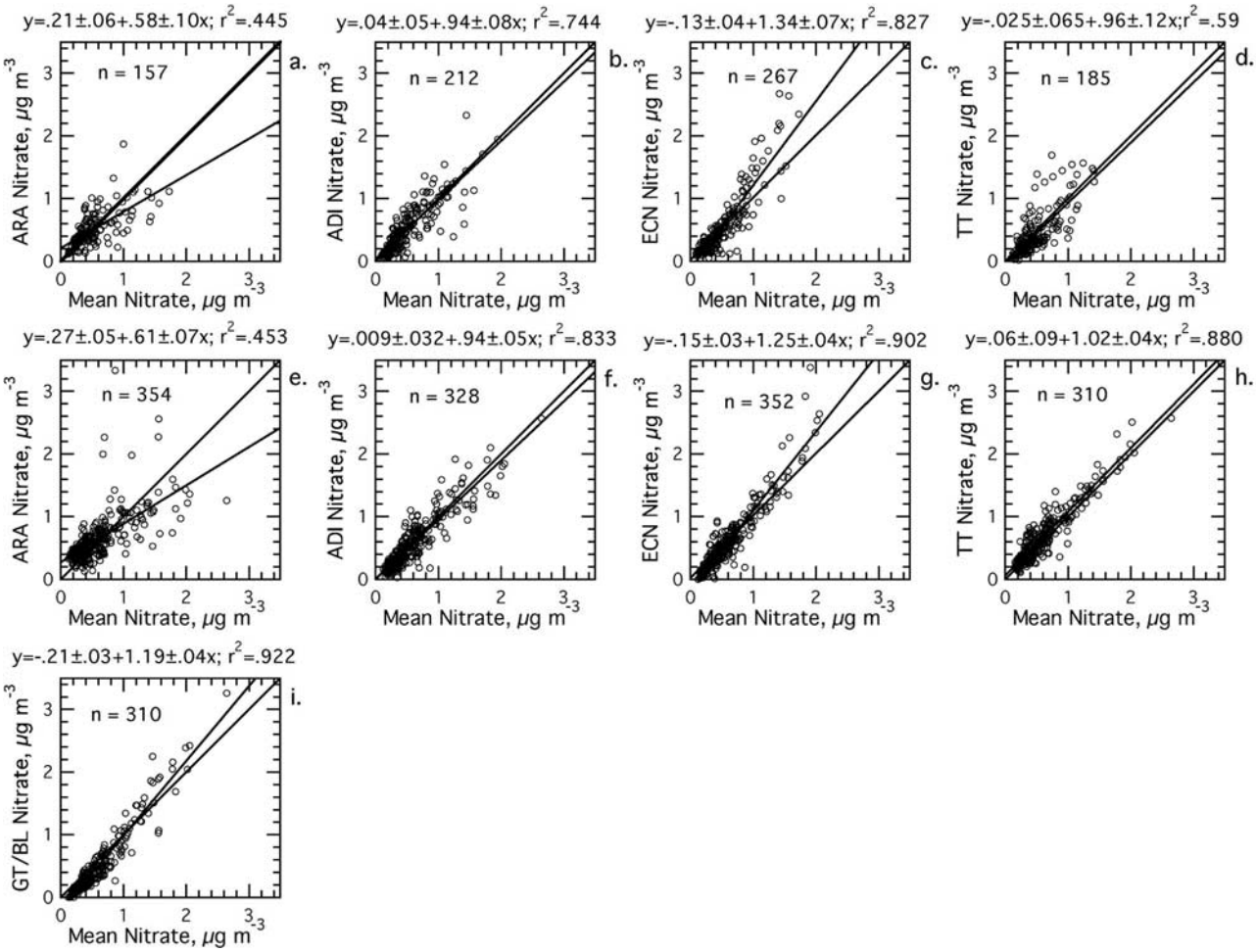

Figure 3. Comparison of each semicontinuous measurement of nitrate to the mean of all semicontinuous measurements. Each plot contains the 1-to-1 line, the linear regression fit (equation with coefficient uncertainty at a 95% confidence interval), r^2, and the number of data points. (a)–(d) Comparisons of measurements from the first half of the study, 3–16 August. (e)–(i) Measurements from the second half of the study, 17–31 August. A summary of the statistics comparing differences of each device from the semicontinuous mean can be found in Table 3.

