

A Comparison of Particle Mass Spectrometers

During the 1999 Atlanta Supersites Project

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Abstract: During the Atlanta Supersites Project, four particle mass spectrometers were operated together for the first time: NOAA's PALMS (Particle Analysis by Laser Mass Spectrometry), U. C. Riverside's ATOFMS (Aerosol Time-of-Flight Mass Spectrometry), U. Delaware's RSMS-II (Rapid Single-Particle Mass Spectrometer II), and Aerodyne's AMS (Aerosol Mass Spectrometer). Although these mass spectrometers are generally classified as similar instruments, they clearly have different characteristics due to their unique designs. One primary difference is related to the volatilization/ionization method: PALMS, ATOFMS, and RSMS-II utilize laser desorption/ionization whereas particles in the AMS instrument are volatilized by impaction onto a heated surface with the resulting components ionized by electron impact. Thus, mass spectral data from the AMS are representative of the ensemble of particles sampled and those from the laser-based instruments are representative of individual particles. In addition, the AMS instrument cannot analyze refractory material such as soot, sodium chloride, and crustal elements, and some sulfate or water-rich particles may not always be analyzed with every laser-based instrument. A main difference among the laser-based mass spectrometers is that the RSMS-II instrument can obtain size-resolved single particle composition information for particles with aerodynamic diameters as small as 15 nm. The minimum sizes analyzed by ATOFMS and PALMS are 0.2 and about 0.35 μm , respectively, in aerodynamic diameter. Furthermore, PALMS, ATOFMS, and RSMS-II use different laser ionization conditions. Despite these differences, the laser-based instruments found similar individual particle classifications and their relative fractions among comparable sized particles from Atlanta were broadly consistent. Finally, the AMS measurements of the nitrate/sulfate mole ratio were highly correlated with composite measurements ($r^2 = 0.93$). In contrast, the PALMS nitrate/sulfate ion ratios were only moderately correlated ($r^2 \sim 0.7$).

1. Introduction

During August 1999, the U. S. Environmental Protection Agency and the Southern Oxidants Study conducted a PM_{2.5} (particulate matter smaller than 2.5 μm in diameter) Supersites Project in Atlanta, GA [see *Solomon et al.*, this issue]. Two of the overall objectives of this experiment were: 1) to test and characterize the performance of emerging and/or state-of-the-science particulate matter measurements, and 2) to compare and contrast the precision and consistency of similar and dissimilar PM measurements. During the experiment, four particle mass spectrometers were operated together for the first time: NOAA's PALMS (Particle Analysis by Laser Mass Spectrometry), U. C. Riverside's ATOFMS (Aerosol Time-of-Flight Mass Spectrometer), U. Delaware's RSMS-II (Rapid Single-Particle Mass Spectrometer II), and Aerodyne's AMS (Aerosol Mass Spectrometer). The general techniques and history of on-line particle mass spectrometers were reviewed recently by *Suess and Prather* [1999]. The designs of the four instruments deployed in Atlanta have been described previously [*Thomson et al.*, 2000; *Gard et al.*, 1997; *Mallina et al.*, 2000; *Jayne et al.*, 2000]. Their performance and results from Atlanta have been evaluated individually and reported in separate manuscripts [*Lee et al.*, 2002, this issue; *Liu et al.*, this issue; *Wenzel et al.*, this issue; *Phares et al.*, 2002; *Rhoads et al.*, this issue; *Jimenez et al.*, this issue]. The current paper focuses on the similarities and differences among the designs of four particle mass spectrometers deployed in Atlanta. We also present comparisons of individual particle types obtained by the laser-based mass spectrometers (PALMS, ATOFMS, and RSMS-II) where the spectra were classified by different programs. Finally, we show comparisons of nitrate/sulfate ion ratios from the PALMS instrument with nitrate/sulfate molar ratios from the more quantitative AMS instrument and their correlations with other measurements.

2. Instrumentation

2.1. Sampling Inlets and Operation

The four instruments had different sampling inlets and hours of operation. PALMS and AMS used cyclones in their sampling inlets to remove particles larger than $2.5\ \mu\text{m}$ in aerodynamic diameter (URG Corp., models URG-2000-30ED and URG-2000-30EN, respectively). The other two instruments could discriminate against the larger particles with either the inlet (RSMS-II) or data analysis (ATOFMS) (see sections below). The sampling inlets for PALMS and RSMS-II were designed for laminar flow. Nafion dryers were used in the sampling inlets for PALMS (for 17 days) and RSMS-II, whereas PALMS (for 4 days), ATOFMS, and AMS were operated without dryers. ATOFMS was operated 24 hours a day every day for most of the campaign. PALMS was operated for the first 3 weeks of the campaign usually between 6 and 18 EST and during the night on Aug. 5, 10, and 15. Since the RSMS-II and AMS instruments had not been extensively field tested, they were operated less consistently at the beginning of the campaign and more consistently at the end.

2.2. Instrument Inlets and Aerosol Transmission

All of the particle mass spectrometers are vacuum instruments that drop the pressure of ambient air by at least 7 orders of magnitude (760 Torr to 10^{-5} Torr or lower). Schematic diagrams of the four instruments are shown in Figure 1. PALMS, ATOFMS, and RSMS-II have differential inlets with orifices and/or skimmers, and many particles are pumped away with the ambient air. Particle trajectories and aerosol transmission depend on aerodynamic diameter and particle shape. The sampling (transmission plus optical detection) efficiency for the PALMS instrument is approximately 2 % for latex spheres greater than $0.8\ \mu\text{m}$ in diameter and 2×10^{-5} for $0.22\ \mu\text{m}$ latex spheres [Middlebrook *et al.*, 2000]. Between 0.35 and $0.9\ \mu\text{m}$ in diameter, the transmission is roughly proportional to the diameter cubed or particle mass. The PALMS Atlanta data were not corrected for sampling biases as a function of size due to the rough estimate of particle size [Lee *et al.*, 2002]. The sampling (transmission plus detection via particle time of flight) efficiency of the ATOFMS is roughly proportional to the third power of the

diameter [Allen *et al.*, 2000; Wenzel *et al.*, this issue]. Because the ATOFMS can obtain accurate size information, the ATOFMS data can be first-order corrected for sampling efficiency by using ambient size or mass distributions measured upstream of the ATOFMS inlet. The sampling efficiency for the RSMS-II instrument ranges from about 1.5×10^{-4} for particles with aerodynamic diameters between about 20 to 55 nm to 6×10^{-6} for 100 nm particles [Mallina *et al.*, 2000]. The AMS instrument focuses particles with an aerodynamic lens, so that a beam of particles is formed and fewer particles are pumped away with the ambient air [Jayne *et al.*, 2000]. Although particle transmission in the AMS also depends on aerodynamic diameter and particle shape, transmission is close to 100 % for spherical particles with aerodynamic diameters between 60 and 600 nm. Note that full corrections would require knowing the instrument's sampling efficiency and hit rate (see below) as a function of particle density, shape, optical properties, and composition as well as size. For the comparisons in this paper, the data were not corrected for sampling efficiency since transmission is roughly comparable for the three laser-based instruments in the size range examined and the PALMS data could not be corrected due to approximate sizing (see below).

2.3. Particle Detection and Sizing

The different methods for particle detection/sizing and size ranges are summarized in Table 1. Both the ATOFMS and AMS instruments size particles by aerosol time of flight. ATOFMS uses light scattering between two diode pumped Nd:YAG lasers to measure particle velocity [Gard *et al.*, 1997] and had a minimum size of 0.2 μm in aerodynamic diameter during the Atlanta campaign. The maximum size measured by ATOFMS is not restricted, since data from particles larger than 2.5 μm in diameter can be omitted if desired during data processing. The AMS aerosol time of flight is initialized by a chopper wheel and detected by the mass spectrometer signal [Jayne *et al.*, 2000]. Because of the aerodynamic lens properties, very small particles can be sized with the AMS instrument. In practice, the minimum size is considered to be 50 nm for which transmission from the inlet is about 50 %. The PALMS instrument sizes by

light scattering from a Nd:YAG laser [Murphy and Thomson, 1997; Lee *et al.*, 2002] and the minimum optical size during the Atlanta campaign was 0.22 μm in diameter, determined in the field with dry ammonium sulfate particles from a differential mobility analyzer. This minimum optical size corresponds to approximately 0.35 μm in aerodynamic diameter for ambient particles (see Table 1). Since the scattered light intensity is roughly indicative of the particle size, approximate optical sizes can be determined [see Lee *et al.*, 2002] and adjusted to the aerodynamic diameter as in Table 1. Note that although individual particles cannot be sized with the PALMS instrument, size trends emerge when the data are averaged as a function of scattered light intensity [e.g., Lee *et al.*, 2002, this issue]. The RSMS-II instrument sizes aerodynamically by varying the inlet pressure to focus a specific size within the ionization region [Mallina *et al.*, 2000]. RSMS-II can focus arbitrarily small aerodynamic sizes, but can only detect particles down to 15 nm depending on composition [Mallina *et al.*, 2000; Kane and Johnston, 2000]. Particles are detected in the RSMS-II instrument when a mass spectrum is recorded. During Atlanta, sizes selected by the RSMS-II instrument were 0.015, 0.03, 0.05, 0.06, 0.10, 0.15, 0.20, 0.25, 0.35, 0.50, 0.82, 1.0, and 1.3 μm in aerodynamic diameter with a geometric standard deviation of 1.14.

