

BEARPEX - Biosphere Effects on AeRosols and Photochemistry Experiment

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I. Overview

The Blodgett Forest 2007/2008 project is designed to study the chemical processes occurring in urban plumes and the chemistry occurring both within and above forests. Our goals are to develop an improved mechanistic understanding of chemical and ecological processes affecting atmospheric composition, and to use this improved understanding to provide a clearer and more accurate evaluation of how chemical processing of biogenic and anthropogenic emissions affects the composition and radiative properties of the atmosphere on urban, regional and global scales. The project is designed around two themes: 1. chemical evolution of urban plumes, day and night, and 2. forest-atmosphere interactions. Within these themes we plan to pay particular attention to three crosscutting issues: a) chemistry downwind of urban areas where there is high VOC reactivity (due to emissions from forests) and low NO_x , b) understanding the full oxidation sequence and subsequent fate of biogenic VOC and c) the processes leading to formation and removal of biogenic secondary organic aerosol (SOA) and the associated chemical and optical properties of SOA.

The following questions are the target of our planned experiments:

1. Chemical evolution of urban plumes

- a. *How well do we understand coupling of HO_x , NO_x , O_3 and VOC photochemistry under conditions of high VOC reactivity and low NO_x ?*
- b. *What happens to NO_x and VOC oxidation products at night? In the nocturnal boundary layer? In the residual layer? How does this chemistry affect NO_x , VOC, O_3 and aerosol production at night and on the following day?*
- c. *What factors affect the time scales for production and removal of 1st, 2nd, 3rd, etc. generation products of biogenic terpenoid (isoprene, monoterpenes, sesquiterpenes, oxyterpenes) oxidation?*
- d. *How do these terpenoid reactions impact the photochemical production and loss of ozone, OH, NO_y species, and aerosols?*

2. Forest-Atmosphere Interactions

- a. *What ecosystem and environmental variables control the biosphere-atmosphere exchange of reduced carbon gases, nitrogen containing gases, and aerosols?*
- b. *What variables control the rate of chemistry and the gradients of these rates within the forest canopy? What are the consequences of within-canopy chemistry for the composition of the boundary layer immediately above and downwind of forests?*
- c. *What is the composition of secondary organic aerosol? Which products of forest emissions are incorporated into such aerosol? How do the climatically related properties of aerosol (scattering, hygroscopicity, etc) vary with its chemical composition?*

In addition to these fundamental questions, these experiments are motivated by some specific, controversial conclusions we have come to based on past observations at the Blodgett Forest site. These include a) a high flux of terpenoid and terpenoid oxidation products out of the forest canopy, b) a large flux of ozone into the forest canopy that can only be explained by chemical loss to reactions with terpenoid compounds, c) calculations of high OH concentrations within the canopy that are a product of these terpenoid + ozone reactions and d) upward fluxes of both HNO₃ and total peroxyoxynitrate compounds as well as downward fluxes inferred for NO_x (based on NO₂ fluxes and calculations of NO flux) that provide evidence that the high OH is present in the canopy removing NO_x and converting it to higher oxides on timescales of less than 10 minutes. All of this evidence leads us to believe that the within-canopy OH is about five times that above the canopy. This is unprecedented and should most certainly be checked by direct observation including observations of OH, independent observations of nitrogen oxides and fluxes and independent observations of terpenoids. At the same time, assuming the conclusions are correct, there are numerous consequences of the high OH, (and high associated RO₂ and HO₂) that should be investigated including the effects on aerosol and O₃ photochemistry.

In defining these goals, we are motivated by the need to improve our understanding of the evolution of urban plumes in downwind regions where the initial emissions have largely been reacted away, where secondary VOC with longer chemical lifetimes have accumulated, and where new emissions from rural forests, grasslands or agriculture have been added (e.g. [Murphy, *et al.*, 2006a] and references therein). Technologies capable of observing a wide suite of the multifunctional secondary VOC that are expected to be produced during these oxidation sequences have only recently begun to be used in field experiments and new technologies are emerging that bring us closer to being able to account for all of the gas and aerosol phase carbon during VOC oxidation [Bartenbach, *et al.*, 2007; Crounse, *et al.*, 2006; Kwan, *et al.*, 2006; Lee, *et al.*, 2006; Slusher, *et al.*, 2004; Warneke, *et al.*, 2001; Williams, *et al.*, 2006]. The effect of ambient levels of nitrogen oxides on the product distribution of VOC oxidation and on aerosol yields has not been studied in as much detail as we require, either in the field or in the lab [Presto, *et al.*, 2005b]. The fate of urban emissions of nitrogen oxides as they are transported to rural and remote regions also remains a subject of discussion because techniques for observing the higher oxides of nitrogen are also difficult to deploy and because rural emissions are not well understood [Day, *et al.*, 2003; Sillman, 1999]. Many of the key chemical transformations are mediated by HO_x radicals in the daytime, NO₃ radicals at night, and by O₃ throughout the day and night. At high NO_x and high VOC mixing ratios characteristic of urban centers that have minor contributions from biogenic VOC to their reactivity, observations indicate that models and HO_x chemistry are largely accurate [Emmerson, *et al.*, 2005; Kovacs, *et al.*, 2003; Ren, *et al.*, 2003] but that there is much to learn about the contributions of NO₃ because of complex vertical structure of the nocturnal boundary layer and the residual layers [Brown, *et al.*, 2006]. However, observations of HO_x at low NO_x and high VOC reactivity characteristic of continental regions outside of the densest centers of cities and even in high NO_x regions with large biogenic VOC sources are much less consistent with models [Emmerson, *et al.*, 2005; Faloon, *et al.*, 2001; Heard, 2006; Martinez, in preparation; Ren, *et al.*, submitted; Tan, *et al.*, 2001; Thornton, *et al.*, 2002] and there are few observations or analyses of the role of NO₃ chemistry in these regions. While there have been some field studies of the effects of O₃ on VOC oxidation rates [Cahill, *et al.*, 2006] and some that included observations of products of ozone oxidation [Holzinger, *et al.*, 2005; Warneke, *et al.*, 2001; Wiedinmyer, *et al.*, 2001] no experiment to date has combined detailed observations of primary emissions and secondary products of ozonolysis in a manner that directly tests current understanding.

