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Semi-Continuous Measurements of Aerosol Chemical Composition during the Summer 2002 Yosemite National Park Special Study

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Semi-continuous Measurements of Aerosol Chemical Composition During the Summer 2002 Yosemite National Park Special Study

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ABSTRACT

Semi-continuous measurements of fine particle composition were made over a period of several weeks in summer 2002 in Yosemite National Park, California. These included measurement of aerosol ionic composition (by PILS - Particle-Into-Liquid System) and aerosol carbon (by dual wavelength aethalometer and an R&P particulate carbon monitor). The data reveal that aerosol composition at the site is highly variable in time, with a strong diurnal cycle. Interestingly, however, different diurnal cycles were sometimes observed for different chemical constituents of the particles. Organic carbon was observed to dominate fine particle mass, with some periods apparently associated with influx of smoke from wildfires in the western U.S. Measurements of fine particle carbon isotopes revealed the fraction of carbon from biogenic sources to range from approximately 73 to 95%. The ionic fraction of the aerosol was usually dominated by ammoniated sulfate. During most periods, $PM_{2.5}$ nitrate was found primarily in sea salt particles from which chloride had been displaced. Strong variations in the extent of ammonia neutralization of sulfate were also observed. The ability to observe rapid changes in aerosol composition using these semi-continuous aerosol composition measurements is helpful for understanding the dynamic chemical composition of fine particles responsible for regional haze.

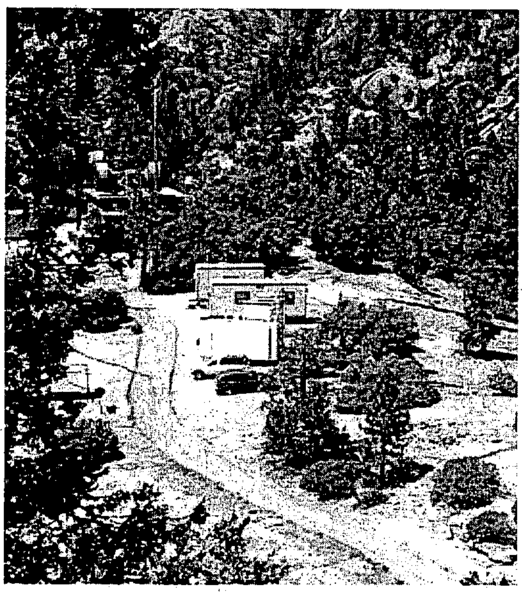
INTRODUCTION

Many processes influence the temporal evolution of fine aerosol mass and composition. Aerosol composition may change on timescales as short as a few minutes as a result of changes in meteorological transport, atmospheric oxidation, gas-particle partitioning, or other factors. While traditional measurements of aerosol composition rely on time integrated sample collection with later chemical analysis, an increasing number of measurement techniques are becoming available that permit near real-time monitoring of aerosol composition. We report here on the application of several of these semi-continuous techniques in the examination of fine particle composition in Yosemite National Park and its contributions to regional visibility degradation.

EXPERIMENTAL

$PM_{2.5}$ aerosol was sampled and analyzed during summer 2002 at Turtleback Dome in Yosemite National Park. The trailers housing several of the measurements are depicted in Figure 1. Turtleback Dome, located above the western entrance to Yosemite Valley, is also host to the Yosemite IMPROVE aerosol monitoring site. Measurements were made from mid-July through early September. Equipment deployed for the summer 2002 aerosol and visibility special study included instruments to measure aerosol size distributions, particle hygroscopicity, dry and ambient relative humidity particle light scattering, and aerosol composition.

Figure 1. View looking down at the measurement site.