2.4. Volatilization/Ionization

The four instruments are mainly differentiated by their volatilization/ionization methods (see Table 1). Three instruments (PALMS, ATOFMS, and RSMS-II) use single laser pulses for laser desorption/ionization (LDI) to ablate and ionize particle constituents: PALMS and RSMS-II use ArF excimer lasers with a wavelength of 193 nm and ATOFMS uses a Nd:YAG laser (fourth harmonic wavelength = 266 nm). Typically only a small fraction of the molecules in the particles are ionized (on the order of 10^{-5} - 10^{-6}) [Thomson *et al.*, 1997] and LDI can easily detect a wide range of particle components such as sulfate, nitrate, organic species, sea salt, soot, and mineral dust [see Suess and Prather, 1999]. Pure sulfuric acid, ammonium sulfate, and water have relatively high ionization thresholds using these laser wavelengths [Thomson *et al.*,

1997; Kane and Johnston, 2000], with the shorter wavelengths being able to produce ions more easily than longer ones [Thomson *et al.*, 1997]. The different laser mass spectrometers use a wide range of laser fluence (see Table 1), which may also affect the ionization efficiencies and fragmentation patterns in the spectra. In general, more fragmentation of organic species occurs with higher laser fluence. Fragmentation may also depend to a lesser degree on wavelength, with longer wavelengths producing fewer fragments.

In contrast, the AMS instrument volatilizes and ionizes particles in two separate steps: it volatilizes particles by impacting them onto the roughened surface of a cartridge heater at 550 °C and then ionizes the components separately with electron impact. The fraction of molecules ionized is around 10^{-6} to 10^{-7} [Jayne *et al.*, 2000]. Species that do not volatilize rapidly at that temperature, such as mineral components, sea salt, and soot, are not detected or analyzed by the AMS instrument. For the species that do volatilize, the AMS probably has fewer matrix effects than the single-step LDI.

2.5. Ion Detection

The three laser-based instruments have time-of-flight (TOF) mass spectrometers with microchannel plate detectors (see Table 1). In conjunction with volatilization/ionization occurring in a short pulse, the TOF mass spectrometers provide full mass spectral information for individual particles. Because the PALMS instrument has a low noise preamplifier and a log amplifier on the detector signal, it has a large dynamic range of ion signals with signal-to-noise ratios (defined as the total signal divided by the minimum peak area) typically higher than 1000 and often higher than 10,000 [Murphy and Thomson, 1997; Thomson *et al.*, 2000; Lee *et al.*, 2002]. Both the PALMS and RSMS-II instruments are capable of operating in either a positive or negative ion mode and the ion polarity to be analyzed by their single TOF mass spectrometers is pre-selected. For the RSMS-II instrument, spectra were archived only in the positive ion mode since negative ion signal intensities were much lower for particles less than a few hundred nanometers [Rhoads *et al.*, this issue]. The ATOFMS instrument detects both positive and

negative ions from the same particle using dual TOF reflectron mass spectrometers [*Gard et al.*, 1997]. When using peak areas, the signal-to-noise ratio with the ATOFMS instrument is ~ 500 -1000, but signals from a few species (e.g., sodium and potassium) occasionally exceeded the range of the data acquisition board during the Atlanta campaign. Multiple data acquisition boards, one with attenuation, are currently being used in the ATOFMS instrument to resolve this problem. The AMS instrument has a quadrupole mass spectrometer with an electron multiplier detector and measures mass-weighted size distributions for a pre-selected molecular or fragment positive ion (i.e. mass-to-charge setting of the quadrupole) [*Jayne et al.*, 2000]. During the Atlanta field campaign, single mass distributions were generated from approximately 20,000 particles. Furthermore, typically more than 50 % of the mass was from about 2 % of the particles. The AMS instrument can also completely scan the mass-to-charge scale, producing a composite mass spectrum for an ensemble of particles.

2.6. Particle Hit Rates

The PALMS and ATOFMS instruments have two independent particle detection methods. The first detects particle presence within the instrument (and particle size), using light scattering in PALMS and particle time-of-flight between two lasers in ATOFMS. The second detection method is the mass spectrometric signal of components from the particle. Since the ionization lasers are not fired unless a particle is detected in the instrument by the first method, a "hit rate" can be defined as the ratio of the number of particles with a mass spectrum to the number of particles detected in the instrument by the first method. Note that hit rate as defined here is different from particle transmission efficiency discussed above. Hit rate includes the efficiencies of both detection methods, e. g., particles of a given type and size may be transmitted into the first detection region but not "hit" because their mass spectrometric signal is too small, either due to the particle not being transmitted into the ionization laser beam or the ionization efficiency is too low. Consistently high hit rates preclude under analyzing a significant class of

particles due to the inability to form ions, especially for those containing sulfate in the laser-based instruments [Thomson *et al.*, 1997; Kane and Johnston, 2000].

An instrument's hit rate is affected by particle transmission between the two detection methods and laser ionization conditions. In the PALMS instrument, the continuous YAG laser beam for particle detection by light scattering is approximately 100 μm above the ionization laser beam along the particle beam axis [Thomson *et al.*, 2000]. This results in a high hit rate: for Atlanta, the overall hit rate was 87 % [Middlebrook *et al.*, 2000]. The most consistent hourly averaged hit rates for PALMS ranged from 98-100 % and were obtained during a four-day period (Aug. 17-20) when the highest laser fluences were used, the light-scattering and ionization lasers were not moved, and the particles were dry, regardless of sulfate concentration in the ambient particles. The hit rate varied slightly more (from 88 to 100 %) during the next four days (Aug. 21-24) when the lasers were in the same position and the particles were not dried. For the earlier part of the campaign (Aug. 3-16), the lasers were automatically aligned and the hit rate varied widely (ranging from 14 to 100 %). Some of the low hit rates during this period occurred when the sulfate concentrations were high or when the laser fluence was decreased step-wise. However, the overall variability in the hit rate was probably due to a combination of varying sulfate concentrations, laser fluences, and laser positions relative to the particle beam.

In contrast to PALMS, the ATOFMS instrument does not have relatively high hit rates because the distance between the second diode laser beam and the ionization laser in the ATOFMS instrument is 12 cm [Gard *et al.*, 1997]. While this allows for very accurate timing to pulse the ionization laser, particles can deviate from the ionization laser beam position and the hit rate was roughly 25-30 % for Atlanta. The ATOFMS data occasionally had hit rates as low as 5 % during the Atlanta campaign and those events occurred when sulfate concentrations were high [Wenzel *et al.*, this issue]. The lower hit rates were probably due to the low ionization efficiency of sulfate particles.

The RSMS-II and AMS instruments only detect particles by their mass spectrometric signals. The RSMS-II instrument does not detect independently when particles are present in the instrument and fires its laser at a fixed rate. The AMS instrument continuously vaporizes particles as they strike the heater and their volatile and semi-volatile components are detected by the mass spectrometer. However, no mass spectrometric signal is recorded for particles that do not vaporize. Thus, the concept of hit rate is not applicable to the RSMS-II and AMS instruments and chemical biases are difficult to detect.

2.7. Data Collection, Processing, and Analysis

All four instruments use custom software for data collection, processing, and analysis. PALMS has a fitting and peak-weighting program to determine the best scaling factors to convert ion arrival time to ion mass-to-charge ratio. PALMS and RSMS-II use a low voltage gradient in the source region of the mass spectrometer to reduce the need for time to ion mass-to-charge ratio calibrations on each spectrum. Since the AMS ionizes the vaporized particle constituents via an electron impact process, this instrument can in principle take advantage of the available standard electron impact ionization databases for molecular identification of the detected fragment ions. The data from the three laser mass spectrometers can be analyzed by peak identification (peak ID) for determining variations of species among individual and averaged spectra as well as by pattern recognition programs to classify individual particle spectra (see Table 1). With peak ID, combinations of peaks are selected by the user to search for spectra containing a particular species.

The ATOFMS and RSMS-II data were analyzed using ART-2a, an artificial neural network for classification of single particles [Song *et al.*, 1999; Liu *et al.*, this issue; Phares *et al.*, 2001; Rhoads *et al.*, this issue]. ART-2a is briefly described here. The mass spectra were initially converted into normalized vectors with integrated peak areas as a function of mass-to-charge ratio within ± 0.5 mass units. Spectra were then selected randomly and compared with a set of normalized weight vectors by taking their dot products. The spectrum was combined with

the weight vector with the highest dot product according to a learning rate and the weight vector was renormalized. If the highest dot product with the current set of weight vectors was below a certain threshold called the vigilance parameter, the spectrum generated a new weight vector. Thus, the first weight vector was created from the first spectrum and additional weight vectors were generated as the remaining spectral vectors were examined. Successive iterations on the entire set of spectral vectors were performed using the previous set of weight vectors. The final set of weight vectors was grouped manually to form general classifications.

The PALMS data were classified using regression tree analysis [*Murphy et al.*, manuscript in prep.]. Spectral data were first compressed into a lower resolution spectrum (every 0.25 mass units) of the raw data and a list of peak areas (every mass unit). Each spectrum started as a normalized classification vector by itself. If the dot product of two classification vectors was within a certain threshold, they were combined into a new classification. Unlike ART-2a, which had a fixed learning rate for combining classifications, the new classification vector was a running average of the classifications being combined. In subsequent steps, the threshold for combining classifications was continuously lowered until a reasonable number of classifications remained. Before the first iteration, the data were divided into smaller blocks for ease of computation. After the final iteration, each spectrum was compared individually with the entire set of classification vectors. Classifications were also combined manually. Regression tree analysis was used for the PALMS Atlanta data because classifying it with ART-2a did not converge due to continua between different classifications in the data (see below).

The ART-2a algorithm has recently been tested using spectra from laboratory-generated particles [*Phares et al.*, 2001]. The same set of laboratory spectra was also classified using regression tree analysis and the results were similar [*Murphy et al.*, manuscript in prep.]. Errors in classification by either method were mainly due to impurities that generated significant signals in the laser desorption/ionization mass spectra. Furthermore, particles composed of various pure organic compounds were classified together by both methods in hydrocarbon fragment classes more often than in distinct classes, indicating frequent fragmentation of organic molecules.