We are also motivated by the understanding that exchange of chemicals between the atmosphere and forests are well known to be important to ozone, aerosol and greenhouse gases with direct consequences on regional scales for health of people, animals, agriculture and ecosystems and with implications for managing global climate change [Davidson and Artaxo, 2004; Moorcroft, 2003; Sanderson, et al., 2003; Steiner and Chameides, 2005; Steiner, et al., 2006]. These chemical exchanges are also important to the biogeochemical cycles of carbon and nitrogen providing links between atmospheric chemistry, climate and ecological systems on long time scales [Aber, et al., 1998; Holland, et al., 2005; Ollinger, et al., 2002; Sievering, et al., 2001; Vitousek, et al., 1997]. Recent observations indicate that interactions between forests and the atmosphere are even more important and more complex than we had thought. Two notable examples include recent observations showing that tetrols, 3rd or 4th generation oxidation products of isoprene are found in aerosol all over the world [Cahill, et al., 2006; Claeys, et al., 2004; Henze and Seinfeld, 2006; Pun and Seigneur, 2007], and observations showing that at least some forests emit reactive VOC at rates that can result in significant enhancements of both production and destruction of OH [Di Carlo, et al., 2004; Farmer and Cohen, 2007; Farmer, et al., 2006; Holzinger, et al., 2005; Lamanna and Goldstein, 1999]. Here again, new technological developments are enabling scientists to ask much more sophisticated questions about the oxidation mechanisms of biogenic VOC and NO_x and thus how these emissions interact chemically both near their sources and downwind.

Finally, we are motivated by observations that SOA are ubiquitous in the atmosphere, with potentially important implications for understanding the natural and human influences on clouds and radiative forcing [Henze and Seinfeld, 2006; Kanakidou, et al., 2005; Tunved, et al., 2006]. Current mechanisms for describing SOA formation are clearly inadequate, and there is a growing understanding based on these references and on the global organic carbon balance [de Gouw, et al., 2005; Goldstein and Galbally, 2006; Heald, et al., 2005; Heald, et al., 2006; Volkamer, et al., 2006] that SOA production from VOC oxidation must be much larger than current models predict. A new suite of ideas developed in concert with laboratory and field measurements are needed to understand and describe the formation and atmospheric lifetime of SOA. Different mechanisms are expected to be at work in daytime and nighttime providing important contrasts in a field study.

The experiment we propose is designed to build on the extensive body of knowledge accumulated over the last few years about the chemistry, ecology and atmospheric transport along the western slopes of the Sierra Nevada Mountains in the region between the city of Sacramento and Lake Tahoe. A detailed reference list appears in the appendix of this White paper. Results from many papers are briefly summarized here. The UC-Blodgett Forest Research Station atmospheric chemistry site is situated in the middle of this transect and it provides a unique window into chemical processing of the Sacramento urban plume, and of forest emissions because it is situated in a rural area 4 hours downwind of the suburban edges of the city of Sacramento. As a result of strong orographic forcing, the winds in the region are nearly constant in speed and direction from day to day. During the daytime, air flows upslope from the West. It leaves the city and suburbs loaded with NO_x, aerosol and some anthropogenic VOC, passes over a band of isoprene-emitting oak trees, and then into the foothills where mixed conifer forest dominates the landscape emitting oxygenated VOC (particularly methylbutenol) and mono and sesquiterpenes. At night the flow reverses and returns to the valley. The transport is stronger in summer than winter, but the basic pattern persists year-round. Since 1997 there has been a series of field measurements building understanding of these processes. Recent observations have quantified fluxes and vertical gradients

of terpenes, sesquiterpenes and some oxidation products of these species along with the presence of some of their oxidation products in SOA. Tetrols presumed to result from isoprene oxidation and terpene oxidation products have been observed in the aerosol at the site indicating the biogenic contribution to the aerosol is important.

The geometry, flow and ecological structure at Blodgett Forest all contribute to observable features of the chemistry that we plan to use for testing and expanding current knowledge of mechanistic controls over the composition of gas and aerosol in the atmosphere. These features are described in more detail below. Briefly,

1) regular upslope-downslope flow results in unusual reproducibility for an atmospheric monitoring station [Carroll and Dixon, 2002; Dillon, *et al.*, 2002; Murphy, *et al.*, 2006a]. As a result, a relatively short experiment (~8 weeks), can capture statistics of the effects of variability in some key parameters that are uncorrelated with the winds, including day-of-week variations in NO_x concentrations [Murphy, *et al.*, 2006b; c] and how temperature affects the chemical evolution of the plume and the local photochemistry and emissions at UC-BFRS itself [Day, *et al.*, in preparation].

2) little NO_x is emitted beyond the suburbs, and little isoprene is emitted beyond the oak belt. Thus at UC-BFRS we can study the chemical effects of these emissions downwind, but without the confusing inputs of local sources.

3) ponderosa pine forests are strong emitters of sesquiterpenes, compounds believed to have large aerosol formation potential and also large potential to provide a source of OH following their reaction with O₃ [Bonn and Moortgat, 2003; Goldstein, *et al.*, 2004; Helmig, *et al.*, 2006].

In addition to these motivations, as we noted above, there are controversial observations indicating steep OH gradients within the forest canopy at Blodgett Forest that should be tested by additional independent measurement methods and more detailed analyses than have been completed to date. These include measurements of vertical gradients in presumed very reactive biogenic VOC (VR-BVOC, e.g. sesquiterpene) oxidation products and measurements [Holzinger, *et al.*, 2005] of upward fluxes of HNO₃ [Farmer and Cohen, 2007; Farmer, *et al.*, 2006]. Both are indirect indicators of high OH. Oxidation of sesquiterpenes is presumed to occur by reaction with O₃ producing OH and to result in a chemical flux of ozone into the canopy [Kurpius and Goldstein, 2003]. Calculations of the oxidation rate, and OH yield in combination with an estimate of the OH loss rate were used by Goldstein *et al.* to suggest OH of $0.5\text{-}3 \times 10^7$ molecules/cm³ is the average OH over the 12 m height of the forest canopy [Goldstein, *et al.*, 2004]. Measurements of HNO₃ concentrations and upward fluxes of HNO₃ by [Farmer and Cohen, 2007; Farmer, *et al.*, 2006], have been used to infer that HNO₃ production within the canopy results in a peak in HNO₃ below the canopy top from which fluxes occur both up and down. Using an estimate of the deposition rate and assuming OH+NO₂ is the sole source of HNO₃, they derive an OH concentration of about 5×10^6 above the forest canopy and 3×10^7 within the canopy from the HNO₃ concentration and flux measurements. Upward fluxes of total acyl peroxy nitrates and downward fluxes of total alkyl nitrates are observed. The total acyl peroxy nitrates fluxes imply a similar OH mixing ratio reacts with acetaldehyde within the canopy. The total alkyl nitrate measurements are consistent with the HNO₃ results if the total alkyl nitrates react with OH to produce either HNO₃ or NO₂ with a 20% yield (the 80% balance producing multifunctional nitrates). The 20% yield is lower than values used in some current models but there is very limited data from laboratory measurements and no analyses of field data that provide unambiguous evidence for or against such a value.