[30] As expected, comparisons to the group mean produced higher correlation coefficients than individual paired comparisons, but the results tend to be the same. Figure 3 shows the scatter plots for each device compared to the 1-hour mean semicontinuous nitrate. In each graph the one-to-one line, the linear regression fit and equation with coefficient uncertainties calculated at 95% confidence intervals, and the r^2 values are given. The first row of plots is for the first half of the study and the second and third rows for the study second half. During the first half the ADI and ECN measurements had the least amount of scatter (r^2 equal to 0.74 and 0.83, respectively). For the study second half, for all instruments, except ARA, the scatter decreased and the slopes for the linear fits to the semicontinuous average were closer to one.

[31] Focusing on individual instruments it is noted that the ARA instrument generally was unchanged between the first and second half of the experiment. This technique was least correlated with the other nitrate measurements. The scatter is seen to occur over all nitrate concentrations and may in part be due to the uncertainties associated with a difference method. Given that NO_x concentrations were significantly higher than nitrate throughout the study, the uncertainty in this technique would be highest when nitrate concentrations are low (i.e., difference between channels is small). This is supported by review of contemporaneous NO_y data, which indicate that the ARA denuders were only 25–60% efficient at removing ambient NO_x. This resulted in a fairly high background signal throughout the study and hence, raised the lower detection limit to a study-wide estimated value of approximately 0.5 $\mu g\ m^{-3}$. Note that this detection limit varies since it depends on the background NO_x concentrations, which are variable. The scatter plots in Figure 3, however, show that the ARA nitrate was scattered over the complete measurement range (up to $\sim$2 $\mu g\ m^{-3}$) suggesting additional interference's may also have been involve as well. ARA is currently testing a much more efficient NO_x removal approach, based on carbon honeycomb denuders, at several locations in and near Atlanta.

[32] From the scatter plots, the ECN instrument generally measured higher nitrate concentrations than the mean, since regressions between ECN and the semicontinuous average

Table 3. Comparison of Each 1-Hour Average Semicontinuous Measurement of Nitrate to the Mean of All Semicontinuous Measurements for the Second Half of the Experiment[a]

Investigator	Mean of Absolute Relative Difference, %	Standard Deviation of Absolute Relative Difference, %	Mean of Absolute Difference, $\mu g\ m^{-3}$	Standard Deviation of Absolute Relative Difference, $\mu g\ m^{-3}$	N
ARA	43.3 ± 2.1	39.0	0.20 ± 0.01	0.2	354
ADI	23.0 ± 1.0	18.5	0.12 ± 0.01	0.1	328
ECN	25.0 ± 1.1	20.7	0.12 ± 0.01	0.1	351
GT/BL	30.1 ± 1.1	17.9	0.16 ± 0.01	0.1	258
TT	24.6 ± 1.3	23.8	0.12 ± 0.01	0.1	310

[a]Absolute relative difference is the absolute difference of the specific semicontinuous method from the mean of all semicontinuous measurements divided by the mean. Absolute difference is the absolute difference between the measurement and the semicontinuous mean. The error associated with the mean is one standard deviation divided by the square root of the number of comparisons (standard error). N is the number of comparisons.

have slopes of 1.34 ± 0.07 and 1.25 ± 0.04 for the first and second half of the study, respectively. The GT/BL instrument also recorded generally higher nitrate concentrations, especially when nitrate concentrations were highest. In this case the regression slope was 1.19 ± 0.04. Both the TT and ADI instrument recorded nitrate concentrations very close to the overall average with slopes equal to one within a 95% confidence level. One explanation for the higher nitrate concentrations in the steam systems (ECN and GT/BL) is that some nitrate could be generated in the system by NO_x conversion to nitrate. This artifact would be most significant at highest NO_x concentrations. However, the differences in nitrate between the steam systems (ECN and GT/BL) and filter-based system (TT) are not correlated with NO_x concentrations suggesting this may not be a significant artifact.