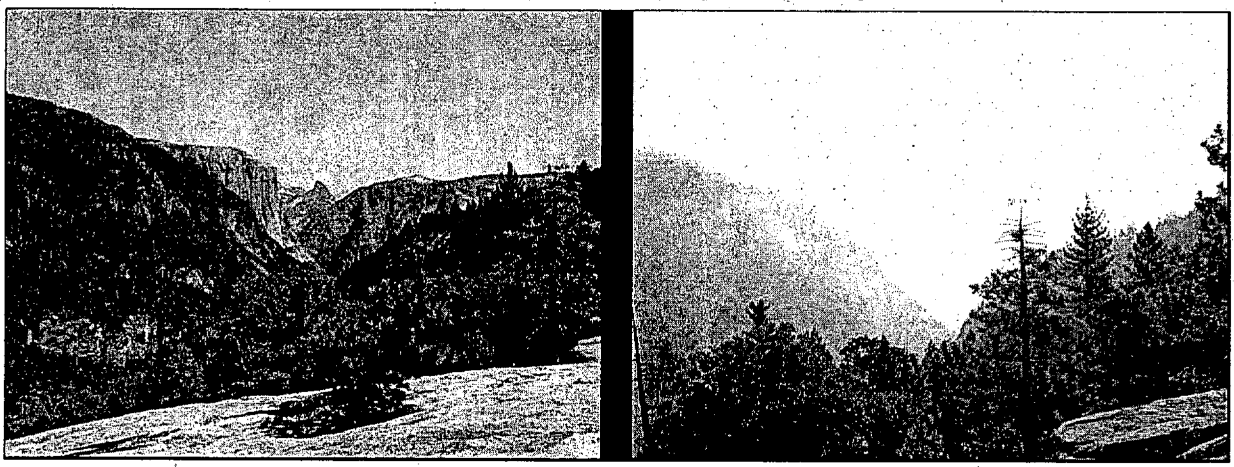
Composition measurements included collection of filters and denuders to measure time-integrated aerosol composition as well as several instruments to provide semi-continuous measurements of aerosol black carbon. A Particle Into Liquid System (PILS) was used to measure $PM_{2.5}$ aerosol ion (NO_3^-, Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) concentrations at 15 minute time intervals. Denuders located upstream of the PILS were used to remove interfering soluble gases, including nitric acid and ammonia. A Rupprecht & Patashnick Model 5400 particulate carbon monitor was used to measure aerosol carbon concentrations at one hour intervals. A Magee Scientific dual wavelength (UV and visible) aethalometer was used to measure aerosol black carbon concentrations.

Quartz fiber $PM_{2.5}$ HiVol filters were also collected for carbon isotope analysis at Lawrence Livermore National Laboratory in order to determine the fraction of aerosol carbon from biogenic vs. fossil fuel sources.

RESULTS AND DISCUSSION

Fine aerosol concentrations and visibility degradation at the site varied strongly over the course of the measurements. Figure 2 shows photographs taken from the measurement site toward Yosemite Valley on days with strongly contrasting visibility.

Figure 2. Photos taken from Turtleback Dome looking into Yosemite Valley. Left panel: 7 August 2002, Right panel: 27 July 2002.



Fine aerosol mass at the site was observed to be dominated by organic carbon. Total fine particle carbon concentrations during the study typically varied between 2 and 14 $\mu g/m^3$ (see Fig. 3). These concentrations are significantly higher than the long term average carbon concentrations measured at Turtleback Dome by the IMPROVE program. Most of the carbon was observed to be present as organic, rather than elemental carbon. Figure 3 depicts the low black carbon concentrations measured during the study using the aethalometer.

During several periods, black carbon concentrations reported by the aethalometer UV measurement significantly exceed black carbon concentrations measured in the visible range (see Figure 4). This difference is consistent with the present of smoke particles, which provide enhanced UV absorption.

During the period of the study there were several large forest fires in the western United States. Figure 5 depicts the locations of several fires on August 20th along with back-trajectories computed from the San Joaquin Valley west of Yosemite using the NOAA Hysplit model. The trajectories in this figure suggest an influence of the large fires burning in southwest Oregon on fine particle concentrations in the region just upwind of Yosemite. Figure 4 shows this is also a period when enhanced aerosol UV absorption is present.

Figure 3. Timeline of study $PM_{2.5}$ carbon concentrations. Total carbon concentrations were measured using an R&P Model 5400 Particulate Carbon Monitor while black carbon concentrations were measured using a UV-Vis Magee Scientific Aethalomter.