II. Experiment Outline and Participants:

The BEARPEX 2007/2008 project will bring together a team of researchers with common interests in the above questions and with established capabilities for observing a wide suite of trace gases and aerosol properties, it will also serve as a venue for testing some new ideas for instrumentation that are targeted at the conditions and issues that are the focus of this project. Measurements are required that have capabilities for 1) verifying some of the unusual aspects of the chemistry that have been reported (but greeted with skepticism) at the site—including inferences of high within-canopy OH that cause upward fluxes of Σ PNs and HNO_3 , and reports of steep gradients in the oxidation products of sesquiterpenes that are the presumed source of this OH, 2) for observing a much wider range of VOC and VOC oxidation products than have been studied before, 3) for observing gradients of as many VOC and nitrogen oxides as possible so that the carbon and nitrogen balance at the site can be assessed and 4) for studying the physical, chemical and optical properties, and composition of aerosol over a wide size range.

Measurements proposed include a very broad array of HO_x , NO_x , VOC, and aerosol properties, with many groups interested in measuring both concentrations and fluxes. Each measurement phase will be approximately 6-8 weeks long to insure that we take full advantage of chemical changes induced by the 35% weekend/weekday changes in NO_x and gather statistics on the effect of variations in NO_x on the chemistry. Measurements during 2007 will begin late in mid-August to accommodate key participants who are also planning to participate in the NASA TC-4 project. Measurements in 2008 will begin earlier in the season and will build on what we learn in 2007.

Participants will submit their data to a common archive maintained at UC-Berkeley and will join in pre- and post-mission workshops to discuss the observations and encourage collaborative writing of manuscripts. A significant site upgrade is required to support the suite of measurements. We plan to add a large platform scaffolding tower and to install a new high-powered generator with the latest particle filtration and NO_x removal technology. A subset of instruments will be located on one or more platforms that can be raised beyond the canopy top for measuring vertical gradients. Participants will be charged an infrastructure fee of \$7000 for the first year of their participation and \$3500 for the second year. A workshop soon after the 2007 campaign will be held to set dates for the 2008 experiment.

Key measurements planned include:

PI (alphabetical order)	Measurement Purpose (questions)
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Atlas	Multifunctional organic nitrates 1A,B, D
Baker/Guenther	Vertical profiles of T, O_3 , humidity, etc using tethered balloon 1A,B
Brune	OH, HO_2 , RO_2 concentrations and gradients 1A,B,C,D; 2A,B
Brune	OH reactivity 1A,B,C,D; 2A,B

Brune	Potential aerosol 2C
Brune	Eppley radiometer 1A,B,C,D; 2A,B
Cohen gradients	NO, NO ₂ , ΣPN, ΣAN, HNO ₃ , and NO _y concentrations, fluxes, and 1A,B,C,D; 2A,B
Cohen	NO ₃ and N ₂ O ₅ concentrations 1A,B,C,D; 2A,B
Cohen	HONO concentrations and fluxes 1A,B,C,D, 2A,B
Chuang	Cloud condensation nuclei 2C
DeGouw GC)	*VOC concentrations, vertical gradients (PTR-IonTrap-MS, PTRMS, 1A,B,C,D; 2A,B; 3
Faloona	H ₂ CO—midIR 1A,B,C,D; 2A,B
Goldstein	O ₃ concentrations, fluxes, and gradients 1A,B,C,D; 2A,B; 3
Goldstein Eddy	*VOC concentrations, fluxes, and gradients (PTRMS, GC, PTRMS- Covariance) 1A,B,C,D; 2A,B; 3
Goldstein/Hering	*Organic aerosol speciation (TAG – new in-situ hourly instrument) 1B,C, D; 2B,C
Keutsch	Glyoxal and H ₂ CO—UV/Vis LIF 1A,B,C,D, 2A,B
Nemitz/Jimenez	* Size-resolved composition and chemically-resolved aerosol fluxes 1B,C, D; 2B,C
Thornton	*Acyl peroxy nitrates concentrations, fluxes, gradients 1A,B,C,D; 2A,B
Vong/Covert	Particle size and number fluxes, hygroscopic growth effects on particle fluxes 1C,D; 2A,C

Tentative additions for 2008

Abbatt/Leitch	*Size dependent composition (AMS) 1B,C, D; 2B,C
Wennberg	*Organic peroxides, HNO ₃ fluxes 1A,B,C,D; 2A,B

*Note on VOC/peroxy/peroxide/organic aerosol measurements: This group of measurements provides unique and greatly expanded observational capabilities through application of multiple new chemical ionization mass spectrometry techniques (PTR-MS, PTR-IT-MS, PTR-LIT, triple Quad, various types of negative ionization techniques) and aerosol measurement techniques, bringing together significant new capabilities for observing isoprene and terpene oxidation products as well as products of the reactions that terminate the HO_x and NO_x free radical chains (organic peroxides, HNO₃).

III. Background

III.a Transport and source gases from upwind

The major circulation patterns in the San Francisco Bay and Sacramento regions begin with air from the West entering through the gap in the coast range at the mouth of the San Francisco Bay. The flow continues along the northern arm of the Bay entering the Central Valley over the Sacramento delta (shown in Figure 1a) or flows south and crosses through the gaps in the East Bay hills leading through the Livermore Valley on its way into the Central Valley, as seen in Figure 1. Air in the Central Valley flows both north into the Sacramento valley and south to the San Joaquin Valley. This flow pattern is coupled to the orographic forcing of the mountain-valley system which drives a strong and regular pattern of daytime upslope and nighttime downslope flow as shown in Figure 1a [Hayes, *et al.*, 1984; Zaremba and Carroll, 1999]. The pattern in the flow persists year-round although the strength of the Mountain-Valley circulation and the extent to which it progresses upslope decrease in winter [Dillon, *et al.*, 2002; Murphy, *et al.*, 2006a].

