

6. Air Pollution Transport

6.1 Background

Air parcels containing pollutants move through the atmosphere as winds and general weather patterns distribute them. The pollutants may detectably persist a short distance or, given certain meteorological regimes, occasionally cross continents and oceans. The impact of the pollutant transport depends on the magnitude and rate of emissions from sources (i.e., source strength) and any additional pollutant input during transport. The impact of the pollutant transport also depends on the meteorological variables that control deposition, transformation, and dissipation within the air parcel, the movement to other locations, and, in the case of transport above the surface layer, the downward mixing to the earth's surface at the receptor location.

Transported air parcels that encounter clouds have their pollutant load subject to additional chemical transformations interacting with droplets within clouds and physical transformation as soluble gases dissolve in the droplet or particles absorb water to create larger particles. Air pollution transport is a most complex phenomenon.

The focus of LTADS was primarily on quantifying direct dry deposition of nitrogenous compounds, phosphorus, and particulate matter to Lake Tahoe and on better characterizing the pollutant sources. As part of that characterization, the transport of nitrogen oxides into the Sierra Nevada, which serves as an upper limit of transport to the Tahoe Basin, received the greatest attention. Potential particulate matter transport to the Tahoe Basin is addressed tangentially in this report via discussion of atmospheric processes as they constrain PM transport and related PM studies. For example, the transport of Asian dust is discussed in Appendix B (Analysis of Historical Aerosol Data). This chapter attempts to characterize the various atmospheric processes influencing the potential transport of pollutants, such as reactive oxides of nitrogen, particulate matter, and ozone, to the Tahoe Basin. A formal, quantitative analysis of the transport of air pollutants to the Tahoe Basin is beyond the purview of LTADS personnel and is left to future investigators.

As noted earlier, phosphorus is found in the atmosphere in very low concentrations and measurements of phosphorus usually encounter analytical difficulties. The phosphorus data collected in LTADS did not provide the measurement sensitivity (low concentrations and short measurement period) sufficient to address potential phosphorus transport to the Tahoe Basin. The study of phosphorus transport to the Tahoe Basin will remain in the theoretical arena until better measurement methodologies are developed and self absorption correction factors are refined for XRF analysis of PM larger than 2.5 μ m. These are fundamental challenges that will limit any analyses of phosphorus transport in the near future.

Reactive nitrogen species, such as nitric acid and organic nitrates, potentially part of the Sacramento plume that may reach the Tahoe Basin, were targeted for study (Cohen and Murphy, 2005). Although ammonia measurements were made with the network of Two-Week-Samplers and with an annular denuder on the aircraft, the results were less

definitive than desired because of high blank values. Although natural sources of ammonia exist (e.g., animals, soil microbes), it is likely that the prodigious emissions of ammonia from agricultural and livestock operations in the Central Valley overwhelm other sources. However, a study of potential ammonia transport (particularly aloft as transformation and deposition likely significant in surface layer) to the Tahoe Basin is left to future investigators due to the limited measurements of ammonia aloft and characterization of natural and anthropogenic sources. The bulk of this chapter investigates potential reactive nitrogen species transport to the Tahoe Basin and is primarily excerpts from the Cohen and Murphy final report.

The Tahoe Basin is located to the east-northeast of the San Francisco Bay Area and the Sacramento metropolitan region. Because the synoptic winds at this latitude are typically westerly (i.e., from the west), there is the potential for polluted air to be transported from these areas to the Tahoe Basin. However, the impact of transported pollutants is not solely a function of the amount of emissions from upwind areas. Emissions undergo chemical reactions, diffusion, dispersion, and deposition after being released. Thus, ambient concentrations of primary (directly emitted) pollutants generally decline with time and distance transported from the source. Furthermore, the concentrations of secondary pollutants also eventually decrease due to dispersion, deposition, and chemical reaction.

Meteorological conditions strongly influence the ambient concentrations of pollutants resulting from their emission, transformation, advection, and deposition. Ambient temperatures influence emission rates (biogenic and evaporation), chemical reaction rates, winds, and vertical mixing of the atmosphere. Wind direction and speed, as well as vertical mixing, primarily determine the dispersion and ultimately the ambient concentrations resulting from the emissions. Lastly, the Sierra Nevada mountain range acts as a barrier to reduce the potential impact of transported emissions and reaction products from the Central Valley. Emissions from upwind areas such as San Francisco and Sacramento are diluted during transport, which takes many hours. For example, pollutants emitted in Sacramento into a 10 mph surface wind would take about 10 hours to traverse the distance to Lake Tahoe. However, wind speeds of this magnitude and faster typically cause low pollutant concentrations.