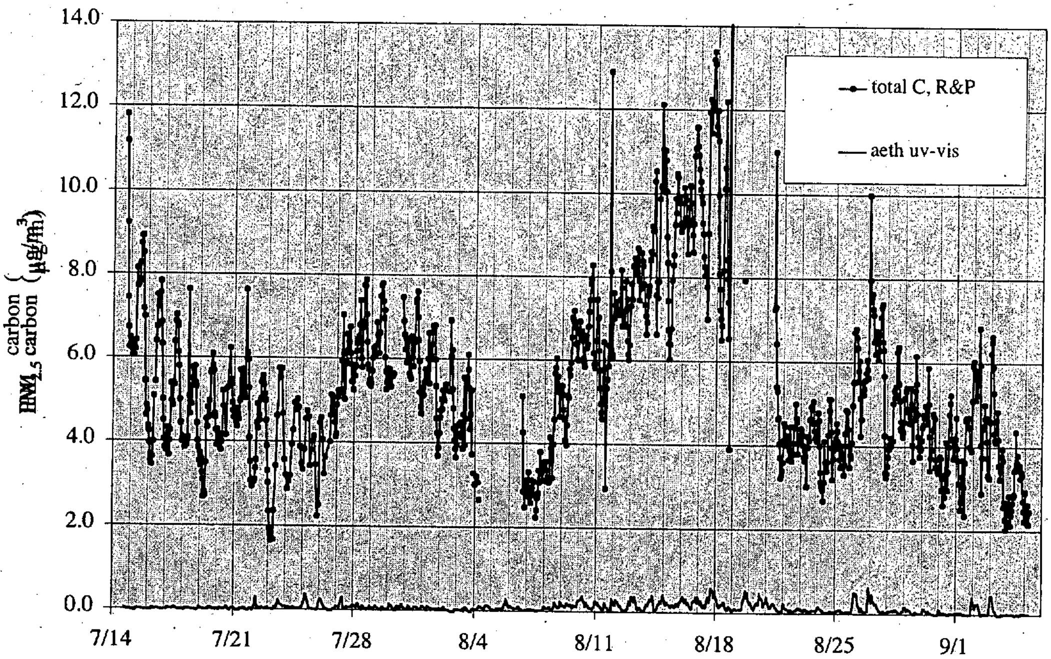


Figure 4. Black carbon (BC) concentrations measured during the study by the dual wavelength aethalometer. Periods when the UV-BC signal exceeds