3. Common Individual Particle Types

A number of individual particle types were identified in the Atlanta data by the laser-based instruments. Four primary classifications found by all three instruments and shown in Figures 2, 3, and 4 were organic (and sulfate), sodium/potassium sulfate, soot/hydrocarbon, and mineral. Table 2 shows the frequencies in these four classifications for all the particles sampled by each instrument for the entire field study. Note these frequencies were not adjusted for particle transmission and that the instruments analyze different sizes and were not operated at the same time for the entire study. The particle classifications could not be independently verified since other single particle data from Atlanta (electron microscopy with X-ray fluorescence) were not available for comparison.

The main PALMS particle classifications for positive spectra are shown in Figure 2 and their frequencies are listed in Table 2. Organic and sulfate (at $m/z = 64/65, 81, \text{ and } 99$) peaks were nearly always present in the positive ion spectra. Lead (Pb) appears as a minor peak in several classification vectors and was present in a high fraction of the PALMS spectra [Lee *et al.*, 2002]. However, other minor peaks such as barium (Ba) appear in some classification vectors and yet were not present in all of the spectra of that classification. The frequencies of the classifications identified by regression tree analysis (Table 2) are comparable to those determined using peak ID [Lee *et al.*, 2002].

The PALMS organic and sulfate classification (Figure 2) is representative of a continuum in the actual data where the relative peak intensities of organic and sulfate peaks varied. Furthermore, relatively large sulfate ion peaks were more common when high laser fluence was used for ionization whereas predominantly organic peaks were more common with low laser fluence. Continua across other particle classifications were also observed. In particular, the Na/K-sulfate classification differs primarily from the organic/sulfate classification by the relative peak intensity for the potassium (K) peak and the presence/absence of sodium and potassium sulfate cluster peaks (Na_3SO_4^+ , K_2HSO_4^+ , and K_3SO_4^+). In addition, the soot/hydrocarbon

classification was mainly distinguished from the organic/sulfate classification by the appearance of high mass C_n fragments (above $n = 9$).

In the PALMS data, the organic/sulfate and soot/hydrocarbon spectra appeared more frequently in smaller (less than about $0.7\ \mu\text{m}$ in aerodynamic diameter) particles and mineral spectra were more common in larger particles (greater than about $1\ \mu\text{m}$ in aerodynamic diameter). These size dependencies were also observed using peak IDs for analyzing the PALMS Atlanta data [Lee *et al.*, 2002]. The sodium/potassium sulfate spectra were observed in both smaller and larger particles. The PALMS classifications are discussed in more detail in a separate paper [Middlebrook *et al.*, manuscript in prep.].

Some individual particle spectra representative of the ATOFMS classifications determined by peak ID are shown in Figure 3. Note that these spectra are from individual particles rather than classification or weight vectors and that both positive and negative spectra were obtained from each particle. The organic/sulfate type contains organic peaks in the positive spectrum whereas sulfate and nitrate peaks are in the negative spectrum. Carbon cluster peaks are prevalent in both the positive and negative spectra of soot/hydrocarbon particles. Although the organic/sulfate and soot/hydrocarbon spectra show a clear distinction between the two classifications, the relative intensities of the organic carbon peaks and carbon cluster peaks varied continuously in the actual data. The carbon-containing classifications (both organic and elemental) were more common among the submicron particles and the sodium-, iron-, or dust-containing particles were more common in the supermicron size range. Potassium was observed in both sub- and super-micron particles. The frequencies reported in Table 2 were not corrected for sampling transmission and the higher fraction of mineral particles in the overall ATOFMS data may be related to sampling biases. More details of these ATOFMS classifications and additional particle types are presented in another paper [Liu *et al.*, this issue].

Some peak weight vectors for several ART-2a classifications of the RSMS-II data are shown in Figure 4. These classifications also indicate that organic components were common in many of the Atlanta particles (see Table 2). Sulfate was infrequently detected in the positive ion

spectra from RSMS-II. The organic classification contains only small carbon fragments whereas the soot/hydrocarbon classification contains the higher mass C_n fragments (up to $n = 15$) in addition to the smaller fragments. The organic spectra also contain lead and were more common for the smaller size particles. Soot/hydrocarbon and sodium/potassium sulfate spectra were more common in the accumulation mode particles (about 0.1 to 0.5 μm in aerodynamic diameter). The mineral type was predominantly observed in the larger sizes sampled (greater than 0.3 μm) and contained aluminum, calcium, and iron. These classifications and others are discussed in more detail in another publication [Rhoads *et al.*, this issue].

A direct comparison of the frequencies of the common particle types is shown in Table 3. For each instrument, the frequencies are reported for particles between about 0.25 and 0.5 μm in aerodynamic diameter during overlapping sampling periods from Aug. 12-19. Sizing from the PALMS instrument is less certain than for the RSMS-II and ATOFMS instruments. Since aerosol transmission is roughly comparable among the three instruments over the size range examined and the PALMS data cannot be corrected for transmission, uncorrected frequencies are shown in Table 3. The four classifications (organic/sulfate mixtures, sodium/potassium sulfate, soot/hydrocarbon, and mineral) represent over 95 % of the data for overlapping time periods from each of the three instruments. All of the instruments indicate that organic particles internally mixed with sulfate were very common during the Atlanta study in this size range. Since there were continua among the organic/sulfate, sodium/potassium sulfate, and soot/hydrocarbon classifications, differences in their frequencies among the three instruments are likely to be related to differences in laser ionization conditions and the way spectra were classified. More fragmentation is observed with higher laser fluence and the classification programs typically place spectra with short organic/hydrocarbon fragments into the organic/sulfate classifications. Furthermore, the RSMS-II and ATOFMS instruments are less sensitive to sulfate and could have relatively fewer organic/sulfate particles. Differences in classification frequencies may also be due to transmission and sizing differences. For example, during the overlapping time period, the RSMS-II data indicate that a higher fraction (13 %) of

the 0.25 μm particles were soot/hydrocarbon particles whereas only 6 % of the 0.35- to 0.5- μm particles were soot/hydrocarbon. Nevertheless, the sodium/potassium sulfate and soot/hydrocarbon particles were generally found by all three instruments to be less common than the organic/sulfate particles, and mineral particles were even less common.

4. Nitrate/Sulfate Ratios

One method of comparing the AMS with the laser-based instruments is to examine how the molar and ion ratios of nitrate/sulfate correlate with composite nitrate/sulfate mole ratios from other measurements (Figure 5). Ion current from the laser-based spectra tends to be more reliable for measuring relative concentrations than for absolute concentrations because the shot-to-shot variability in the absolute ion yields is greater than that for the relative ion yields [Gross *et al.*, 2000]. Because the peaks in the PALMS data were not saturated, peak areas can be determined without extrapolation. Furthermore, PALMS had relatively high hit rates. Thus, only the PALMS data are shown in this comparison. Comparisons of the ATOFMS data with the semi-continuous measurements from Atlanta will be discussed in a separate paper [Prather *et al.*, manuscript in prep.].

For the AMS data, molar concentrations were obtained by integrating the $m/z = 30$ (NO^+) and 46 (NO_2^+) peaks for nitrate and $m/z = 48$ (SO^+) and 64 (SO_2^+) peaks for sulfate [Jimenez *et al.*, this issue]. To convert the ion signals into mass concentrations, the AMS data were scaled to fit Georgia Tech's Particle in Liquid Sampler with Ion Chromatography (PILS-IC) data by a constant calibration factor (order of magnitude 1) every few days. This scaling was needed due to changes in AMS sensitivity that were not calibrated for as frequently as it would have been required during this campaign. The use of two fragments for each species allows the detection of interfering species, which will generally contribute to one of the peaks but not the other. No major interferences were observed for the AMS nitrate and sulfate measurements in this study.

The ion ratios for the PALMS data were determined from the integrated peak intensities in the negative spectra at $m/z = 46$ (NO_2^-) and 62 (NO_3^-) for nitrate and at $m/z = 64$ (SO_2^-), 80

(SO_3^-), 81 (HSO_3^-), 96 (SO_4^-), 97 (HSO_4^-), 99 ($\text{H}^{34}\text{SO}_4^-$), 177 ($\text{SO}_3\cdot\text{HSO}_4^-$), and 195 ($\text{H}_2\text{SO}_4\cdot\text{HSO}_4^-$) for sulfate. The particles sampled by PALMS during the time period shown in Figure 5a were not dried. The undried particles do not represent most of the PALMS data but were the only data available during an overlapping time period with the AMS. All of the data from both instruments during the overlapping time period were used and were not corrected for aerosol transmission.

The time series plot (Figure 5a) includes composite nitrate/sulfate mole ratios derived from semi-continuous measurements at the site [Hering *et al.*, this issue]. Both the AMS and PALMS data track the composite mole ratios during this time period. Furthermore, the nitrate ion yield from PALMS was approximately a factor of 100 lower than the sulfate ion yield during this period. A diurnal trend in nitrate was observed by many methods during the entire study [Weber *et al.*, 2001; Hering *et al.*, this issue; Lee *et al.*, this issue].

The scatter plot (Figure 5b) shows that both the AMS and PALMS ratios were positively correlated with the composite mole ratios. However, the AMS data were clearly more correlated than the PALMS data ($r^2 = 0.93$ for the AMS whereas $r^2 = 0.65$ for the PALMS). In fact, the AMS nitrate and sulfate measurements over a period of 2 weeks generally agreed well with the data from the semi-continuous aerosol composition instruments present in Atlanta [Jimenez *et al.*, this issue]. Independent calibration procedures are being developed for the AMS instrument.