The scenarios potentially transporting pollutants from the Central Valley to Lake Tahoe involve one-day surface transport during summer, multi-day surface transport, and pollutants transported in winds above the surface layer. Most commonly, the pollutants from the upwind regions act to raise regional background concentrations entering the Tahoe Basin rather than directly causing exceedances (e.g., of the State 1-hour ozone air quality standard - not to exceed 0.09 ppm) in the Tahoe Basin (Carroll et al., 1998; Carroll et al., 2000). The relatively low ambient pollutant concentrations, combined with the complex topography and low spatial density of meteorological and air quality monitoring locations in the Tahoe region, make evaluations of transport difficult. Data from infrequent aircraft flights to sample air quality aloft in the Sierra Nevada and Tahoe Basin (Carroll et al., 1998) do not support the transport of an "intact" polluted air mass to the Tahoe Basin. However, ozone measurements at ground-level and aloft in many

largely rural areas of California that are located downwind of major urban centers frequently have elevated regional background ozone concentrations of about 50 ppb (Carroll et al., 1998; CARB, 1997). Another factor that must be considered to properly assess the impact of transport on air quality in the Tahoe Basin is the semi-permanent thermal inversion layer located about 10-11,000 feet MSL over the Basin. When present, this inversion would inhibit the mixing of air above it into the air below it. Because transport of pollutants in the surface layer is limited by diurnal variations in upslope and downslope airflows, the most effective altitude for potential transport to the Tahoe Basin would be about 8-10,000 feet MSL (i.e., above the Sierra Nevada but below the elevated inversion). Furthermore, pollutant concentrations transported into the Basin in that layer of air would undergo some dilution when mixed with the cleaner air below (i.e., between 6-8,000 feet MSL).

6.2 Reactive Nitrogen Species

Nitrogen oxide and ammonia deposition to the Lake Tahoe basin and more broadly throughout the Sierra Nevada may have negative consequences associated with changing the nutrient balance and pH of lakes and streams. It may also alter ecosystem function by changing nitrogen-limited systems to ones that are saturated with available nitrogen. One study (Korontzi, Macko, et al. 2000) showed that nitrogen deposition to the forests of the San Bernardino Mountains, west of the Los Angeles Basin, has shifted the ecology in low lying regions from nitrogen limited to nearly nitrogen saturated conditions. They also report a correlation between nitrogen deposition and increased NO_3^- in the region's watersheds.

Species-specific effects on California's ecology have also been the subject of discussion. For example, Keeley and Fotheringham (1997) argue that NO or NO_2 may be a signaling agent for seed germination in fire sensitive species. Downwind of urban areas, the implication is that many species may be perpetually germinating instead of germinating only after the clearing effects of fire. Nasholm, Ekblad, et al. (1998) report direct uptake of artificially deposited organic nitrogen compounds (amino acids) and this raises the question of whether atmospheric organic nitrates might be directly assimilated, either as nutrients or with toxic consequences. Recent work at the plant and leaf scale show that the mechanisms for nitrogen oxide exchange are complex and that there may be a compensation point controlling biosphere-atmosphere fluxes of some nitrogen oxides (Lerdau, Munger et al. 2000; Sparks, Monson et al. 2001). A compensation point is an atmospheric concentration below which nitrogen oxides are in the net emitted and above which they are, in the net, deposited to an ecosystem.

A large fraction of the input of nitrogen to Lake Tahoe is thought to occur by wet and dry deposition of atmospheric reactive nitrogen (both nitrogen oxides, collectively known as NO_y , and ammonia) to surfaces (water, leaves, soils, etc.) within the Tahoe Basin. Atmospheric NO_y in the form of the chemical species NO and NO_2 (collectively known as NO_x), gas and particle phase nitric acid, and organic nitrates (in gas and particle phases) deposit to the materials on the Earth's surface at different rates because each pollutant has a different solubility and reactivity. Further complicating the situation, it is