the visible-BC signal are suggestive of the presence of smoke.

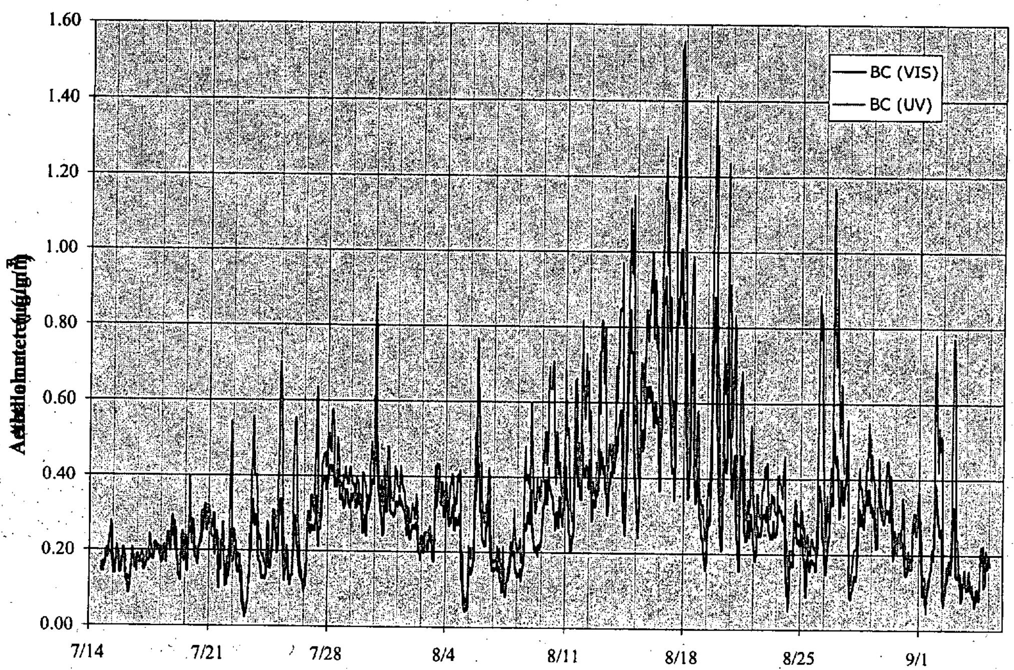
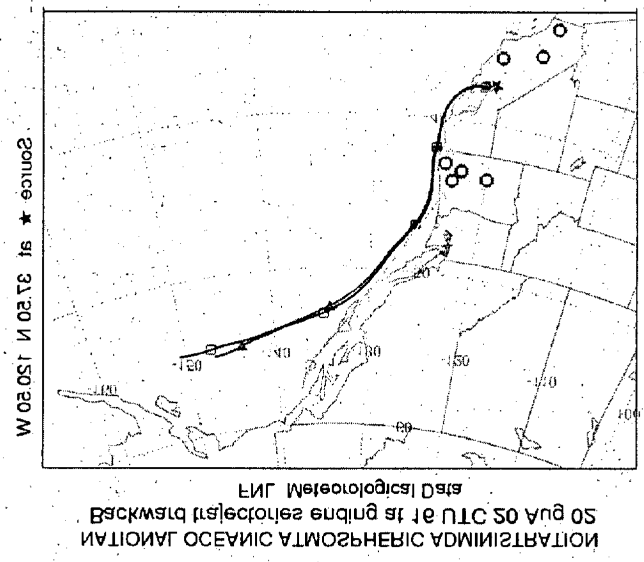
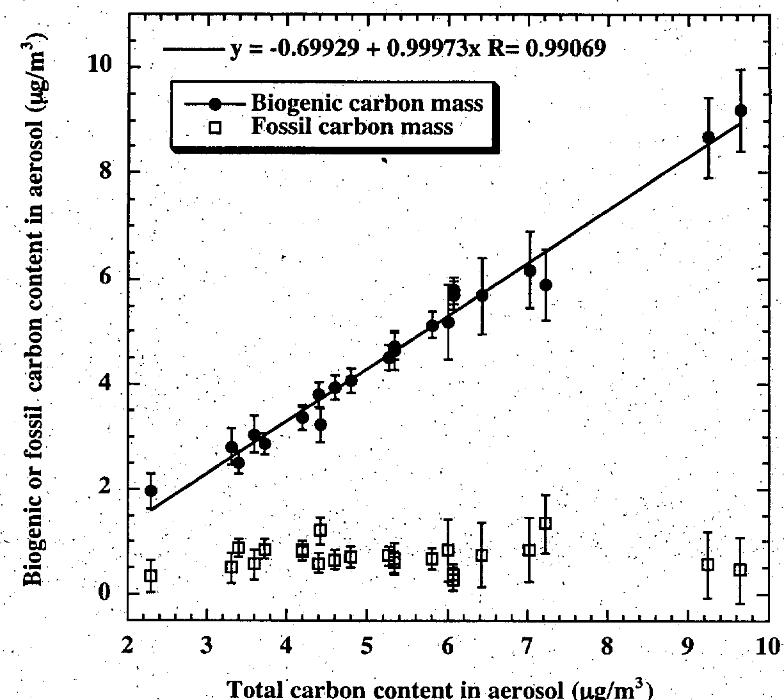