[33] Because the linear regression fits are dominated by the deviations from the mean at higher concentrations, an additional approach for comparing the instruments was performed. In this case each semicontinuous instrument was compared to the mean by calculating the absolute difference between each instrument and the semicontinuous mean for every hour of merged data. Table 3 summarizes results from these comparisons for the second half of the study. Note that in this approach, instruments with higher data densities (N in Table 3) are biased toward a lower mean difference. Relative and the actual differences are shown in the table. The relative difference is the absolute value of the difference divided by the mean, whereas the actual difference is just the absolute difference between the measurement and the mean. Because nitrate concentrations were so low throughout the study, the relative differences were at times quite high. For example the ARA instrument was on average 43% lower than the semicontinuous mean, which corresponds to an actual mean difference of only 0.2 $\mu g\ m^{-3}$. The variability of the differences between each instrument and the mean was also fairly high. Standard deviations of the relative differences were typically near 20%. From an absolute point of view, however, the instruments were typically very close to the mean with values generally within 0.1 $\mu g\ m^{-3}$. For the limited range in nitrate experienced during this experiment, by the end of the one-month study the semicontinuous nitrate measurements agreed remarkably well.

3.3. Sulfate Semicontinuous Intercomparisons

[34] Four groups measured sulfate aerosol concentrations, with the GT/BL group again only producing data for the second half of the study. Correlation coefficients (r^2) for all pairs of measurements are shown in Tables 4a and 4b. Compared to nitrate, there was less scatter between instruments at the beginning of the study. For example, in the first 13 days of the study, the ADI versus ECN r^2 - value was 0.72, compared to a value of 0.32 for nitrate during the same period. Overall, however, focusing on comparisons during the second half of the study shows that although ambient sulfate concentrations were much higher than nitrate, the various semicontinuous instrument's performance for measuring sulfate and nitrate were similar. Again, the highest correlation was between the two most similar instruments, ECN and GT/BL, with a r^2 of 0.94.

[35] Comparisons of the four sulfate measurements to the 1-hour mean are shown in Figure 4 along with the linear regression fits. The top row of plots is for the first half of the study and the bottom row, the second half. There is slightly less scatter in these comparisons then was observed for nitrate, demonstrated by higher regression r^2 values. Again, the instruments had minimal systematic errors since most regression intercepts are near zero. As with nitrate, the GT/BL regression slopes to the semicontinuous mean was higher than unity by ~11% and is likely due to a flow calibration error. The TT slope was lower by about 10% and the ADI and ECN slopes were one, within 95% confidence intervals.

[36] The statistical results from the calculations of the difference of each measurement from the 1-h mean for the second half of the study is shown in Table 5. Because

Table 4a. Sulfate Correlation Coefficients (r^2) for the First Half (3–16 August) and the Second Half (17–31 August) of the Atlanta Supersite Experiment[a]

	ADI		ECN		GT/BL	
	First	Second	First	Second	First	Second
ECN	0.723	0.802				
GT/BL	–	0.762	–	0.936		
TT	0.516	0.564	0.475	0.823	–	0.820

[a]Instrument acronyms are defined in Table 1.

Table 4b. Sulfate Number of Comparisons for the First Half (3–16 August) and the Second Half (17–31 August) of the Atlanta Supersite Experiment[a]

	ADI		ECN		GT/BL	
	First	Second	First	Second	First	Second
ECN	252	322				
GT/BL	0	288	0	287		
TT	185	306	144	278	0	249

[a]Instrument acronyms are defined in Table 1.