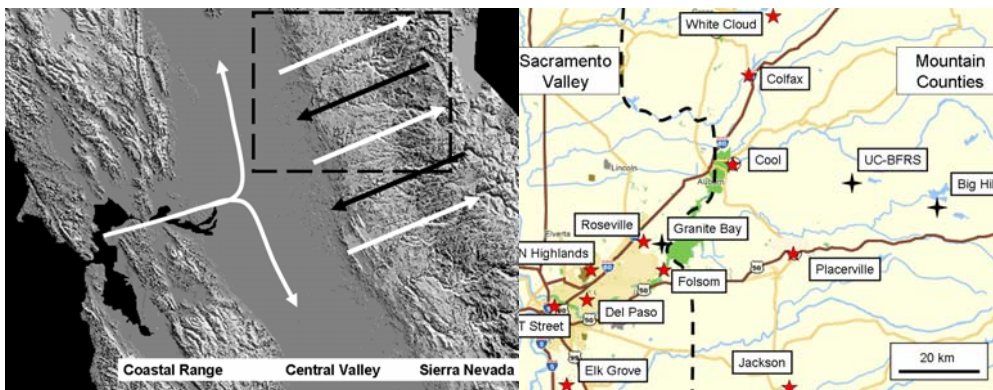


Figure 1. (a) Typical flow pattern for air entering California in the San Francisco region. (b) The location of the monitoring sites in the Sacramento Valley and Mountain Counties (separated by the dashed line) used in this analysis. The darker shaded area represents to Sacramento municipal area, and the green area to its Northeast is a California State Park. Routine monitoring sites maintained by CARB are denoted with (★) and sites where experiments have been conducted by UC Berkeley researchers are marked with (✦).

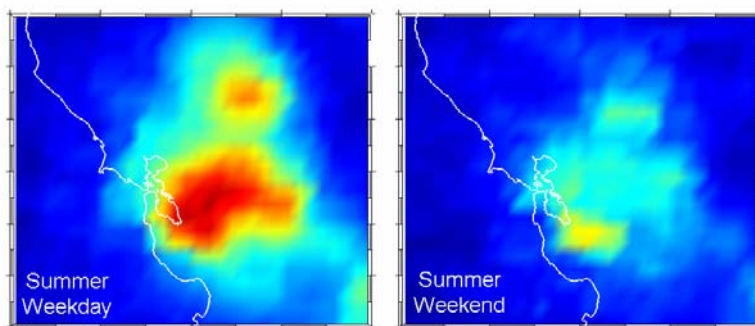


Figure 2 Column average NO₂ densities (SCIAMACHY) in the San Francisco area during the summer (a) weekdays and (b) weekends.

Despite the direct flow path from the San Francisco area, Sacramento is a well-separated area source. As the column average NO₂ measurements (SCIAMACHY) shown in Figure 2 demonstrate

the branch of the flow leaving the Bay area via the northern route is relatively clean compared to the flow exiting to the South. For the purposes of this experiment the clear separation between the SF Bay Area and Sacramento to the Northeast is an advantage because it allows us to think of Sacramento as a relatively isolated area source—a so-called “island city.”

The Sacramento region and its downwind neighbors in the Mountain Counties are in frequent violation of ambient air quality standards for ozone. After improvements in air quality observed in the late 1980’s, air quality in the Sacramento and Mountain counties districts has not improved (Figure 3a). The record in the Mountain Counties begins in 1992 and shows no signs of change.

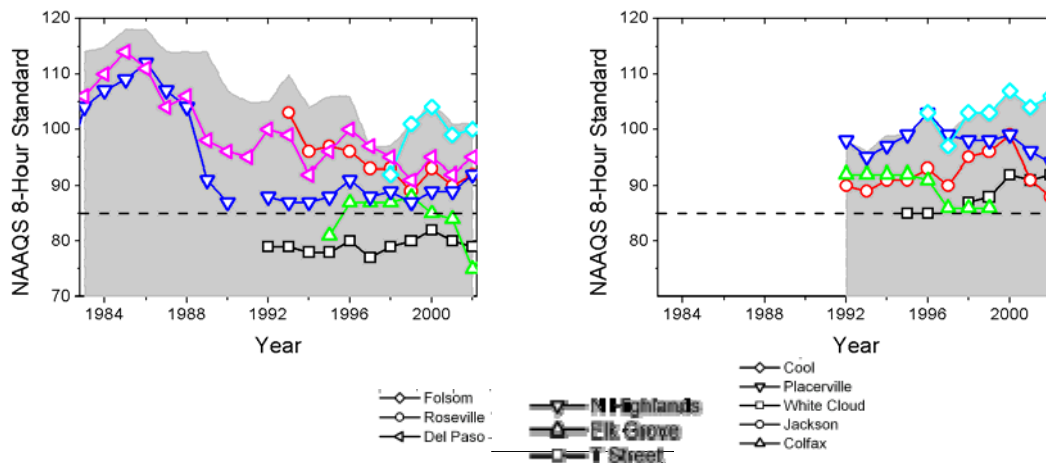


Figure 3 8-h maximum air quality statistic (3 year average of 4th highest value) for the individual sites in (a) the Sacramento Valley and (b) the Mountain Counties. The top of the grey area is the basin-wide statistic of the 4th highest values calculated by finding the highest 8-h maximum each day from any site in the basin.

The UC-BFRS site we propose to use for these experiments sits in the foothills of the Sierra Nevada 1300 m above sea level. During the day the site is 5 hours downwind of the eastern edge of suburban Sacramento, California and at night cleaner air from the high Sierra descends past the site in the downslope flow [Murphy, et al., 2006a]. Although modeling and understanding the detailed patterns of flow over complex terrain is difficult, many aspects of the flow patterns in the region are well understood. Surface flows which as noted above are almost always from the west during daytime and from the East at night, are coupled to flows aloft. During the day, there is a recirculating flow moving back toward Sacramento aloft [Carroll and Dixon, 2002]. This flow serves to reduce the height of the boundary layer in the region to less than 1 km. This capping of the boundary layer height is also reinforced by prevailing flows from the west. As a result boundary layer heights are almost always less than 1 km [Dillon, et al., 2002].