Figure 5. August 20 backtrajectories computed for 3 ending heights in the Central Valley upwind of Yosemite (500, 1000 and 2000 m agl). Major fires locations are denoted by yellow symbols.



Carbon isotope measurements were used to determine relative contributions of fossil vs. biogenic carbon sources. A 2-component model determined the fraction of carbon on each filter derived from biogenic sources, based on the measured $^{14}C/C$ ratio. Results indicate 73 to 95% of the $PM_{2.5}$ carbon was of biogenic origin. Figure 6 depicts variation of biogenic and fossil carbon mass with total $PM_{2.5}$ carbon. Interestingly, the fossil carbon mass concentration varies little; nearly all variability in total carbon mass coming from biogenic carbon concentration changes.

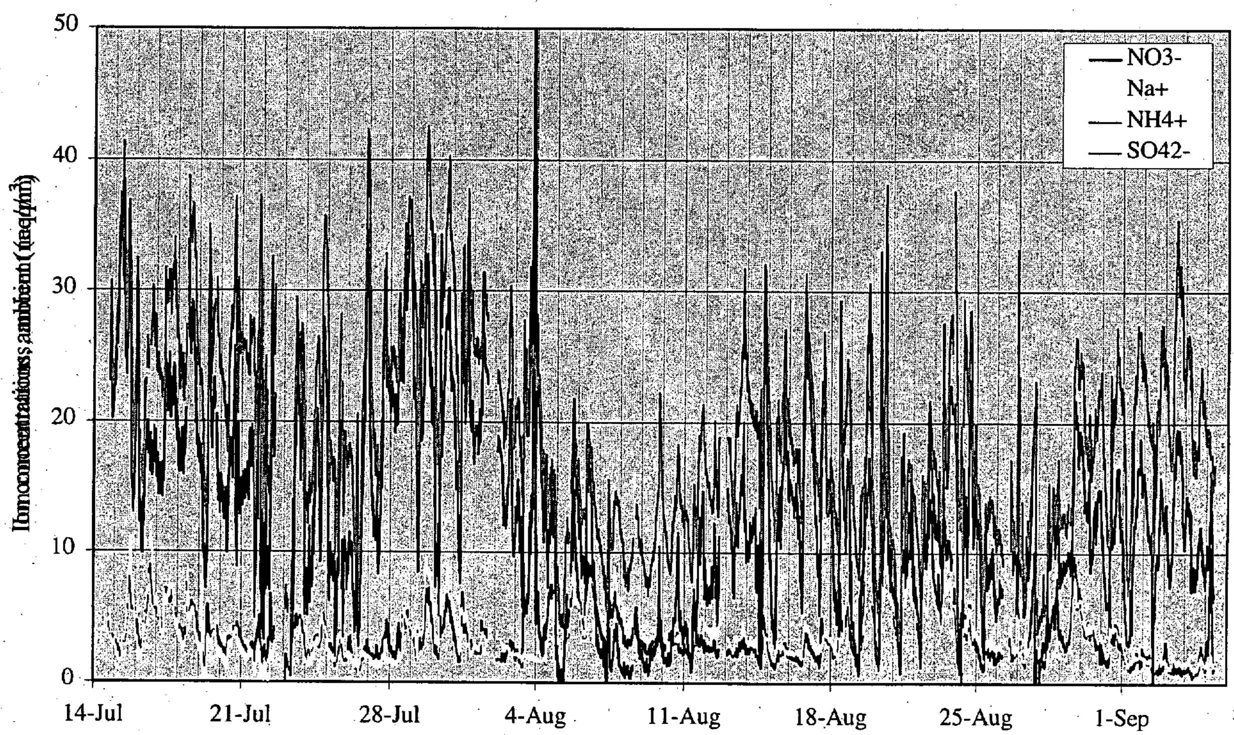
Figure 6. Relationship of biogenic carbon mass and fossil carbon mass to total $PM_{2.5}$ carbon based on carbon isotope measurements.



$PM_{2.5}$ ion concentrations during the study were dominated by sulfate and ammonium. Significant concentrations of nitrate and sodium were also observed. Fig. 7 depicts timelines of the major ion mass concentrations over the course of the study. Concentrations are shown in terms of nanoequivalents (nanomoles multiplied by the absolute value of the ion's charge) per cubic meter, in order to facilitate the comparison of relative concentrations of each species. For example, equal concentrations of ammonium and sulfate on this plot indicate the presence of fully neutralized ammonium sulfate, if these two ions are paired only with each other. Ammonium to sulfate ratios below 1.0 indicate the presence of acidic sulfate. Ammonium bisulfate, for example, would have a ratio of 0.5 in these units.