Figure 5b also includes a correlation of the PALMS nitrate/sulfate ion ratios with the composite nitrate/sulfate mole ratios during a different time period when the PALMS particles were dried. More spectra were averaged for this comparison and the correlation was slightly improved over the results from the undried particles ($r^2 = 0.70$ vs. $r^2 = 0.65$). Furthermore, the nitrate ion yield relative to sulfate appears to be more efficient for the dried particles. There are two key differences between the two PALMS correlations. 1) There may be a matrix effect from the additional water in the undried particles that produces less nitrate ions relative to sulfate ions. A second effect of the undried particles is that their sizes were potentially larger than the dried particles. For particles between 0.35 and 0.9 μm in diameter, transmission into PALMS is

roughly proportional to mass [Middlebrook *et al.*, 2000]. Since the PALMS data were not corrected for particle transmission, changes in the size distribution outside of this size range may affect the correlations. 2) Roughly 50 % higher laser fluences were used during the period when the undried particles were sampled. Large differences in laser fluence could potentially change the relative amount of ions produced from nitrate and sulfate.

This is a first attempt at examining correlations in nitrate/sulfate ratios between different particle mass spectrometers and other measurements in Atlanta. The main purpose of Figure 5 is to demonstrate that the AMS data are clearly more correlated with the composite measurements and hence more quantitative than the PALMS data. Yet, the correlations between PALMS and the composite data indicate that calibration of the laser-based data may be possible for certain ions and that higher ion ratios from the same instrument can represent higher relative concentrations. Indeed, promising comparisons of the ATOFMS data with the semi-continuous measurements from Atlanta have been discovered [Prather *et al.*, manuscript in prep.]. This has also been reported for other field studies [Murphy and Thomson, 1997; Liu *et al.*, 2000; Cziczo *et al.*, 2001]. However, caution must be used since there is a high degree of variability in the laser-based data and quantification is unlikely on a single particle basis. As mentioned above, calibration factors may vary depending on particle matrix [Ge *et al.*, 1998], water content [Neubauer *et al.*, 1997, 1998], size, and laser ionization parameters [Neubauer *et al.*, 1997]. By averaging spectra according to their single-particle classifications, relative humidity during sampling, size, and/or laser ionization conditions, these effects may be minimized.

5. Discussion

In general, there are striking differences among the techniques from the four particle mass spectrometers that operated in Atlanta. The main difference is related to the volatilization/ionization method. Because the AMS instrument uses a separate volatilization step followed by electron impact ionization, it can produce quantitative data. Furthermore, mass spectral data from the AMS are representative of the ensemble of particles sampled. In contrast,

the mass spectra from the laser-based instruments (PALMS, ATOFMS, and RSMS-II) are qualitative and representative of individual particles. In addition, relative ion intensities can indicate relative concentrations in the laser-based data.

Among the laser-based instruments, there are several differences in the resulting individual particle data due to the varying designs.

- 1) The RSMS-II and ATOFMS instruments are able to provide size-resolved individual particle composition. For the RSMS-II instrument, the size range is extended to particles too small to scatter light efficiently. However, since particles are detected by the presence of a spectrum, small particles of certain compositions may be present but not detected [*Kane and Johnston, 2000*]. Furthermore, the inlet pressure was varied stepwise in the RSMS-II instrument so that the size of the particles being analyzed was pre-selected.
- 2) The ATOFMS instrument clearly reveals more information by providing both positive and negative spectra from the same particle. Without the corresponding negative spectrum, the coexistence of organic and sulfate compounds in the same particles may be difficult to discover unless both compounds appear in the same polarity spectrum as they do in the PALMS data [*Lee et al., 2002*].
- 3) The different laser wavelengths and fluences may affect the appearance of some peaks in the spectra, the degree of fragmentation of organic species, and the ability to probe the entire particle or mainly the surface. For example, larger sulfate peaks in the positive ion spectra from PALMS at relatively high laser fluence and the absence of sulfate peaks in the RSMS-II spectra may indicate that a high laser fluence is necessary to efficiently produce positive ions from sulfate. It is also possible that the sulfate was present in the bulk of the particles and organic compounds on the surface. However, the lowest PALMS and RSMS-II laser fluences ($2 \times 10^9 \text{ W/cm}^2$ and $1.4 \times 10^8 \text{ W/cm}^2$, respectively) should have been high enough to probe more than only the particle surface [*Carson et al., 1997*]. Alternatively, the appearance of sulfate in the

PALMS spectra but not in the RSMS-II data may have been due to the high dynamic range of the PALMS detector. This is less likely to cause the difference in sulfate sensitivity because small lead peaks were observed in both data sets and the sulfate peaks were typically larger than the lead peaks in the PALMS data.

- 4) The PALMS spectra have very high signal-to-noise ratios due to the use of a preamplifier on the detector and a high dynamic range due to a log amplifier. These allow the PALMS instrument to be sensitive to very small ion peaks and integration of peaks is relatively simple. Signal saturation was occasionally seen in some of the ATOFMS and RSMS-II spectra from Atlanta.

Due to the complexity of individual particle data and the above differences between instruments, the three laser-based instruments were compared in more detail by examining their particle classifications. Despite the differences, it is interesting to note that the particle classifications from the three instruments had common features. One overriding similarity is the observation of continua between different classifications. Thus, in the Atlanta environment, many particles were not adequately represented by distinct, non-overlapping classifications. Different particle types probably coagulated with the common organic/sulfate particles or organic and sulfate compounds condensed on a variety of particles. Nevertheless, individual particles may be grouped into classifications that contain the major ions in the spectra and these classifications have different size and temporal trends. Furthermore, the number of classes and where the line is drawn to separate classes is somewhat subjective and may be optimized for the type of analysis being performed. While the organic/sulfate classes appear to be very different for the three instruments, the sodium/potassium sulfate, soot/hydrocarbon, and mineral classifications are fairly similar. In addition, minor peaks such as lead (Pb) in the organic/sulfate and sodium/potassium sulfate spectra and barium (Ba) in the mineral spectra were detected by different instruments. Although not indicated in Tables 2 and 3, all of the laser-based instruments found mineral particles were more common in larger particles (greater than 0.3 μm for RSMS-II, greater than about 1 μm for PALMS and greater than 1 μm for ATOFMS) and that

organic/sulfate particles were more prevalent at smaller sizes. These results were reported in the individual papers [Lee *et al.*, 2002; Rhoads *et al.*, this issue; Liu *et al.*, this issue].

6. Summary and Conclusions

The four particle mass spectrometers deployed during the Atlanta Supersites Project have distinct characteristics and advantages. Particle sizes are measured the most accurately with ATOFMS, RSMS-II, and AMS. Furthermore, the RSMS-II instrument can obtain composition information on individual particles as small as 15 nm. Because the AMS instrument has an aerodynamic focussing inlet, particle transmission is close to 100 % for particles 60 to 600 nm in aerodynamic diameter. In the other instruments, particle transmission is as high as 2 % for supermicron particles and as low as 10^{-6} for submicron particles. The ATOFMS data can be first-order corrected for particle transmission. Particles containing pure sulfuric acid, ammonium sulfate, or a high water content are difficult to ionize and may not be detected by the laser-based instruments. The high hit rate of PALMS due to the geometry of the system, the high laser fluence, and shorter wavelength minimizes any systematic bias against these particles. Using a dryer in the sampling line reduces the aerosol water content and enhances ionization of particles that are hard to ionize at high ambient relative humidity.

The AMS instrument utilizes a two-step volatilization/ionization process, which can yield quantitative results. However, the AMS instrument cannot provide single particle mass spectra or analyze refractory species such as soot, sodium chloride, and crustal material. In contrast, the laser-based instruments (PALMS, ATOFMS, and RSMS-II) generate individual particle mass spectra yet provide only semi-quantitative results. Correlation plots of the AMS and PALMS data with the composite measurements demonstrate how quantitative the two mass spectrometers can be ($r^2 = 0.93$ for AMS whereas $r^2 \sim 0.7$ for PALMS). Further comparisons of the AMS and ATOFMS data with the semi-continuous data are shown in separate papers [Jimenez *et al.*, this issue; Prather *et al.*, manuscript in prep., respectively]. The spectra from the laser-based instruments varied mainly due to the different laser fluences (10^8 - 10^9 W/cm²) and wavelengths

(193 nm and 266 nm), which can affect ion yields and fragmentation patterns of organic species. Both positive and negative ion spectra are obtained from single particles with the ATOFMS instrument whereas only one pre-selected polarity spectrum is obtained from either PALMS or RSMS-II. Extremely minor ions can be detected with the PALMS instrument. For example, more than 50 different elements were detected in the PALMS Atlanta data [Lee *et al.*, 2002].

Despite the differences in laser ionization conditions and using different classification programs, single-particle positive ion classifications from the data obtained in Atlanta by the laser-based instruments (PALMS, ATOFMS, and RSMS-II) are broadly consistent and revealed similar trends as a function of size for organic/sulfate and mineral particles. The 0.25 - 0.5 μm spectra from all three instruments during overlapping time periods were dominated by organic particles internally mixed with sulfate and other particle types (soot/hydrocarbon, sodium/potassium sulfate, mineral, etc.) comprised smaller fractions.