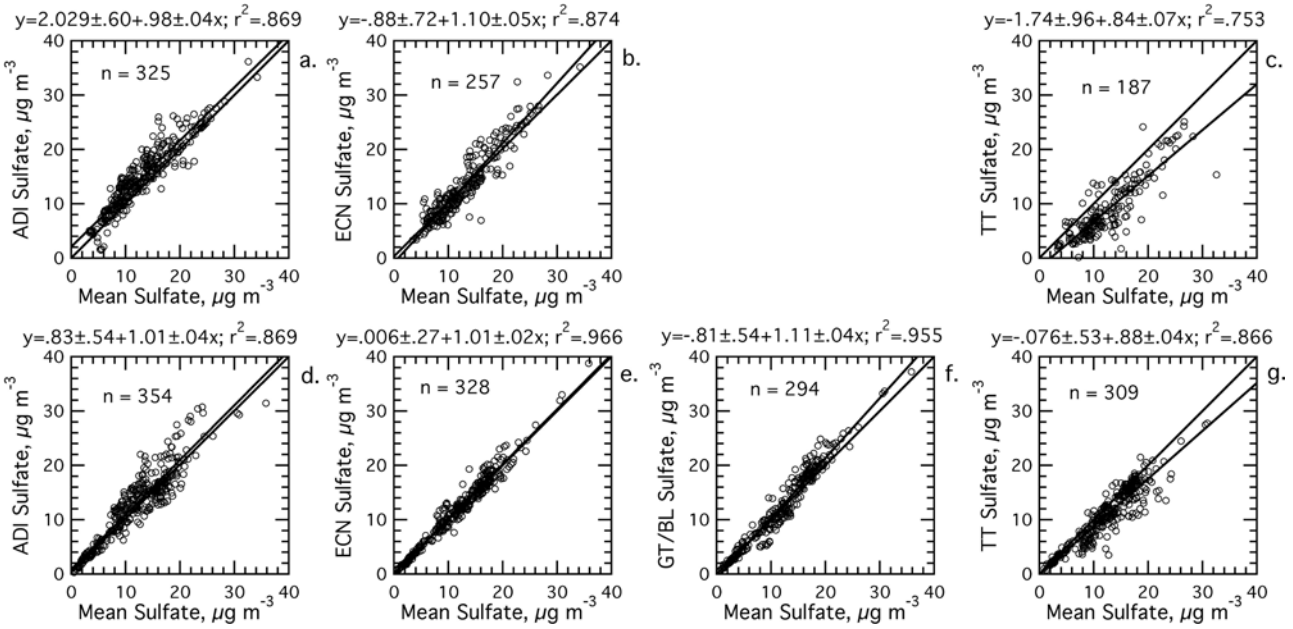

Figure 4. Same as Figure 3, but for sulfate. (a)–(c) Comparisons of measurements from the first half of the study, 3–16 August. (d)–(g) Measurements from the second half of the study, 17–31 August. A summary of the statistics comparing differences of each device from the semicontinuous mean can be found in Table 5.

sulfate concentrations are much higher than nitrate, the relative differences in this case have more meaning. The relative differences for instruments measuring both nitrate and sulfate ranged between about 23 and 30% for nitrate, compared to 8 and 16% for sulfate. For individual instruments, the variation in the measurements from the mean (the standard deviation of the relative difference) for sulfate ranged from about 7 to 14%.

[37] In summary, the comparisons among the semicontinuous measurements show that they were generally within about 10–15% of each other when ambient concentrations were significantly above the instruments detection limits (i.e., focusing only on data from sulfate measurements). To further assess the performance of these rapid measurements, the semicontinuous measurements of nitrate and sulfate are compare to the more traditional filter-based techniques.

4. Results: Comparisons of Semicontinuous to 24-Hour Integrated Filter Measurements of Nitrate and Sulfate

[38] Eight independent techniques used to make 24-hour integrated filter measurements during the Atlanta Supersite study are compared with the semicontinuous measurements. During the one-month study, a total of 15 sets of 24-hour filter measurements were made. Table 6 summarizes the various measurement techniques and investigators. For these comparisons, the individual semicontinuous data were merged onto the 24-hour filter sampling periods.

[39] It should be noted that this intercomparison has some difficulties associated with it. For one, some of the semicontinuous measurements do not sample continuously. For example, TT data effectively represent 15 min averages 2 times per hour, and ECN measures a 15-min average once per hour. Because they only measure a fraction of the time, short-term variability in ambient concentrations (i.e., on times less than one hour) introduces uncertainties when comparing these semicontinuous averages to a true average measured by the filters. A similar problem can arise due to an instrument being off-line during the integration period due to calibrations or instrument difficulties. In an attempt to minimize the latter problem, only those semicontinuous measurements that were operational for 75% of the 24-hour filter-sampling period are compared. (Note that operational means normal running mode. That is sampling at its regular rate, e.g., ECN sampling at 15 min/hour).