known that NO and NO₂ are both deposited to and emitted from snow, soils and terrestrial plants depending on chemical and meteorological conditions at the surface and in the surrounding atmosphere. Emissions of species other than these three are possible. For example, HONO emissions from surfaces are thought to be important to the OH chemistry of urban areas--but little is known about emission rates of other reactive nitrogen species. In the Lake Tahoe region, significant deposition of nitrogen oxides is thought to be occurring both directly to the lake surface and to the surrounding basin followed by runoff into the lake. Understanding the sources and the chemical speciation of nitrogen oxides in the atmosphere upwind of the Tahoe Basin is essential for evaluating models used to design control strategies aimed at reducing the nitrogen inputs to the Lake. Sources of atmospheric nitrogen oxides may include 1) emissions from the Central Valley (specifically, the southern Sacramento Valley and northern San Joaquin Valley) and the San Francisco Bay Area (e.g., combustion, bacterial modification of fertilizers, and natural bacterial emissions) that are then transported to the Tahoe Basin, 2) anthropogenic emissions within the Tahoe Basin (e.g., motor vehicles and wood burning), and 3) emissions from bacterial sources in the soils and forests surrounding the lake.

Despite this wide range of policy relevant and scientifically interesting issues, the difficulty of accurately measuring nitrogen oxides and their deposition rates has prevented the development of an accurate, complete and detailed mechanistic understanding of nitrogen oxide deposition from emerging. The work by Cohen and Murphy was aimed at understanding the contribution of atmospheric nitrogen from west of the Tahoe Basin to the nitrogen oxide burden within the basin. The goals were to provide a detailed baseline of high time resolution observations of the annual cycle of four different types of reactive nitrogen oxides just to the west of the Tahoe Basin, to make those observations available to other investigators within ARB or elsewhere and to develop analyses using this data set. Further, the Big Hill observations were combined with data from separately funded work at UC Blodgett Forest and with data sets from other ARB investigators to provide a more quantitative understanding of the mechanisms and processes that establish the amount of each different nitrogen oxide species in the air to the west of the Tahoe Basin. The location at Big Hill permitted only characterization of air outside the basin. Nonetheless, the constraints developed from the Big Hill data set provide a maximum estimate of the contributions of transport from the west to the composition of air at the peak of the Sierra Nevada and the western edge of the Tahoe Basin.

6.3 Chemistry of Nitrogen Oxides

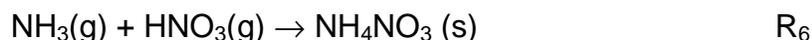
Nitric oxide (NO) is the primary reactive nitrogen compound emitted by biological activity and as a byproduct of combustion. Once emitted NO rapidly (~100 seconds) interconverts with NO₂



Collectively NO and NO₂ are referred to as NO_x and the sum of NO_x and all higher oxides of nitrogen is referred to as NO_y. Higher oxides of nitrogen are formed in reactions of the radicals OH, HO₂ and RO₂ with NO and NO₂.



These reaction products have very different properties. Peroxynitrates are thermally unstable and form a reservoir for NO_x, in which the partitioning depends on the ambient temperature. HNO₃ and hydroxyalkyl nitrates (R'' = ROH) are very water soluble while the peroxy nitrate and alkyl nitrate products of R₄ and R₅ are only weakly water soluble. As a result of its solubility, HNO₃ is rapidly (on a time scale of hours within the planetary boundary layer) removed from the atmosphere by deposition to the Earth's surface and/or rapidly scavenged in water rich aerosol, which then deposit to the Earth's surface. Less is known about the deposition rates of hydroxyalkyl nitrates but measurements of their Henry's law solubilities strongly suggest that their deposition rates should be similar to that of HNO₃. Deposition of NO₂, alkyl nitrates, and peroxynitrates are a factor of 10 slower than deposition of HNO₃ (Wesely and Hicks 2000). The most abundant peroxynitrate, PAN, is a known phytotoxin at the concentrations (~5 ppb) encountered immediately downwind of Sacramento (Cape 2003). HNO₃ also reacts with NH₃ in the gas phase or within particles to produce an ammonium nitrate salt: NH₄NO₃. The equilibrium is shifted toward ammonium nitrate aerosol at low temperature and high relative humidity, and the particles may have different atmospheric lifetimes than gas phase HNO₃ (Seinfeld and Pandis 1998).