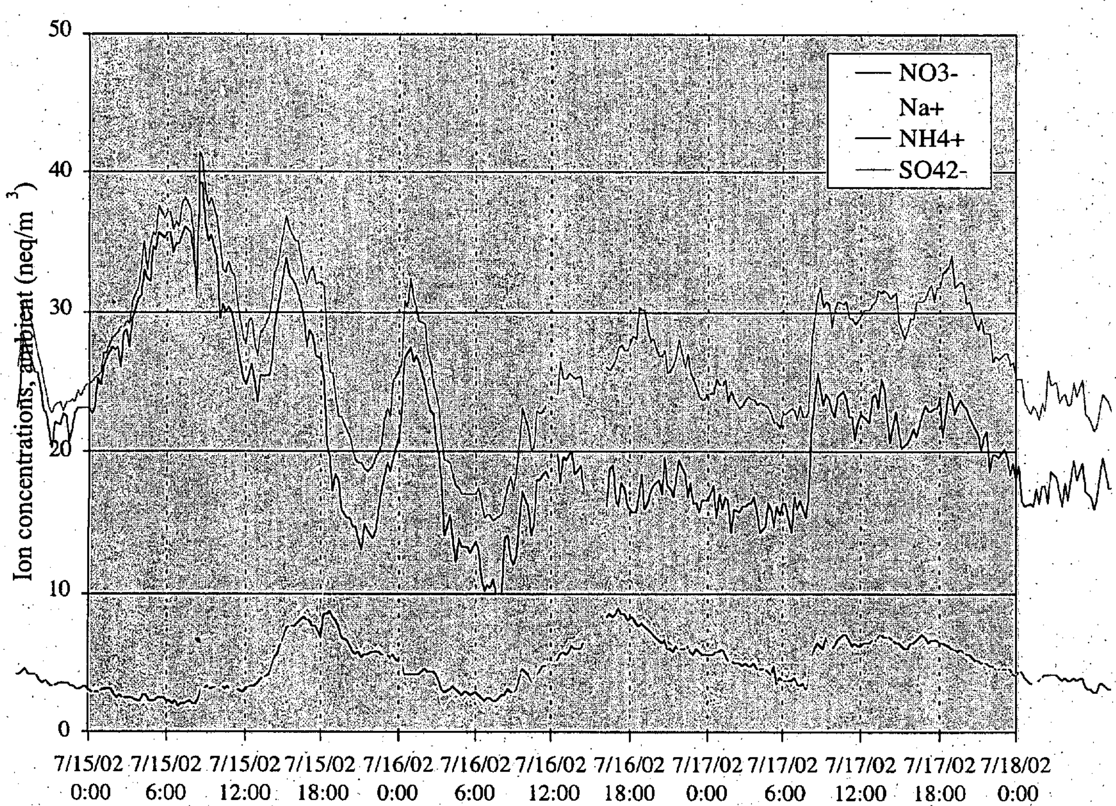
It can be seen that there is insufficient ammonium in the aerosol during most periods to neutralize sulfate, indicating the frequent presence of an acidic fine particle mode. One consequence of the absence of sufficient ammonia to fully neutralize sulfate is that $PM_{2.5}$ nitrate measured at the site was generally present in the form of $NaNO_3$, resulting from reaction of gas phase nitric acid with sea salt particles. Comparison of the timelines of NO_3^- and Na^+ concentrations shows that these two species generally appear together and track each other quite closely. Only when the molar concentration of Na^+ exceeds the molar concentration of NO_3^-, is significant Cl^- present (not shown). The presence of NO_3^- concentrations in excess of Na^+ concentrations occurs during a few periods when sufficient ammonia is present to completely neutralize sulfate and permit ammonium nitrate formation. The occurrence of significant ammonium nitrate concentrations is limited, however, to only a few periods over the course of the study.

Figure 7. Timeline of $PM_{2.5}$ ion concentrations measured using the PILS sampler.



Significant diurnal fluctuations are observed in fine particle mass as well as fine particle concentrations of carbon, sulfate, and nitrate. In general, fine particle mass and carbon concentrations are higher in daytime, consistent with upslope transport of air to the site and suggestive of diurnal patterns in biogenic fine particle carbon sources. Note, however, that all species do not consistently follow this trend. Sulfate concentrations, for example, sometimes peak during the night, possibly reflecting interception at the site of a sulfur plume located above the boundary layer. An example is shown in Figure 8, where a peak in the sulfate concentration at the site was observed during the afternoon followed by another large peak at approximately 2:00 AM. Nitrate concentrations, by contrast, do not increase at this time. Another interesting period is evident at approximately 08:30 AM on the morning of July 17th, when concentrations of sulfate, ammonium, nitrate, and sodium are all seen to climb dramatically, over a time period of just a few minutes, in conjunction with the initiation of upslope flow at the site.

Figure 8. Major $PM_{2.5}$ ion concentrations measured from July 14-17, 2002.



CONCLUSIONS

Semi-continuous measurements of aerosol composition provide considerable additional insight into factors influencing local aerosol composition and visibility degradation than are possible from longer, time-integrated measurements. Close tracking of NO_3^- and Na^+ concentrations, for example, provides strong evidence of the upwind reaction of nitric acid with sea salt. Strong diurnal patterns in fine particle carbon concentrations, combined with results from carbon isotope measurements, suggest an important influence from diurnal biogenic emissions of fine particle carbon and its gas phase precursors. Diurnal concentration trends of many species are also quite clearly tied to changes in atmospheric transport associated with mountain-valley winds. For example, sulfate and other ion concentrations frequently change dramatically over a few minute period in the morning in conjunction with the the initiation of upslope flow at the site.

Future comparison of these semi-continuous aerosol composition measurements with time-integrated composition measurements and study measurements of other aerosol properties, including particle size distributions and hygroscopicity, promise to greatly aid our understanding of factors influencing regional haze and visibility degradation in Yosemite National Park. Application of a suite of similar semi-continuous aerosol measurements is encouraged for other regions in order to better understand factors controlling aerosol composition and fine particle concentrations.

ACKNOWLEDGEMENTS

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