Since the Atlanta study, many of the instruments have been improved or modified. The AMS has an improved vacuum system to reduce background and a larger-diameter quadrupole to increase ion detection efficiency. The combination of both improvements has resulted in up to two orders of magnitude higher sensitivity than in the Atlanta study (as of mid-2001). Its data acquisition and analysis software has also evolved to the point where mass loadings and size distributions can be plotted as they are being obtained. In addition, the inlet has been redesigned to increase the transmission of smaller and larger particles. For the PALMS instrument, a new digitizer and software modifications have dramatically increased the data acquisition rate and an aerodynamic lens has been used to increase particle transmission. Furthermore, the ion source region is currently being modified to measure aerodynamic particle size with two continuous Nd:YAG laser beams. Detection of sulfate particles is now accomplished with the RSMS-II using dual polarity mass spectrometers. Multiple data acquisition boards of varying attenuation levels are now being used on the detectors of the ATOFMS and RSMS-II instruments to increase their dynamic range. The ATOFMS instrument also currently has an aerodynamic lens to increase particle transmission. Finally, quantification of the laser-based data can be improved

for specific organic compounds by using separate lasers for ionization and desorption [*Morrical et al.*, 1998; *Cabalo et al.*, 2000].

This is the first study comparing the performance of several particle mass spectrometers. The field is rapidly growing with new and evolving individual instruments and methods of disseminating their complex results. Each of the particle mass spectrometers described here is a research instrument designed to excel at specific problems with various objectives. The AMS instrument has the capability to show how size-resolved particle composition varies on short time scales. The strength and primary focus of the laser-based instruments are their ability to find associations between different chemical species in individual particles with high time resolution. Classification of the mass spectra is a relatively new tool to study these associations. With single particle mass spectra, specific source signatures can be identified [*Liu et al.*, 1997; *Bhave et al.*, 2001a] and used to track particle origins, transformations, and transport [*Murphy et al.*, 1998]. Furthermore, heterogeneous chemistry can be detected at the single particle level [*Gard et al.*, 1998] and the differences in the chemistry of various particle types can be identified [*Lee et al.*, this issue].

The ability for all of the particle mass spectrometer data to be quantified is being extensively tested to assess the potential and limitations. As shown here, averaged laser-based data do indicate changes in relative concentrations of particle components. In some situations these changes may be quantified [*Murphy and Thomson*, 1997; *Liu et al.*, 2000; *Cziczo et al.*, 2001; *Ferguson et al.*, 2001; *Bhave et al.*, 2001b]. The data from all of the instruments described here are intended to be complementary to other techniques and comparisons with other measurements are very important. Because the laser-based instruments return complex data, their rich data sets have yet to be fully explored by the atmospheric science community. By obtaining chemical information on the single particle level, these instruments are providing a unique perspective on the composition of atmospheric particles.

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Figure Captions:

Figure 1. Schematic diagrams of the four particle mass spectrometers that operated during the Atlanta Supersites Project. The ATOFMS diagram is adapted from *Gard et al.* [1997], RSMS-II is from *Rhoads et al.* [this issue], and AMS is from *Jimenez et al.* [this issue].

Figure 2. Common single particle classification vectors for positive ion spectra from the PALMS instrument determined by regression tree analysis.

Figure 3. Positive and negative single particle spectra representative of particle classes from the ATOFMS instrument determined by peak identification (ID).

Figure 4. Peak weight vectors generated by ART-2a which are representative of typical single particle classes for positive ion spectra from the RSMS-II instrument.

Figure 5. (a) Time series and (b) scatter plots of nitrate/sulfate ratios from the AMS and PALMS mass spectrometers compared to a composite ratio from semi-continuous measurements [*Hering et al.*, this issue]. The AMS and composite data are reported as mole ratios, whereas the PALMS data are reported as ion ratios. The mass spectrometer data were not corrected for particle transmission and the peaks used in the ratios are listed in the text. Particles sampled by PALMS were not dried during the time period shown in part (a). The scatter plot (b) shows the correlations of the AMS and PALMS data with the composite measurements during the time period shown in part (a) as well as a correlation of the PALMS data with the composite measurements during another time period when the PALMS particles were dried (Aug. 7-12). In the scatter plot, the AMS and undried PALMS data were averaged for 500 points and the dried PALMS data were averaged for 2000 points as a function of the composite mole ratio. The change in the PALMS correlation between the two time periods in (b) is primarily due to a change in ionization efficiencies, most likely from differences in water content and laser fluence.

Table 1. Main Design Characteristics of the Four Particle Mass Spectrometers

	particle detection/ sizing	aerodynamic size range (μm)	volatilization/ ionization method	mass spectrometer	single-particle classification methods
PALMS	light scattering	0.35 ^a -2.5	LDI ^b $\lambda = 193 \text{ nm}$ $2\text{-}5 \times 10^9 \text{ W/cm}^2$	single time of flight reflectron	peak ID ^c / regression tree analysis
ATOFMS	aerosol time of flight	> 0.2	LDI ^b $\lambda = 266 \text{ nm}$ $\sim 10^8 \text{ W/cm}^2$	dual time of flight reflectron	peak ID ^c / artificial neural network
RSMS-II	aero- dynamic focussing	0.015-1.3	LDI ^b $\lambda = 193 \text{ nm}$ $1\text{-}2 \times 10^8 \text{ W/cm}^2$	single linear time of flight	peak ID ^c / artificial neural network
AMS	aerosol time of flight	0.05-2.5	T $\sim 550 \text{ }^\circ\text{C}$ with electron impact	quadrupole	not applicable

^a PALMS' optical lower limit (0.22 μm) was converted into aerodynamic diameter, d_a , by assuming the optical diameter equals the Stoke's diameter, d_s , and $d_a = d_s \times \sqrt{\rho_p C_c / \rho_0}$, where ρ_p is the particle bulk density = 1.5 g cm⁻³ (P. H. McMurry, personal communication), C_c is the Cunningham correction factor = 1.74 for $d = 0.22 \mu\text{m}$, and ρ_0 is the standard density = 1 g cm⁻³ [Hinds, 1982].

^b LDI = laser desorption/ionization

^c ID = identification

Table 2. Classification frequencies^a for all particles sampled during the entire study by the laser-based mass spectrometers.

	RSMS-II 0.015-1.2 μm 15989 spectra ^c	PALMS 0.35-2.5 μm ^b 206131 spectra ^c	ATOFMS 0.2-2.5 μm 455444 particles ^d
organic/sulfate mixtures	75 %	87 %	74 %
sodium/ potassium-sulfate	7 %	7 %	6 %
soot/ hydrocarbon	3 %	3 %	5 %
mineral	3 %	0.6 %	12 %
total	88 %	97 %	97 %

^a Frequencies were not adjusted for particle transmission.

^b The PALMS lower size limit of 0.35 μm is derived from the optical lower limit of 0.22 μm (see footnote a in Table 1).

^c Only frequencies in the positive ion spectra are shown here.

^d Each ATOFMS particle had either a positive or negative spectrum or both.

Table 3. Classification frequencies^a for comparable-sized particles during overlapping sampling periods.

	RSMS-II 0.25-0.5 μm 535 spectra ^{c,d}	PALMS 0.35-0.5 μm ^b 2180 spectra ^c	ATOFMS 0.2-0.5 μm 6963 particles ^e
organic/sulfate mixtures	74 %	89 %	88 %
sodium/ potassium-sulfate	8 %	8 %	3 %
soot/ hydrocarbon	11 %	1 %	8 %
mineral	3 %	0.7 %	0.4 %
total	96 %	99 %	99 %

^a Frequencies were not adjusted for particle transmission.

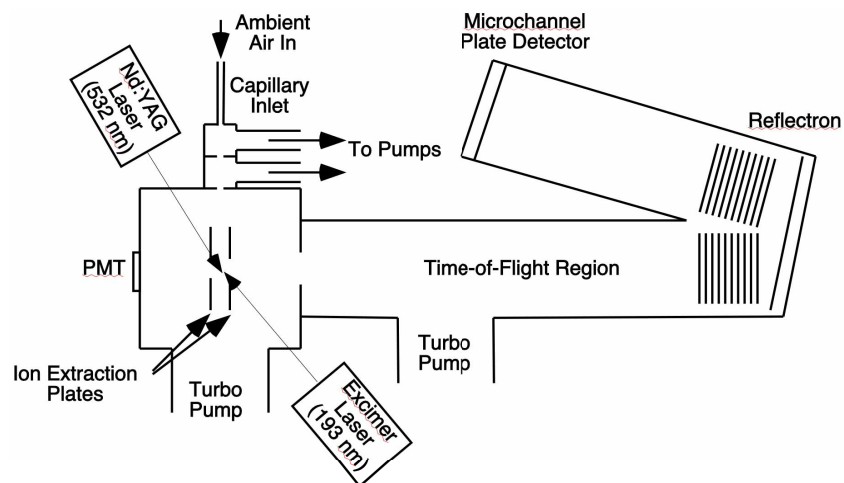
^b The PALMS lower size limit of 0.35 μm is derived from the optical lower limit of 0.22 μm (see footnote a in Table 1). The upper size limit of 0.5 μm is approximate.

^c Only frequencies in the positive ion spectra are shown here.

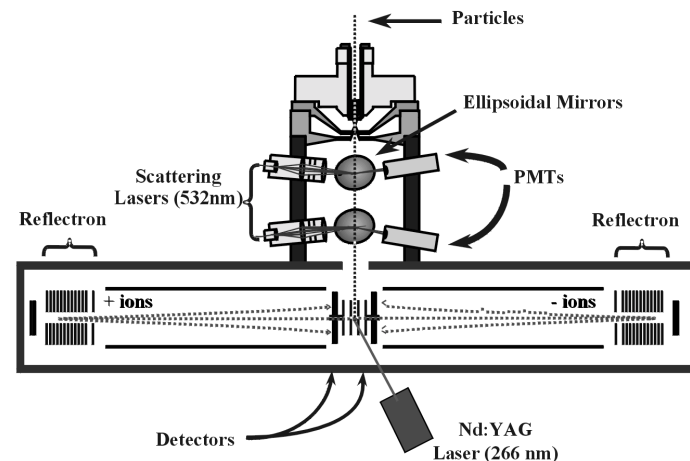
^d Most of these spectra (464) were from 0.25 and 0.35 μm particles.