The nitrate radical, NO₃, is formed from the oxidation of NO₂ by O₃ (R₇). At night, when the very rapid photolysis of NO₃ (R₈) is not occurring, NO₃ accumulates:



and then reacts to form N₂O₅ via R₉:



HONO is also rapidly photolyzed during the day and accumulates at night as a result of mechanisms that are poorly understood, but appear to be equivalent to:



N_2O_5 and HONO are highly reactive with and soluble in water and are likely removed from the atmosphere on contact with most surfaces. The role of these important nighttime compounds in redistributing reactive nitrogen is not well understood. It is likely that some of the N_2O_5 hydrolyzes (reacts with water vapor) to form nitric acid, particularly during winter,



6.4 Transport Concepts

Transport of nitrogen oxides from the Central Valley and the western slopes of the Sierra Nevada to the Tahoe Basin can result from processes that include: a) direct transport within the planetary boundary layer (PBL), b) direct transport above the PBL, and c) accumulation of pollutants in a regional background (**Figure 6-1**). The first two of these mechanisms operate on a daily timescale. Accumulation of pollutants in a regional background and subsequent transport to the Tahoe Basin operates on a longer timescale (i.e., multiple days). All three of these mechanisms are expected to operate, though to differing extents, every day. Research also suggests that biomass burning may be a significant source of atmospheric nitrogen and phosphorus in the Tahoe Basin (Zhang et al. 2002) and it is well known that biomass fires can be significant sources of longer lived pollutants such as CO on a continental scale (Novelli et al. 2003). Fires are episodic in nature, the extent to which their emissions will impact the Basin rests on their frequency, intensity, and proximity to Tahoe.

Figure 6-1 depicts the possible pathways of pollutants originating in the Central Valley that are transported toward the Tahoe Basin. The dotted line is used to suggest the mixing height or upper edge of the planetary boundary layer (PBL). Urban emissions may be transported within the PBL along path 1 or lofted above and transported in the free troposphere by a combined path involving arrows 2 and 3. Emissions in the Sacramento urban area that are advected eastward undergo dilution and chemical reactions as well as receiving additional emissions (anthropogenic and biogenic) and depositing on surfaces. If the westerly air flow (i.e., from the west) is sufficiently strong or persistent during a given day, it may reach the Tahoe Basin. Arrow 4 is dashed to emphasize the uncertainty regarding the duration and strength of conditions that directly transport an air parcel originating in the valley to the east before the winds reverse to downslope at night. While pollutants may not be directly transported to Tahoe within the mixed layer, emissions into an air mass that washes up and down the slope of the Sierra every day may increase the regional background over time, eventually contributing to elevated reactive nitrogen in the air that reaches the Tahoe Basin.

Alternately, some air masses may be lofted high above the floor of the Central Valley and move eastward over the western Sierra disconnected from interactions with the surface (arrows 2 and 3). Air masses that pass over the roughly 3000 m peaks to the west of the Lake Tahoe Basin or flow through canyons may subsequently be mixed

downward and be exposed to the lake surface (arrow 5). The downward mixing of material transported over the Sierra Nevada will be limited by the presence of a semi-permanent temperature inversion above Lake Tahoe between 3,000 and 3,400 meters MSL (indicated by a heavy dashed line). Additionally, the routine presence of surface inversions and seasonal differences in the relative air-water temperatures over the lake can dramatically affect atmospheric mixing and deposition to the Lake. Thus, a detailed understanding of how air mixes vertically within the Tahoe Basin (arrow 5) is necessary to assess the influence of remote nitrogen sources. Pollutants transported aloft via arrows 2 and 3 will have no effect on Lake Tahoe unless they enter the mixed layer above the lake, which would permit their eventual deposition. An assessment of the probability of such events is beyond the scope of this chapter.

The overall impact of remote sources of atmospheric reactive nitrogen on Lake Tahoe depends on the appropriately weighted combination of all the transport pathways noted above. In the summer, the prevailing wind flow is from the west at all altitudes more than 2000 m above the surface. During the day, heating of the western Sierra generates upslope winds that transport air from the valley floor into the mountains, regardless of the dominant flow regime within the Central Valley itself (Zaremba and Carroll 1999). In the winter, significant periods of high pressure in the region cause inland valleys and basins to fill with cold air leading to low mixing heights and weak winds. Local pollutants tend to accumulate and long-range transport of emissions is less likely. While the pattern of upslope/downslope flow is observed on some winter days, the shorter periods of daylight mean that upslope flow persists for a much smaller fraction of the day. **Figure 6-2** shows the summer and winter patterns of upslope/downslope flow at the University of California’s Blodgett Forest Research Station (UC-BFRS, 1400 m ASL).

Figure 6-1. Topographical diagram of airflow along the western slope of the Sierra Nevada and potential surface and aloft inversions over Lake Tahoe that inhibit mixing.