[40] In the following section three types of comparisons for nitrate and sulfate are made: (1) a comparison to look at

Table 5. Comparison of Each 1-Hour Average Semicontinuous Measurement of Sulfate to the Mean of All Semicontinuous Measurements for the Second Half of the Study[a]

Investigator	Mean of Absolute Relative Difference, %	Standard Deviation of Absolute Relative Difference, %	Mean of Absolute Difference, μg m^{-3}	Standard Deviation of Absolute Difference, μg m^{-3}	N
ADI	15.9 ± 0.8	14.2	1.8 ± 0.1	1.8	354
ECN	7.9 ± 0.4	7.4	0.8 ± 0.1	0.8	328
GT/BL	11.1 ± 0.5	9.1	1.2 ± 0.1	1.1	294
TT	14.7 ± 0.7	13.1	1.8 ± 0.1	1.8	309

[a]For column descriptions, see Table 3.

Table 6. Filter Measurements of Nitrate and Sulfate at the Atlanta Supersite Used for Comparisons With the Semicontinuous Measurements

Acronym	Sampler/Investigator
FRM-A	FRM Sampler Platform A/Solomon
AND	Andersen RASS/Solomon
Met	MetOne SASS/Solomon
URG	URG MASS/Solomon
RPS	R&P Speciation Sampler/Solomon
VAPS	VAPS Sampler/Solomon
PCM	Particle Composition Monitor/Baumann
PCB	PC BOSS/Tanner

the variability amongst the filters themselves; (2) a similar analysis to assess the variability amongst the semicontinuous measurements when averaged over 24-hrs; and (3) individual semicontinuous techniques are compared to the average of all filter measurements.

4.1. Nitrate: Semicontinuous Versus Filter Measurements

[41] The variability amongst the eight different nitrate filter measurements can be seen in the scatter plot in Figure 5a. For a more detailed discussion on filter intercomparisons, see P. A. Solomon et al. (unpublished manuscript, 2002). The standard deviation of the absolute difference of the various filter measurements from the mean of all filter measurements is 0.12 μg m^{-3}, or ~22%. In contrast, as shown in Figure 5b, the variability among the semicontinuous devices relative to their 24-hour mean is considerably lower with a standard deviation of the absolute difference being only 0.06 μg m^{-3}, or ~13%.

[42] The higher spread among the nitrate filter measurement compared to the semicontinuous measurement is intriguing and may be due to a number of factors, including; difficulties associated with filter measurement of volatile aerosol species; artifacts from on-filter reactions and filter blanks. The latter being exacerbated in this case by the low ambient nitrate levels throughout the study period. The semicontinuous devices may have comparatively fewer sampling artifacts. Take for example the volatility artifact. Nitrate volatility resulting in nitrate loss from the filter has led to the use of a filter pack assembly in which filters are arranged in series. The first filter collects particles (e.g., nitrate) and the following backup filter collects gaseous species volatilized from the first filter (e.g., nitric acid). Volatility artifacts may be a less significant problem with semicontinuous devices since these measurements integrate over much shorter times and should thus expose samples collected on substrates to less temperature variation. The TT automated filter system, for example, integrates for only 15 min. Moreover, in many of the semicontinuous devices the aerosol is rapidly stabilized through the formation of dilute aqueous solutions (i.e., the steam devices of ECN and GT/BL), or by aerosol humidification (ADI). Finally, the semicontinuous devices should have less scatter due to background interference since unlike filters, these devices are automated and do not require handling collection substrates.

[43] A comparison of each semicontinuous measurement to the filter mean is shown in Figure 5c. The linear regression fit of all the semicontinuous measurements (24-hour average) to filter average gives a r^2 of 0.38. The regression slope is one and the intercept zero within 95% confidence intervals, suggesting that on average the semicontinuous and the filter techniques recorded similar levels of nitrate. Given the degree of scatter in the data, however, this fit is of little significance. Because there is significant data scatter, a further comparison to test if the semicontinuous nitrate measurements tracked the mean filter values in terms of being high when the filters were high and low when the filters were low was done by calculating the Spearman Rank correlation. A value of 0.57 was obtained indicating that the semicontinuous and filters measurements did track fairly well (a value of 1 indicates perfect rank-order correlation and -1 perfect negative rank-order correlation).