The source regions sampled by observations at the UC-BFRS site reflect this transport pattern. During the daytime the city of Sacramento represents a large area source, there are few anthropogenic emissions downwind of the suburbs along the line between Folsom and Auburn. Thus air arrives at UC-BFRS having processed the urban emissions for almost 5 hours with negligible additional anthropogenic input. There are significant biogenic inputs. After passing over the suburbs, air then passes over a narrow (15 km) band of oak trees that lie perpendicular to the

flow. These oak trees are strong emitters of isoprene. Since the flow is almost always perpendicular to this band, isoprene arrives at the UC-BFRS site well after emission and almost always with the same transit time since emission. After passing over the oak band, the flow traverses foothills, which are primarily covered in pine trees that do not emit isoprene, but instead emit alcohols including methyl butenol, monoterpenes, and sesquiterpenes. As a result, the site offers a unique opportunity to study the downwind consequences of isoprene emission. Except for some aircraft profiles over the ocean, measurements at UC-BFRS are the only ones that have observed isoprene oxidation without being located in a region of isoprene emissions. The displacement from the source region is advantageous for studying the chemistry, the fact that the transit time is nominally independent of temperature means that among other things, the temperature dependence of the isoprene chemistry can be separated from the emission rate.

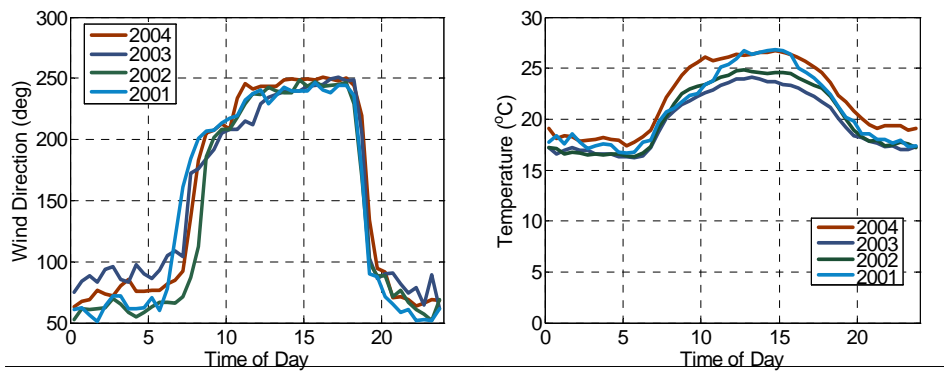


Figure 4 Median diurnal (a) wind direction and (b) temperature during August at Blodgett forest.

The Sacramento urban plume moves into the foothills and mixes both laterally and vertically. Observations 2 hours downwind of UC-BFRS at Big Hill indicate that much of the mixing at that site is vertical. In particular, simple mixing lines of $\text{NO}_{y,i}$ (Figure 5) and water and an increase of HNO_3 at low water observed at the Big Hill site provide evidence for mixing of an urban source with air characteristic of the free troposphere [Murphy, *et al.*, 2006a]. The apparent mixing time ($1/e$) is approximately 4 hours, implying considerable input of boundary layer material into the free troposphere and/or rapid horizontal spread of the urban plume, but also setting the timescale over which chemical processes must act in order to have a substantial effect within the PBL.

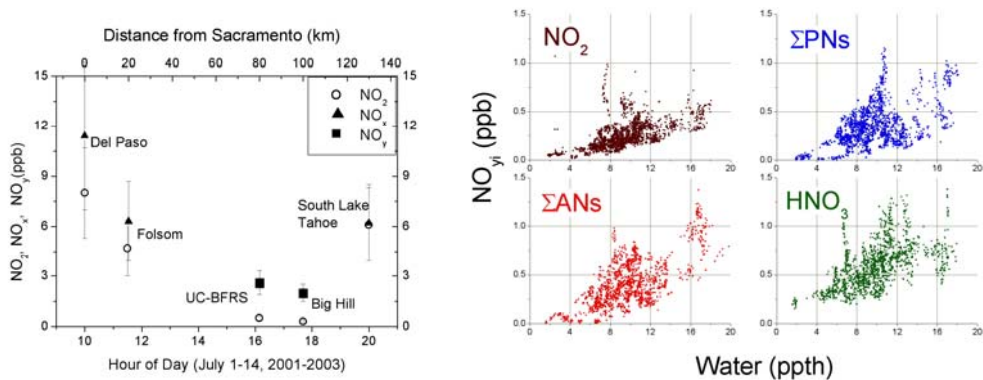


Figure 5 (a) Evolution of the mixing ratios of NO_2 , NO_x , and NO_y during transport of the Sacramento plume. These values are the mean obtained over a two week time period in July 2001-2003. (b) Mixing ratio of several NO_y compounds as a function of water mixing ratios.

Observations at these sites have also established that the strong day-of-week patterns in NO_x emissions in the city of Sacramento have a clear impact on the chemistry at UC-BFRS. This pattern is felt differently by species of differing lifetimes (hours versus minutes). At a site well downwind of the Sacramento NO_x source such as UC-BFRS, one expects OH concentrations that are approximately linear in NO_x [Murphy, *et al.*, 2006a]. Locally then, when NO_x is higher as it is on weekdays (compared to weekends), we expect higher concentrations of OH and lower concentrations of any chemical species whose atmospheric lifetime is controlled by OH and whose lifetime is less than an hour or two. Consistent with this idea isoprene is observed to have higher concentrations on the weekend than it does on weekdays at UC-BFRS because, lower NO_x results in lower OH on weekends and thus a longer lifetime for isoprene (Figure 6). Compounds that have longer chemical lifetimes have their concentrations controlled both by chemistry and transport and can be much more strongly affected by upwind chemistry. For example, both O_3 and HNO_3 have both local and non-local sources that must be taken into account to explain their day-of-week patterns at UC-BFRS. Effects of multi-day accumulation in the region are seen in the increase of long-lived VOC from Monday to Friday followed by a decrease on Saturday and again on Sunday (Figure 6).

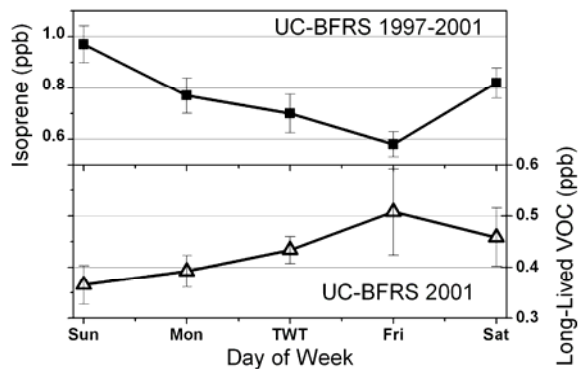


Figure 6. Speciated VOC observations sorted by day of week from UC-BFRS between 12:00 and 20:00. The top panel shows measurements of isoprene made at UC-BFRS from the summers of 1997-2001. The bottom panel shows UC-BFRS measurements in 2001 of long-lived anthropogenic VOC (benzene + butane + isobutene + pentane + isopentane).