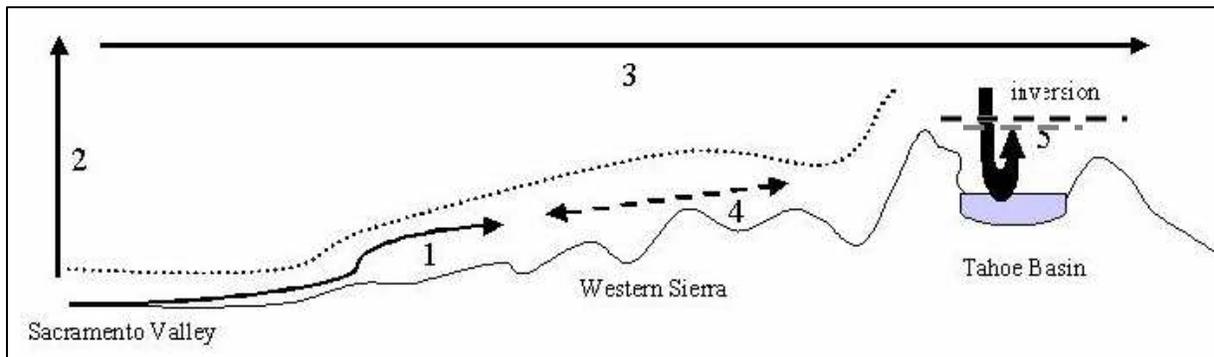
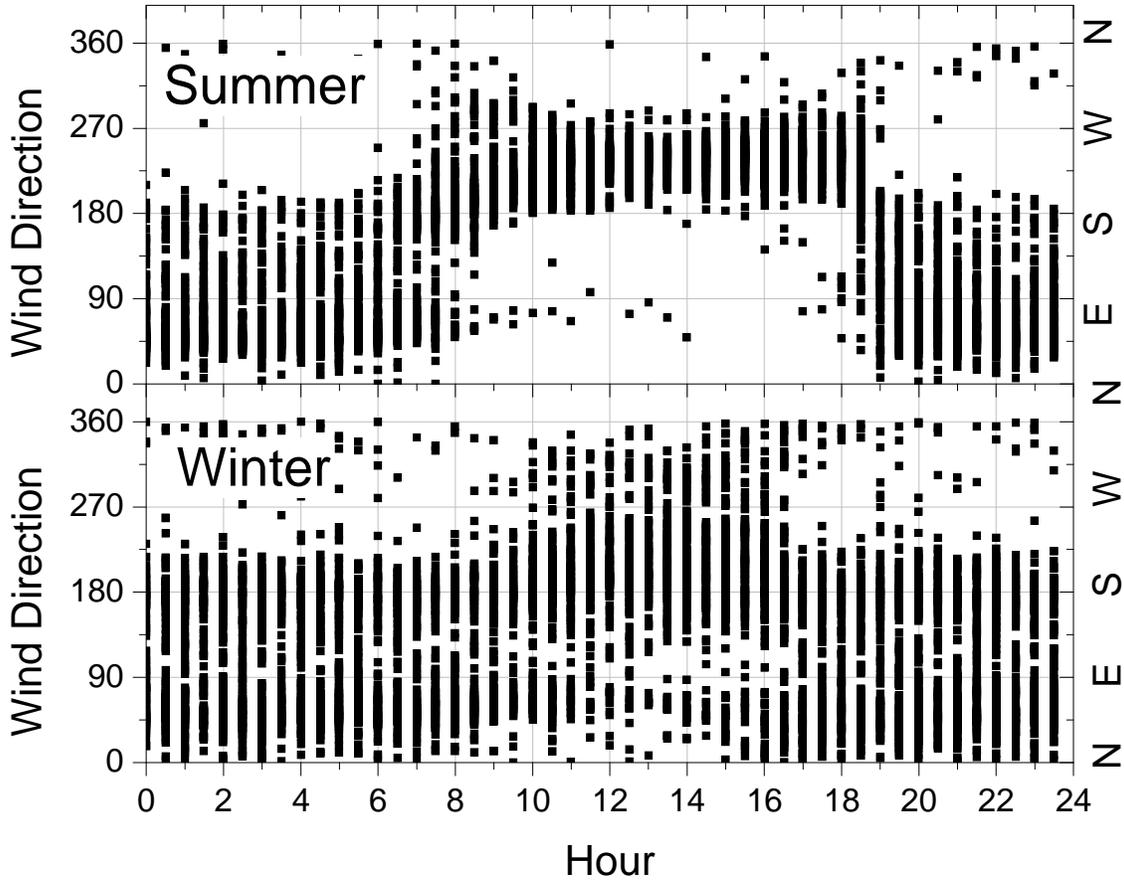


Figure 6-2. Half-hour averages of wind direction observations at Blodgett Forest during 2001. Summer refers to data between day 155 and 255 (June 5- Sep 12) and winter refers to data before day 50 (Feb 20) and after day 300 (Nov 2).