[44] The statistical results from comparing each semicontinuous measurement to the filter mean are given in Table 7a. The range in the relative differences are from about 10 to 25%, (approximately ± 0.1 μg m^{-3} for nitrate)

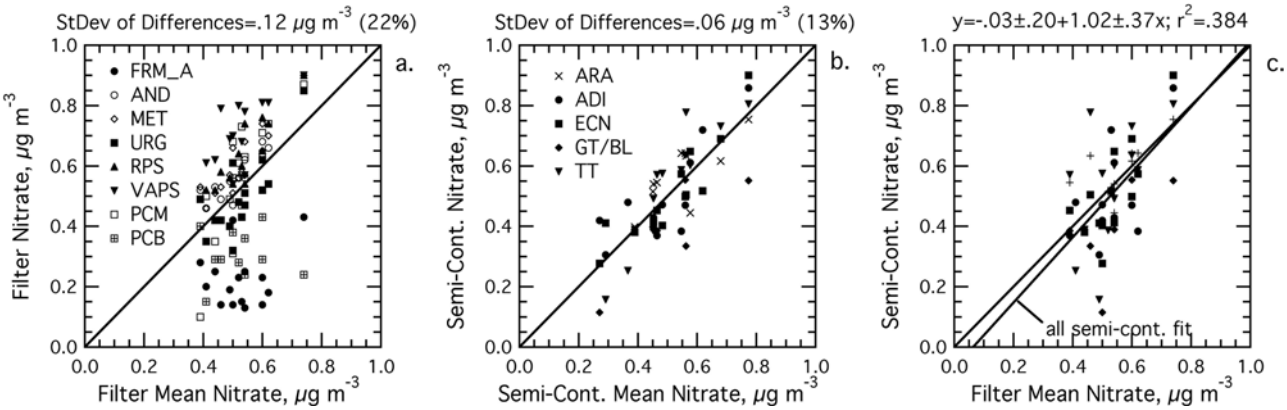

Figure 5. Comparison of semicontinuous measurements of PM2.5 nitrate to 24-hour integrated filter measurements. (a) Variability among the eight different filter measurements. (b) Variability among the five various semicontinuous techniques. (c) Comparison of each semicontinuous measurement to the mean of the eight filter measurements. Figures 5a and 5b also show the standard deviation of the absolute difference between the individual measurements and the measurement mean. Figure 5c shows the linear regression fit with coefficient uncertainty given by 95% confidence intervals and the 1-to-1 line.

Table 7a. Comparison of Each 24-Hour Averaged Semicontinuous Measurement of Nitrate to the Mean of All Filter Measurements for the Complete One-Month Study[a]

Investigator	Mean of Absolute Relative Difference, %	Standard Deviation of Absolute Relative Difference, %	Mean of Absolute Difference, $\mu g\ m^{-3}$	Standard Deviation of Absolute Difference, $\mu g\ m^{-3}$	N
ARA	12.1 ± 4.7	15.1	0.06 ± 0.02	0.06	10
ADI	20.7 ± 3.7	12.2	0.11 ± 0.02	0.07	11
ECN	17.4 ± 2.8	10.0	0.09 ± 0.01	0.05	13
GT/BL	17.9 ± 5.8	13.0	0.10 ± 0.03	0.08	5
TT	25.9 ± 6.3	22.6	0.13 ± 0.03	0.10	13

[a]For column descriptions, see Table 3.

with standard deviations ranging between ~10 and 20%. This is slightly lower than the results comparing each semicontinuous instrument's 1-hour averaged measurement to the semicontinuous mean (Table 3).

[45] Finally, it is noted that the limited dynamic range of the nitrate measurements during this study, and the narrow range of environmental conditions in general, limit the generality of this intercomparison. The instruments might perform differently under conditions not encountered during this brief summertime study.