III.b Chemical composition at UC-BFRS

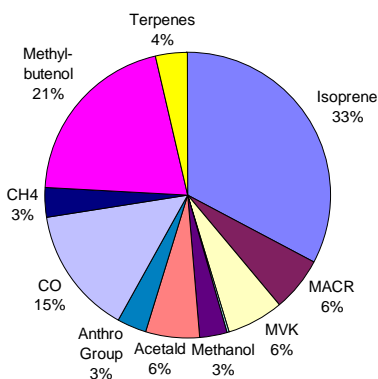


Figure 7 Typical composition VOCs contributing to OH reactivity based on 1997 measurements

The mix of upwind transport and source gas influences, described above, combine with local forest emissions to establish the chemical environment at UC-BFRS. In the summer, the typical mix of VOC contributing to OH reactivity as described by available technology in 1997 is given (Figure 7) [Lamanna and Goldstein, 1999]. Numerous additional VOC have since been observed at the site raising the importance of known biogenic species to the observed reactivity but also providing a strong indication that secondary VOC are abundant in the atmosphere and still poorly characterized. There are longterm records of NO_{yi} , O_3 , numerous VOC and CO (e.g. Figure 8a,b,) that provide a basis for thinking about processes on annual, seasonal, and diurnal time scales.

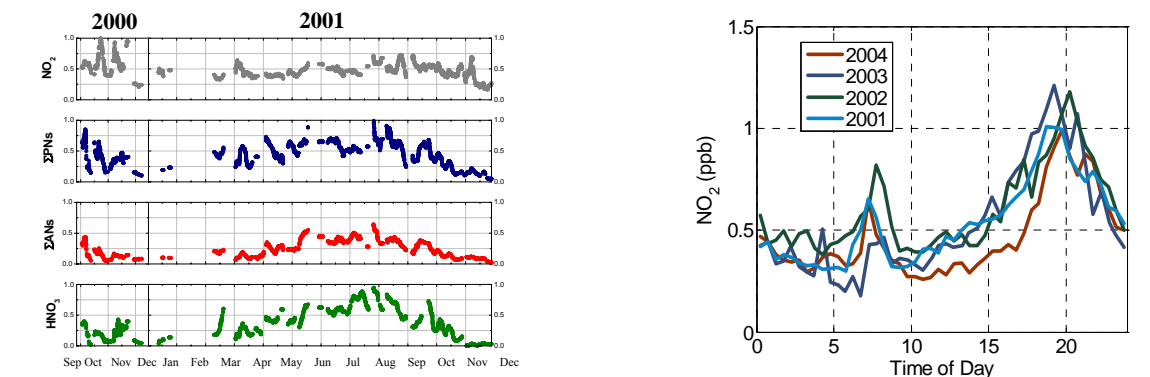


Figure 8 (a) Average daily mixing ratio (ppb) of NO_2 , ΣPNs , ΣANs , and HNO_3 as observed at Blodgett from September 2000 until December 2001. (b) Median diurnal NO_2 mixing ratio during August at Blodgett forest.

A correlation between O_3 and isoprene oxidation has been established (Figure 9a) [Dreyfus, *et al.*, 2002] this correlation is associated with the temperature dependence of the reactivity of OH calculated from observed VOC (Figure 9b) . Temperature has also been shown to affect the partitioning of NO_{yi} species (Figure 9c).

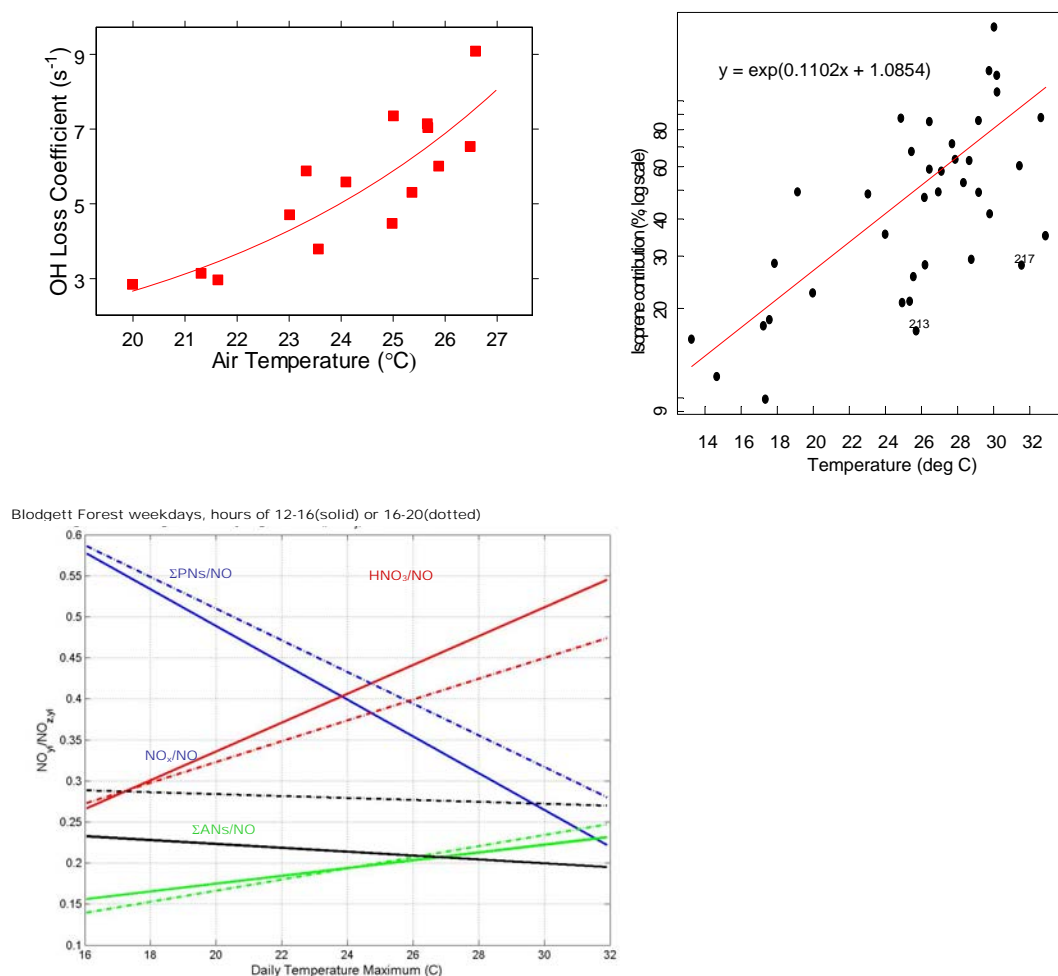


Figure 9 (a) OH loss coefficient as a function of air temperature. (b) Isoprene oxidation as a function of air temperature. (c) Affect of temperature on the portioning of NO_y species during the weekday at Blodgett forest. Note that the solid lines represent hours 12-16 and the dashed lines represent hours 16-20.