^e Both positive and negative spectra were obtained from each particle.

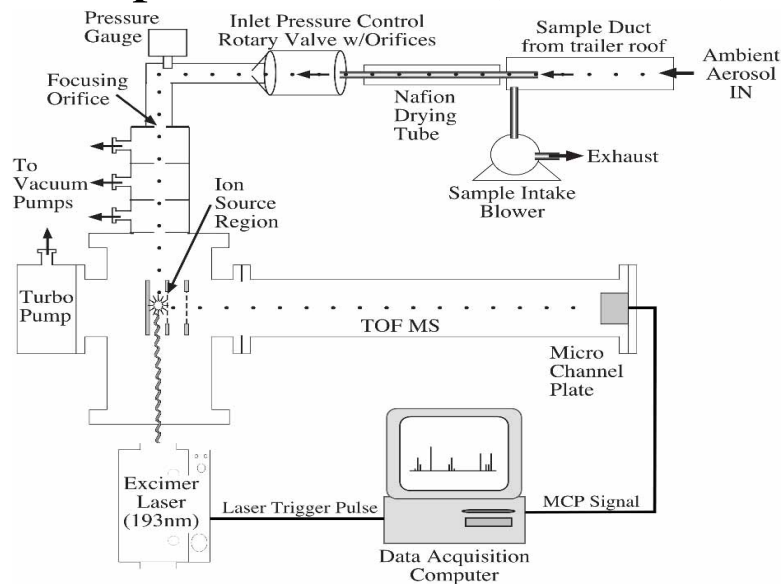
Particle Analysis by Laser Mass Spectrometry (PALMS)



Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)



Rapid Single-Particle Mass Spectrometer II (RSMS-II)



Aerosol Mass Spectrometer (AMS)

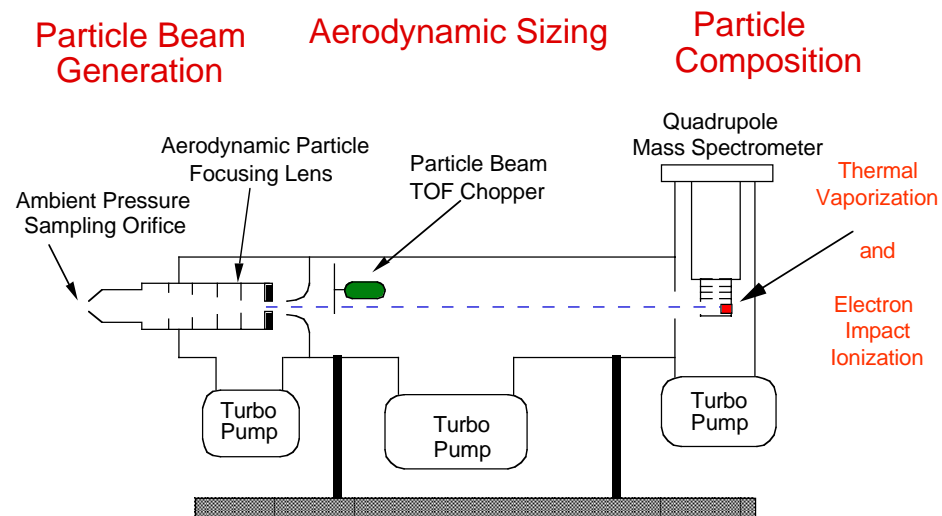
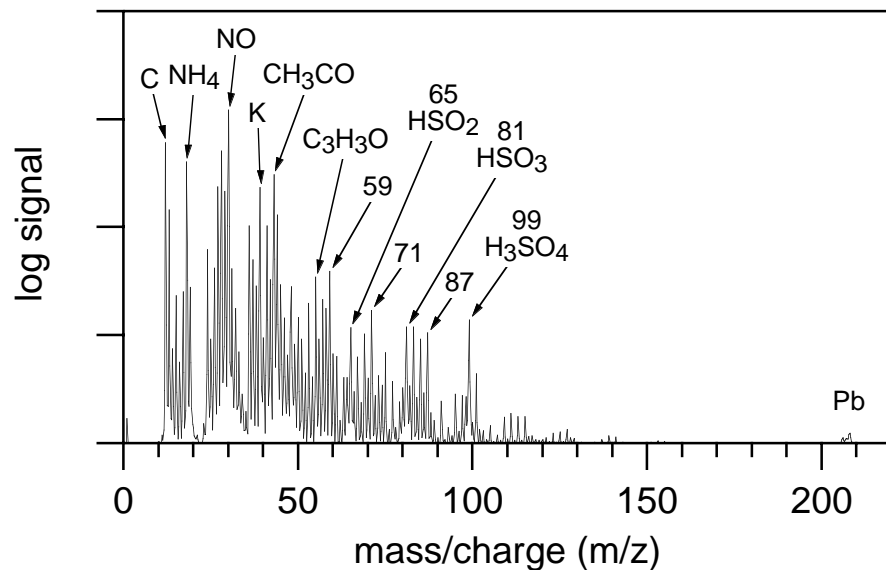
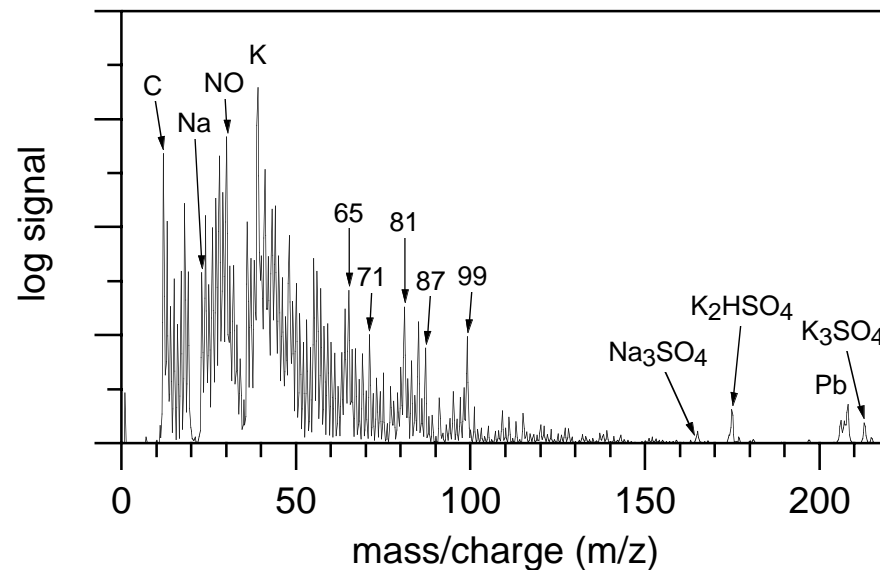