4.2. Sulfate: Semicontinuous Versus Filter Measurements

[46] As with nitrate, similar scatter plots are shown in Figure 6 comparing filters and semicontinuous sulfate measurements. Figure 6a shows how the various filter sulfate measurements compared to the filter mean. In contrast to the similar plot in Figure 5a for nitrate, the filter sulfate measurements show much more uniformity across samplers. The standard deviation of the absolute difference from the mean is about 1 $\mu g\ m^{-3}$, and a relative difference from the mean of only ~8%, significantly lower than the filter nitrate variation of 22%. Unlike the filters, for both sulfate and nitrate the semicontinuous devices had approximately the same amount of scatter when compared to their mean. For sulfate the standard deviation of the relative absolute difference from the mean was 13%, compared to 12% for nitrate. One may speculate that in this case, because sulfate is non-volatile and the concentrations were generally high, filter sampling artifacts and blank uncertainties were minimal, and thus the filter variability for sulfate primarily reflects differences between different operators running similar sampling devices. In contrast, the similar variability among the semicontinuous devices for both nitrate and sulfate may reflect the less significant role of artifacts with these techniques and demonstrate more the variability amongst the various sampling and analytical approaches employed.

[47] Finally, comparing all semicontinuous measurements of sulfate to the filter mean, Figure 6c shows that the semicontinuous and filter measurements were fairly well correlated. The regression slope is 1.15 ± 0.15 (uncertainty is the 95% confidence interval) suggesting no bias between the semicontinuous and filter measurement techniques. Table 7b shows the summary of each semicontinuous instrument compared to the filter mean. Most instruments are within 15–25% of the filter mean.

5. Summary

[48] The unique data provided by the Atlanta Supersite Experiment allow for detailed intercomparisons among a variety of semicontinuous approaches for measuring particle nitrate and sulfate in an urban environment. Despite much lower ambient nitrate concentrations, (about a factor of 10), the intercomparisons between the instruments resulted in similar findings for measurements of both nitrate and sulfate. Overall, the semicontinuous instruments agreed to within approximately 20–35% (±0.1–0.2 $\mu g\ m^{-3}$) for nitrate and 10–15% (±1–2 $\mu g\ m^{-3}$) for sulfate.

[49] A number of broad conclusions can be made from the intercomparison of the semicontinuous measurements amongst themselves and with 24-h integrated filter measurements. All semicontinuous techniques improved over the course of the study suggesting that many of these approaches still require refinements and further experience until they can be considered "routine" measurements. The fact that most measurements converged by the last week of the study, producing very similar data, even at nitrate concentrations down to about 0.1 $\mu g\ m^{-3}$ and sulfate over a range of 0.3–40 $\mu g\ m^{-3}$ attests to the their

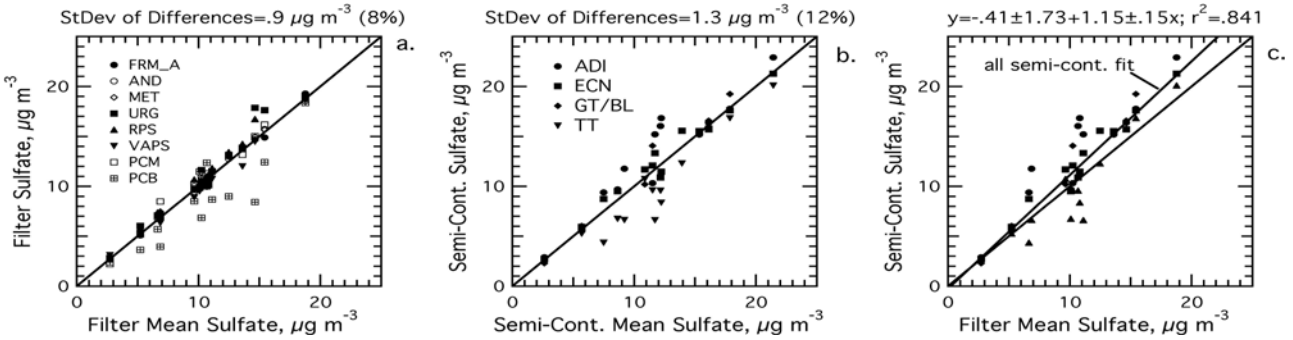

Figure 6. Same as Figure 5, but for sulfate.