Analyses of the daytime patterns in concentration have been used to infer average OH concentrations during advection from Sacramento of about 1×10^7 molecules/cm³ and to infer local OH concentrations above the forest canopy of 5×10^6 at noon. There have been few analyses of the role of nighttime chemistry. Effects of nighttime chemistry are reflected most clearly during the early morning mixing events as the nocturnal boundary and residual layers mix. During this period we observe an increase in NO₂—presumably because there was significant loss of NO₂ in the nocturnal boundary layer relative to the layer above it. Calculations suggest that there are significant NO_x losses due to reaction of biogenic VOC with NO₃, and observations of N₂O₅ during summer and fall 2006 show that NO₃ just above the forest reacts away essentially immediately upon formation [Minejima and Cohen, in preparation]. However the fate of the reaction products of the reactions of NO₃ with biogenics is unclear because the identity of the chemical products and the deposition rate of those organic nitrate reaction products are not well known. Some of these processes are also thought to be important for SOA formation.

III.c Chemistry driven by biospheric emissions at UC-BFRS

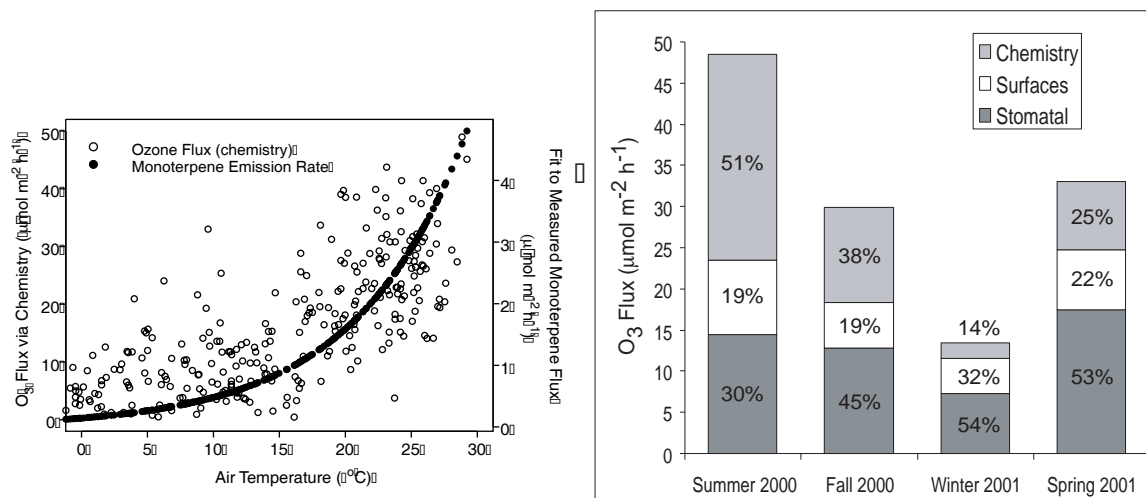


Figure 10 (a) Ozone flux and monoterpene emission rate as functions of air temperature. (b) Contribution of chemistry, surfaces, and stomatal processes on the observed ozone flux in Blodgett by season.

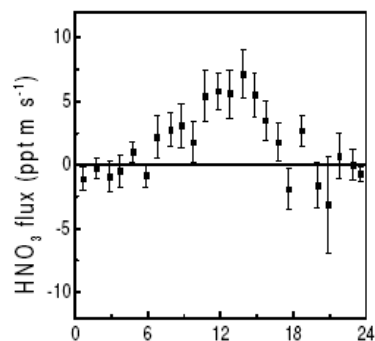
The consequences of biogenic emissions for atmospheric chemistry are manifold. Locally within the UC-BFRS forest canopy emissions have been shown to be a strong sink of ozone (Figure 10). Observations of ozone fluxes have been analyzed to derive a chemical flux term which has been compared to emission rates of monoterpenes and sesquiterpenes and which is shown to vary in proportion to physical factors that control these terpenoid emission rates.

Calculations based on the rate of terpene reactions with O₃ indicate that terpenes should be short-lived with lifetimes of order minutes. Observations of vertical profiles of terpenes are consistent with the idea of rapid removal by reaction with O₃ and products of terpene oxidation have been observed to occur higher in the canopy than the primary emissions.

If the terpene reactions with O₃ are assumed to have near unity OH yields then calculations give a very large non-photochemical OH production rate ($\sim 2 \times 10^8$ molecules/cm³/s) within the canopy, much larger than has been calculated for other canopies (e.g. [Stroud, *et al.*, 2005]) presumably because of the larger emissions of terpenes in this forest. Assuming that the OH loss frequency is ~ 10 s⁻¹ this results in an estimate of the OH concentration of order 2×10^7 molecules/cm³. Observations of upward HNO₃ fluxes are consistent with the presence of high OH assuming that the within-canopy OH is sufficient to react with ambient NO₂ producing a peak in the HNO₃ mixing ratio below the canopy top (Figure 11). Simultaneous flux observations of other NO_y species are consistent with this conclusion, however, the consistency requires making a number of assumptions that can only be verified and examined more fully with new observations. These include the assumption that the reaction of ΣANs with OH produces HNO₃ or NO₂ with a 20% yield [Farmer and Cohen, 2007] and that processes within the canopy such as the mechanisms that have been suggested for producing HONO in forest canopies [Kleffmann, *et al.*, 2005; Zhou, *et al.*, 2002] result in emissions of NO_x from the UC-BFRS canopy that are about double those due to soil NO_x

emissions. It should be noted that the total NO_y flux at the UC-BFRS canopy is not unusual. These observations are the only simultaneous flux measurements of a wide suite of NO_{yi} species and they indicate that the total fluxes observed elsewhere may have much more complicated explanations than is widely assumed.