Figure 1

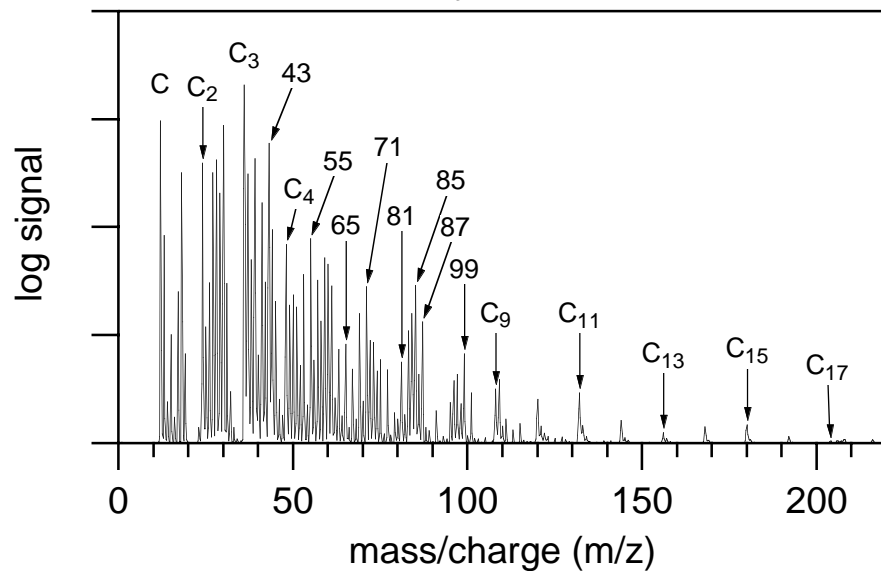
Organic and Sulfate



Na/K-Sulfate



Soot/Hydrocarbon



Mineral

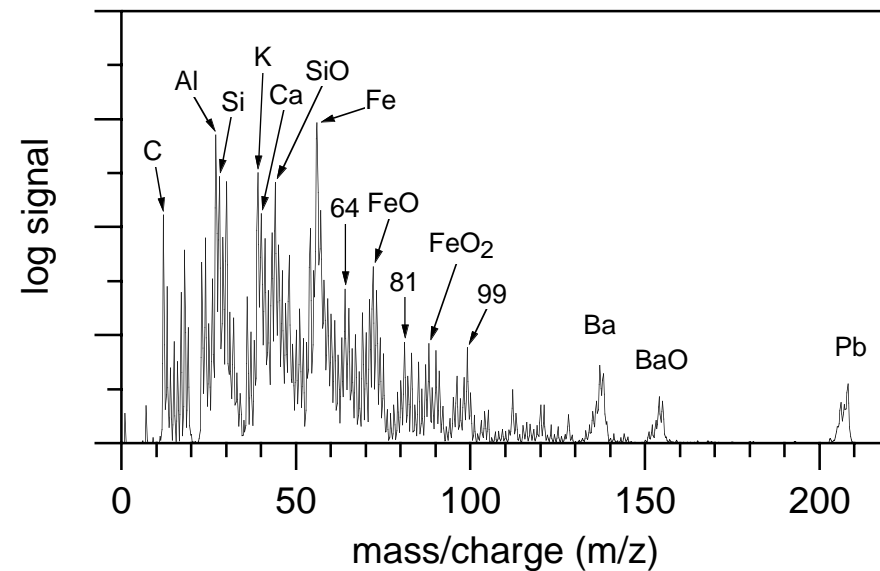
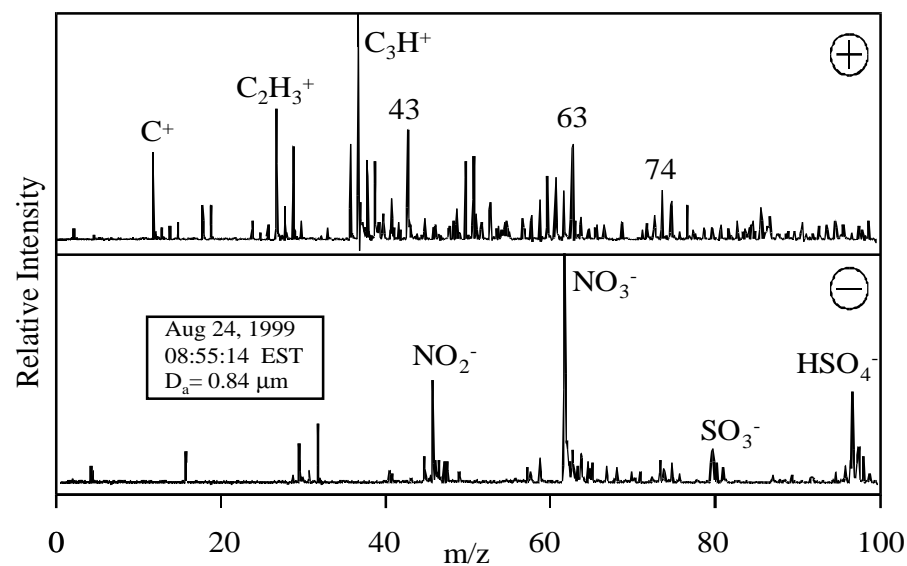
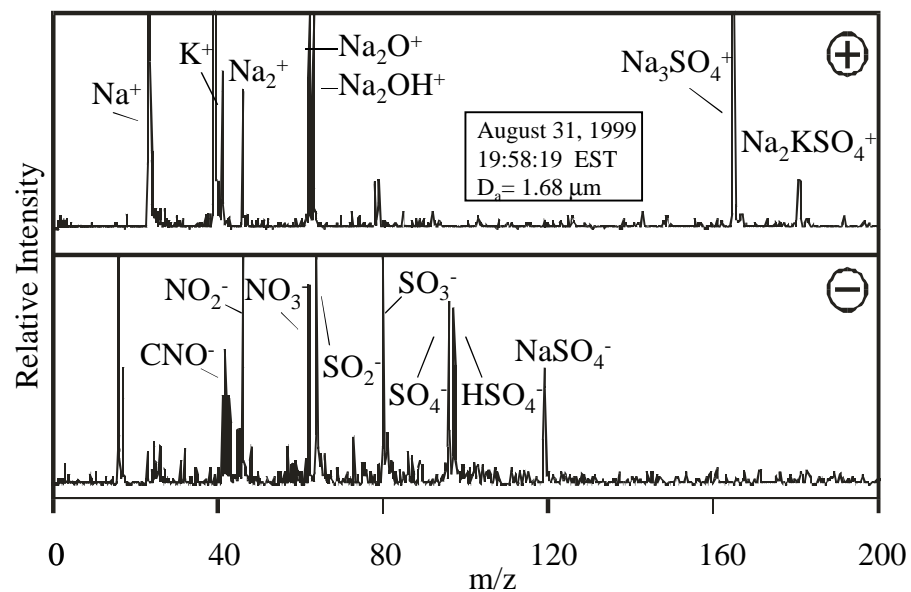