Table 7b. Comparison of Each 24-Hour Averaged Semicontinuous Measurement of Sulfate to the Mean of All Filter Measurements for the Complete One-Month Study[a]

Investigator	Mean of Absolute Relative Difference, %	Standard Deviation of Absolute Relative Difference, %	Mean of Absolute Difference, $\mu g\ m^{-3}$	Standard Deviation of Absolute Difference, $\mu g\ m^{-3}$	N
ADI	25.6 ± 6.4	23.0	2.6 ± 0.6	2.1	13
ECN	13.7 ± 2.4	9.0	1.5 ± 0.3	1.0	14
GT/BL	18.7 ± 4.5	10.9	1.9 ± 0.6	1.5	6
TT	14.7 ± 3.7	13.5	1.5 ± 0.4	1.3	13

[a]For column descriptions, see Table 3.

great potential. Compared to filters, for both nitrate and sulfate, the semicontinuous measurements were typically within 10–25%. However, the semicontinuous instruments did appear to perform better than the filters when the techniques were compared amongst themselves. For example, for both nitrate and sulfate the variability between the semicontinuous instruments was similar with a standard deviation of ~12%. The variability amongst the eight different filter measurements for sulfate was slightly smaller at 8%, but much larger for nitrate at 22%. This may suggest that the semicontinuous approaches are less susceptible to sampling artifacts, such as those associated with aerosol volatility.

[50] For the specific semicontinuous instruments compared, the following observations were made:

1. ARA (only measured nitrate): This instrument was generally the least correlated with all other semicontinuous instruments with typical r^2-values of 0.25–0.3 throughout the study. Based on 1-h averages, it also had the largest differences from the mean of all semicontinuous devices. Much of this may be attributed to the techniques differencing approach, which is most uncertain at low nitrate concentrations; conditions typical throughout the one-month study.

2. ADI: Based on 1-hour averages, the ADI instrument had generally more scatter than the IC-based devices with r^2 values typically near 0.7 for both sulfate and nitrate. This higher variability (lower correlation) may reflect the fact that the instrument employs a different analytical technique where nitrate and sulfate are indirectly measured from the thermally desorbed gases NO_x and SO_2 to determine nitrate and sulfate, respectively. Based on regression fits to the semicontinuous mean and comparisons with 24-hour filter averages, the instrument on average was in good agreement with the other techniques for nitrate and sulfate.

3. ECN: The most similar semicontinuous devices, in terms of design (ECN and GT/BL), were the most highly correlated with r^2 values near 0.9 for both sulfate and nitrate. Overall, the ECN instrument agreed well with the other semicontinuous devices for nitrate and sulfate. However, when nitrate concentrations were highest, both the ECN and the GT/BL instruments (based on similar operating principles) measured significantly higher concentrations. A possible explanation is an artifact associated with these instruments due to nitrate production from NO_x within liquid drops formed by steam condensate. However no correlation between this error and measured NO_x concentrations was observed.

4. GT/BL: This instruments had high correlation's (r^2) when compared to the other semicontinuous measurements. However, the regression slope was 19% higher for nitrate and 11% higher for sulfate. The systematic error is thought to be due to a liquid flow calibration error. At low nitrate concentrations it tended to report lower concentrations than the other semicontinuous devices due to poor automated software integration of the small chromatographic peaks. Overall, it agreed well with the other techniques being within 10–35%.

5. TT: For sulfate, the TT technique showed more data scatter than the other IC-based systems (ECN and GT/BL), but on average, was in good agreement with the semicontinuous mean having a regression slope of only 12% lower than 1. Nitrate was less scattered than sulfate and the measurement was very close to what other instruments detected.

[51] Considering that many of the instruments compared were only recently developed (ARA, GT/BL, and TT), and thus likely to be further improved, this study demonstrates that these instruments are capable of providing real-time, accurate, and quantitative measurements of ambient fine particle nitrate and sulfate under the conditions experienced during the Atlanta Supersite Experiment.

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