(a)



(b)

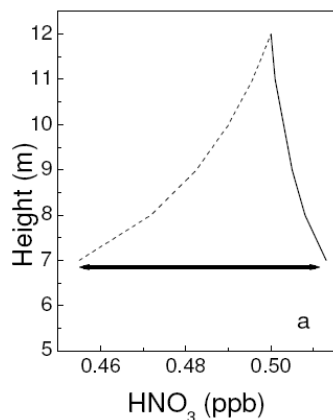


Figure 11 (a) Net daytime flux (ppt m s^{-1}) of HNO_3 upward out of the canopy. Averaged over August 2005. (b) Calculations using the corrected Monin-Obukhov theory for the midday summer gradient HNO_3 required to produce observed flux (solid) and calculation of the deposition fluxes (dashed). Horizontal arrow represents the implied within canopy chemical source of HNO_3 .

III.d SOA composition and production

A further consequence of biogenic emissions at UC-BFRS, and directly linked to the observed ozone chemistry within the forest canopy, is the production of SOA, a potentially important, but poorly understood contributor to climate change. Ozonolysis of monoterpenes leading to aerosol formation is well-documented from lab-based chamber experiments [Glasius, *et al.*, 2000; Griffin, *et al.*, 1999; Hoffmann, *et al.*, 1997; Iinuma, *et al.*, 2004; Koch, *et al.*, 2000; Presto, *et al.*, 2005a; b]. More recently, unknown biogenic VOC oxidation products, detected at UC-BFRS using a PTR-MS, were also observed during smog chamber experiments investigating the ozonolysis of a series of mono- and sesqui-terpenes [Lee, *et al.*, 2006]. Further, these product yields were found to mirror measurements of aerosol yield over the course of the reaction. The importance of these reactions

occurring at UC-BFRS and contributing to regional SOA levels is thought to be significant, with oxygenated BVOCs comprising about 8.6% of the total organic particulate matter (PM₁₀) [Cahill, *et al.*, 2006].

In addition to ozone, NO₃ and OH radicals are also thought to play significant roles in the oxidation of BVOCs, likely influencing the volatility of reaction products and subsequent partitioning into the particle phase. Although no direct measurements of OH or NO₃ have been made at UC-BFRS, there is ample indirect evidence to suggest that their chemistry is significant in SOA formation at the forest. OH radicals, for example, can react with alkanes in the presence of NO_x to form hydroxy alkyl nitrates, which are significantly lower in volatility than the corresponding alkyl nitrates [Lim and Ziemann, 2005]. Evidence has also been found indicating that there is significant OH reactivity with biogenic emissions at a forest site in northern Michigan [Di Carlo, *et al.*, 2004]. Elevated OH levels, as mentioned previously, have been inferred both from the observed nitric acid flux out of the canopy as well as ozone chemical flux and terpenoid reactivity within the canopy. Meanwhile, NO₃ is expected to be a significant nighttime oxidant, and chamber-based studies have shown that reactions with monoterpenes (e.g. [Spittler, *et al.*, 2006] and references therein) and linear alkenes [Gong, *et al.*, 2005] can form condensable products leading to SOA. Many questions surround its atmospheric availability for reaction with BVOCs, however, and more field observations are required.

Concurrently, the role that NO_x plays in the cycling of these three oxidants also becomes important for SOA and will be an important set of observations in studying the anthropogenic effects on SOA formation at remote forest locations. Further, NO_x may play a significant role in controlling the branching reactions in the oxidation sequence of BVOCs. These branching reactions control the extent to which acids, aldehydes, ketones, peroxides, organic nitrates, nitric acid and multifunctional organics are produced, products which span a wide range of volatilities and, as a consequence, have implications on aerosol formation and growth rates. Direct evidence of the role of NO_x in SOA formation exists as one recent lab-based chamber experiment found that the nature of oligomeric isoprene photo-oxidation products were strongly reliant upon initial NO_x concentrations [Surratt, *et al.*, 2006].

While many of the associated precursors to SOA formation have been observed (i.e. O₃, BVOCs, oxygenated BVOCs) or inferred from observations (i.e. OH and NO₃) at UC-BFRS, many additional physical, meteorological, and chemical variables play an important role in this process. To date, only one study [Lunden, *et al.*, 2006] has focused specifically on tying all of these variables together to study SOA at the UC-BFRS site. In this study, direct observations of fine particle growth events were seen on a number of days during the summer of 2002, and, as expected, a strong link to ozone-VOC chemistry within the canopy was suggested. Ambient temperature, wind speed and direction, and relative humidity were some of the meteorological variables studied, and it was concluded that lower temperatures and increased mixing in the atmosphere lead to higher growth rates. There was also found to be a significant anthropogenic influence, as high background particle concentrations arriving from Sacramento were thought to increase the surface area on which oxygenated products could condense, consequently inhibiting new particle growth. The predominant mechanisms for particle formation and growth, however, remain an enormous uncertainty that has significant consequences on SOA production and composition.

Although there is a growing knowledge base in this area, the importance of the results thus far cannot be fully assessed without better time resolution and increased capabilities for investigating factors controlling their production, partitioning, and fate. The purpose of this campaign at UC-BFRS as it pertains to SOA is to determine the composition of SOA and the factors that govern its formation. Further, and what is a central theme to the campaign, the goals are to study the anthropogenic influence on SOA at a remote forest site. Again, UC-BFRS is ideally located in this respect as the diurnal and day-of-week patterns for air transport from urban Sacramento has been well characterized and is relatively consistent during the summer months.

IV. Expected Outcomes

Observations at UC-BFRS continue to yield surprises and we expect this campaign to uncover some more. Nonetheless, some of the outcomes of this project are predictable and we highlight these below.

- 1) Direct observations of OH and HO₂ above and within the canopy will provide evidence for or against the suggestions that within canopy OH is exceptionally high.
- 2) H₂CO and Glyoxal measurements will provide important constraints on the sources of OH and be used to understand oxidation within the canopy and in the urban plume.
- 3) Comprehensive VOC measurements will improve our understanding of biogenic emissions, reactivity of the urban plume, and the availability of SOA precursors.
- 4) NO and HONO measurements will directly test models of their role in the nitrogen budget. Direct measurements of the concentration and fluxes of specific PAN compounds will provide a comparison to the TD-LIF total flux, insight into the extent to which there are unusual PAN analogues in the atmosphere at this location and an interesting test of within canopy chemistry.
- 5) Aerosol composition and flux measurements will provide direct tests of mechanisms describing formation, chemical and physical evolution and residence time of SOA
- 6) Observations of organic nitrates by Atlas will provide comparison for the controversial SAN measurements by Cohen et al. and will provide unique indicators for the role of these species in chemical production of SOA.
- 7) Weekend/weekday variations in all of the different species we observe will provide a unique test of our understanding of mechanisms of atmospheric chemistry and transport

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