Figure 2

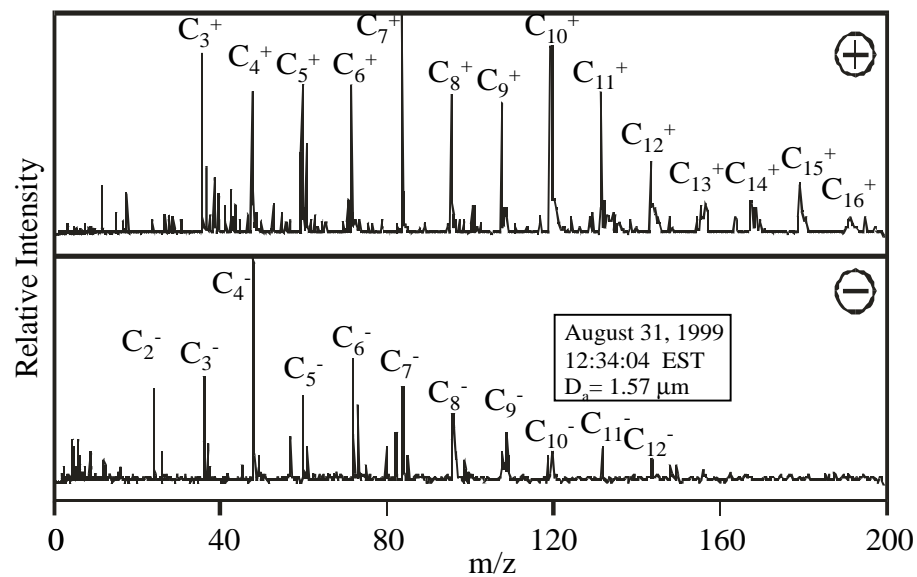
Organic and Sulfate



Na/K-Sulfate



Soot/Hydrocarbon



Mineral

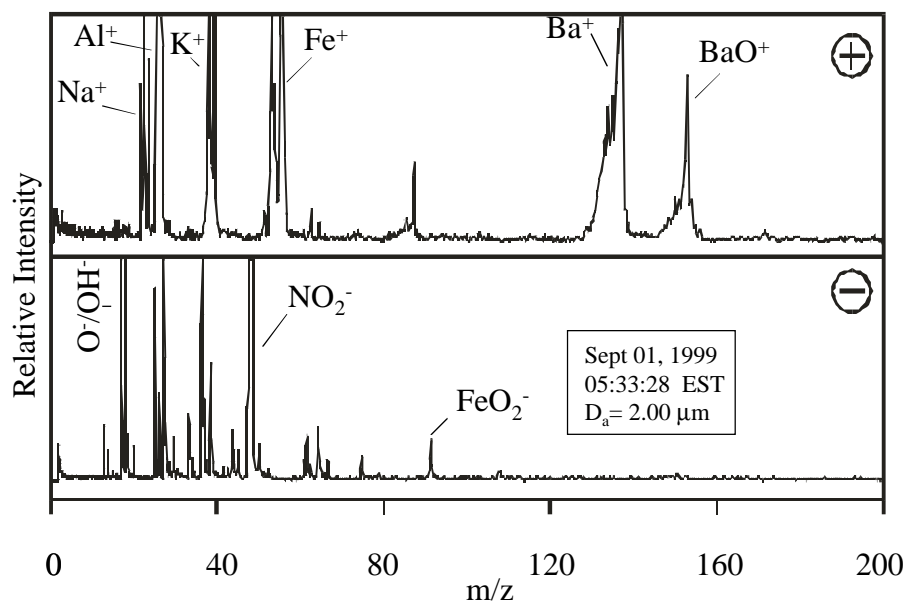


Figure 3

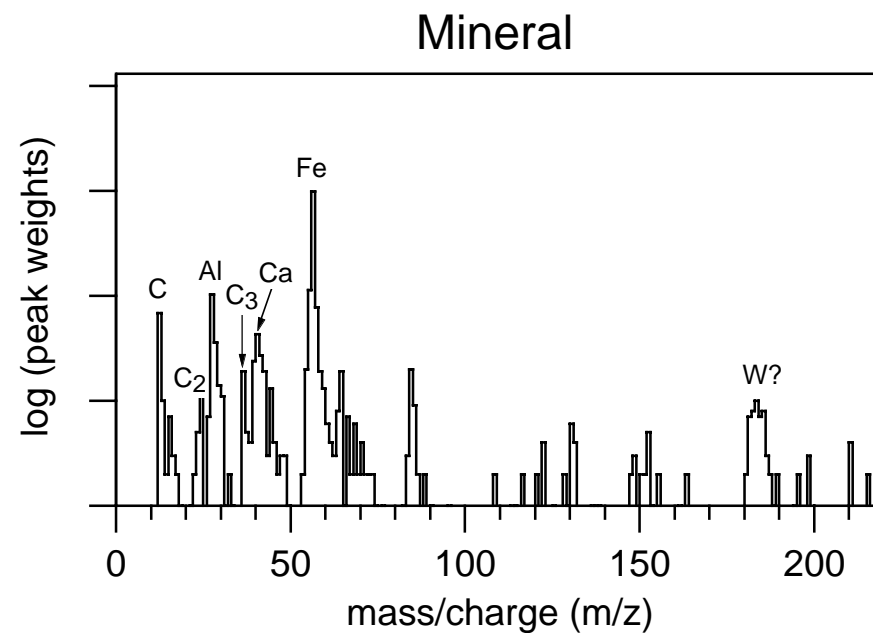
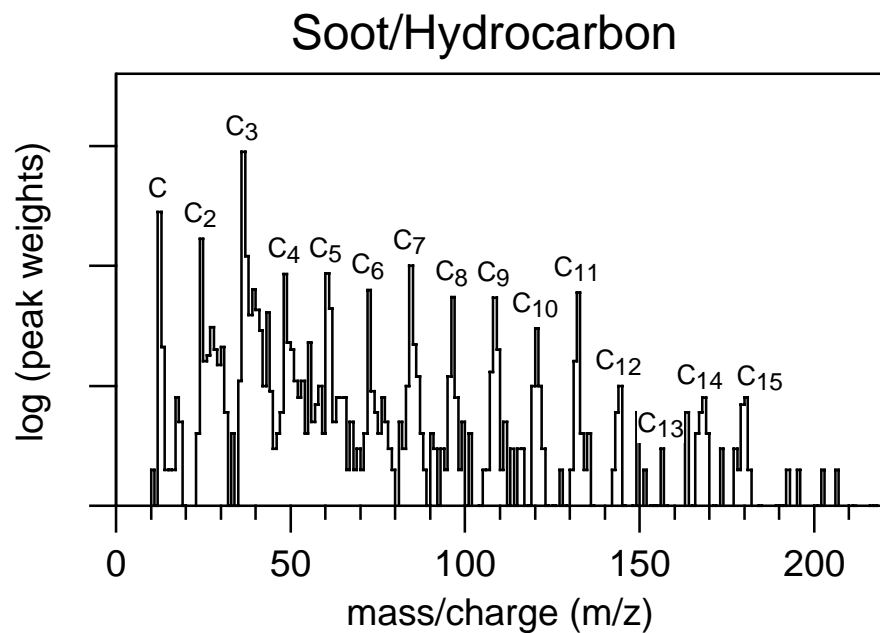
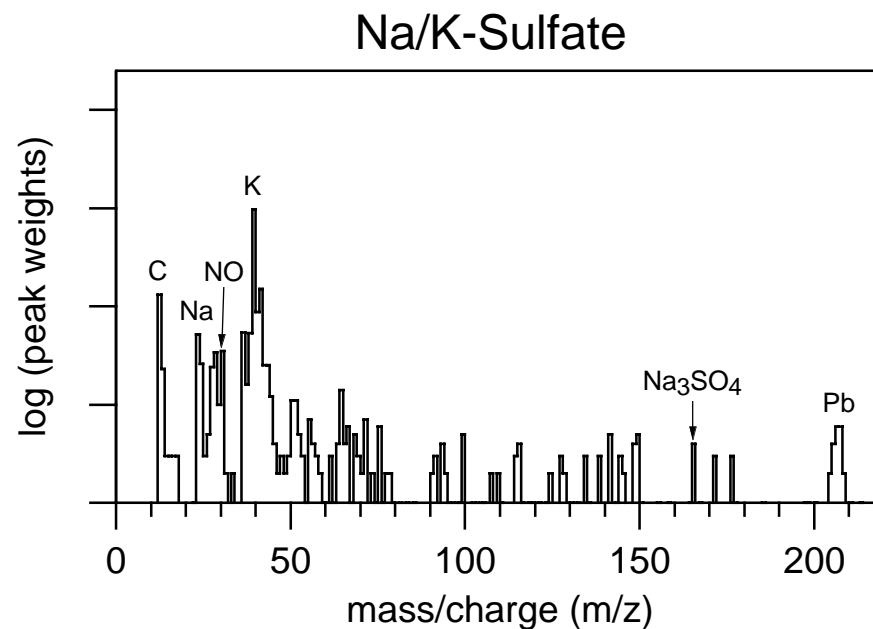
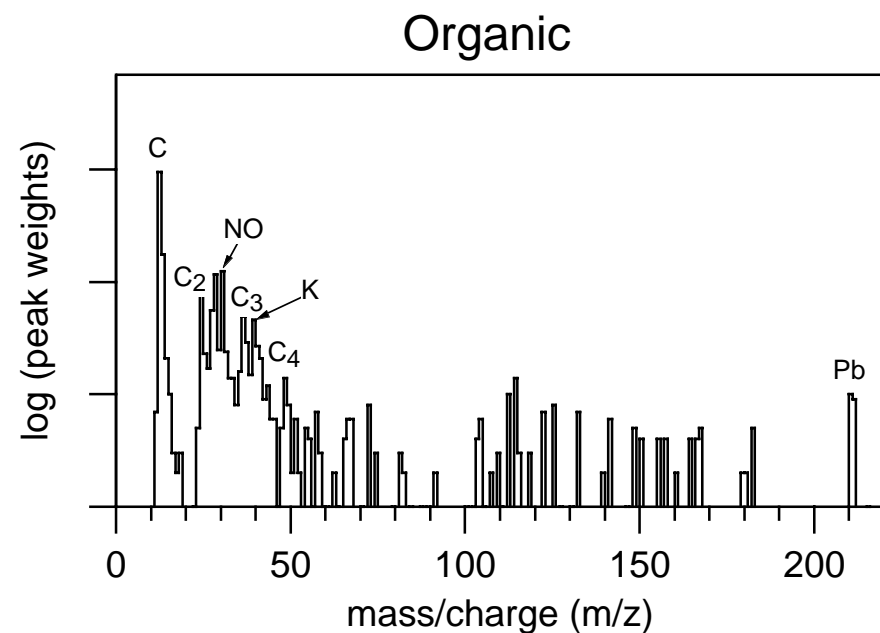


Figure 4

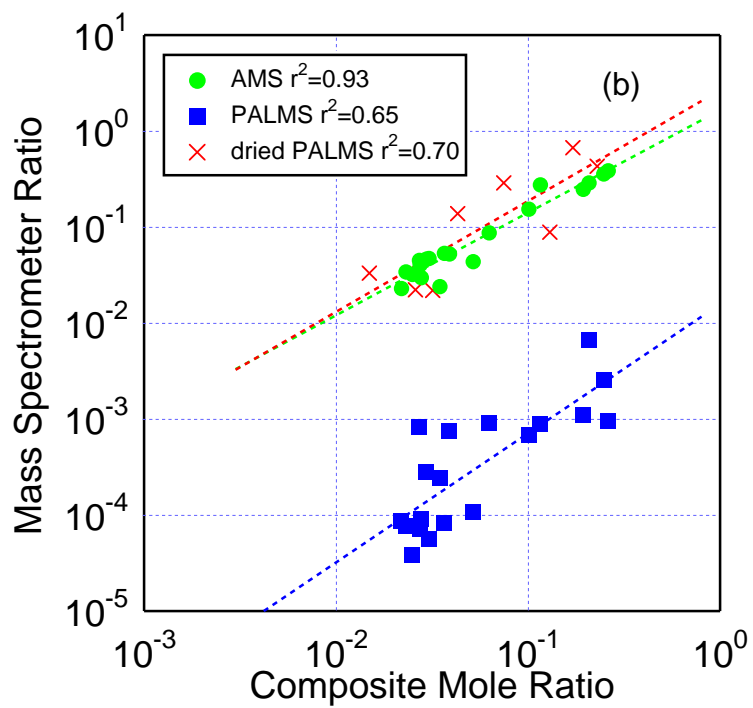
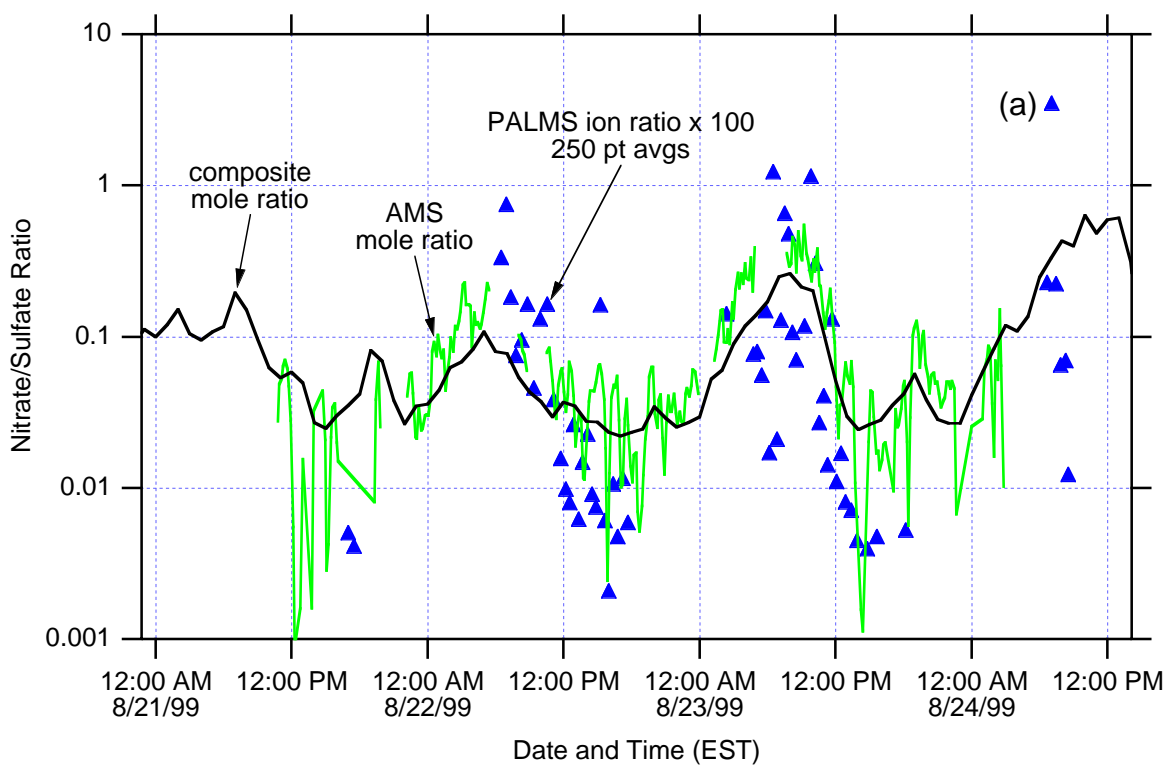


Figure 5