6.5 The Urban Plume

The daily evolution of the Sacramento urban plume during the summer is remarkably consistent. During the day, terrain driven winds blow steadily from Sacramento into the Sierra Nevada foothills – drawing air into the sparsely populated mountains. During the night, the wind reverses and clears out the mountains replacing the urban plume with the regional background. Observations of atmospheric composition and meteorology show this pattern persists to at least 1200 m elevation (Carroll and Dixon 2000).

Transport of anthropogenic emissions from the Sacramento metropolitan area as a result of this meteorological flow pattern is evident in observations of anthropogenic hydrocarbon, ozone, and nitrogen oxide concentrations at the University of California Blodgett Forest Research Station, which peak in the late afternoon/evening and decrease steadily with the downslope flow during the night. *Van Ooy and Carroll (1995)* measured ozone and local meteorological variables (temperature, wind speed, wind direction, relative humidity, and solar radiation) at six sites along a 400 km north-south transect of the Sierra Nevada foothills (1100 – 1200 m elevation) during the summer of 1992. At the three sites where east-west wind patterns are predominant, as they also

are at UC-BFRS, there was a strong correlation between wind direction and ozone concentrations. At these sites, there was a regular diurnal pattern with ozone concentrations peaking at 15:00 to 17:00 PST (Pacific Standard Time) and reaching a minimum at 7:00 PST. At the other three sites where north-south winds were predominant, the diurnal variation in ozone was small. The sites with east-west wind patterns had higher peak ozone abundances and violated the one-hour state ozone standard of 0.90 ppm up to 40% more often than the sites with predominantly north-south winds indicating sites with east-west wind patterns such as UC-BFRS represent a maximum effect of transport. The major climate variables controlling transport in the region (temperature, sunlight, precipitation, relative humidity, and wind) as measured in Sacramento have been nearly constant for 20 years (1980 to 1999) (**Figure 6-3**). Thus emissions in the Central Valley should have been transported with equal efficiency throughout this 20-year period.

These analyses suggest the plume traveling into the foothills of the Sierra from the valley serves as a mesoscale (100 km), daytime flow reactor that can be characterized as a Lagrangian air parcel transported from the valley into the Sierra Nevada. *Dillon et al.* (2002) used comprehensive (ozone, speciated nitrogen oxides, speciated anthropogenic and biogenic hydrocarbons, and meteorology) and extensive (spanning the years 1997 to 2002) observations at Folsom, California and five hours downwind at the University of California – Blodgett Forest Research Station to evaluate transport from Sacramento into the mid-Sierra during the summer (**Figure 6-4**). The observations at Folsom effectively integrate all of the emissions to the west. Dillon (2002) established that a Lagrangian analysis captures the essential features of the chemistry and transport and fit the parameters of a Lagrangian model to the observations. Comparison of ozone and meteorological observations to the north of UC-BFRS at Blue Canyon and to the south at Sly Park support the suggestion that the observations and the model analysis are regionally representative.

Measurements of speciated NO_x and individual NO_y species at UC-BFRS (1998-present) demonstrate pronounced seasonal variability (Day et al. 2002) (**Figure 6-5**). The Lagrangian model has only been applied to summer time conditions when upslope transport is expected to be at a maximum. To obtain an annually complete picture, other approaches are required to interpret the reactive nitrogen measurements because of different source distributions, and more importantly, very different meteorological conditions.

Figure 6-3. Monthly averaged observations at the Sacramento Executive Airport (WBAN 23232) demonstrate the inter- and intra-annual variance of climatological variables in the region from 1980 through 1999. The line with solid squares is the median of monthly means while the gray swath denotes the 1 σ variance. a) maximum daily temperature; b) percent of total possible hours of direct sunlight (no observations were available in 1998 and 1999); c) sum of monthly rainfall; d) the lowest relative humidity recorded each day (typically a late afternoon observation); e) daily origin direction of 24 hour average of recorded winds (also called resultant wind direction); f) 24 hour average of recorded wind speeds.

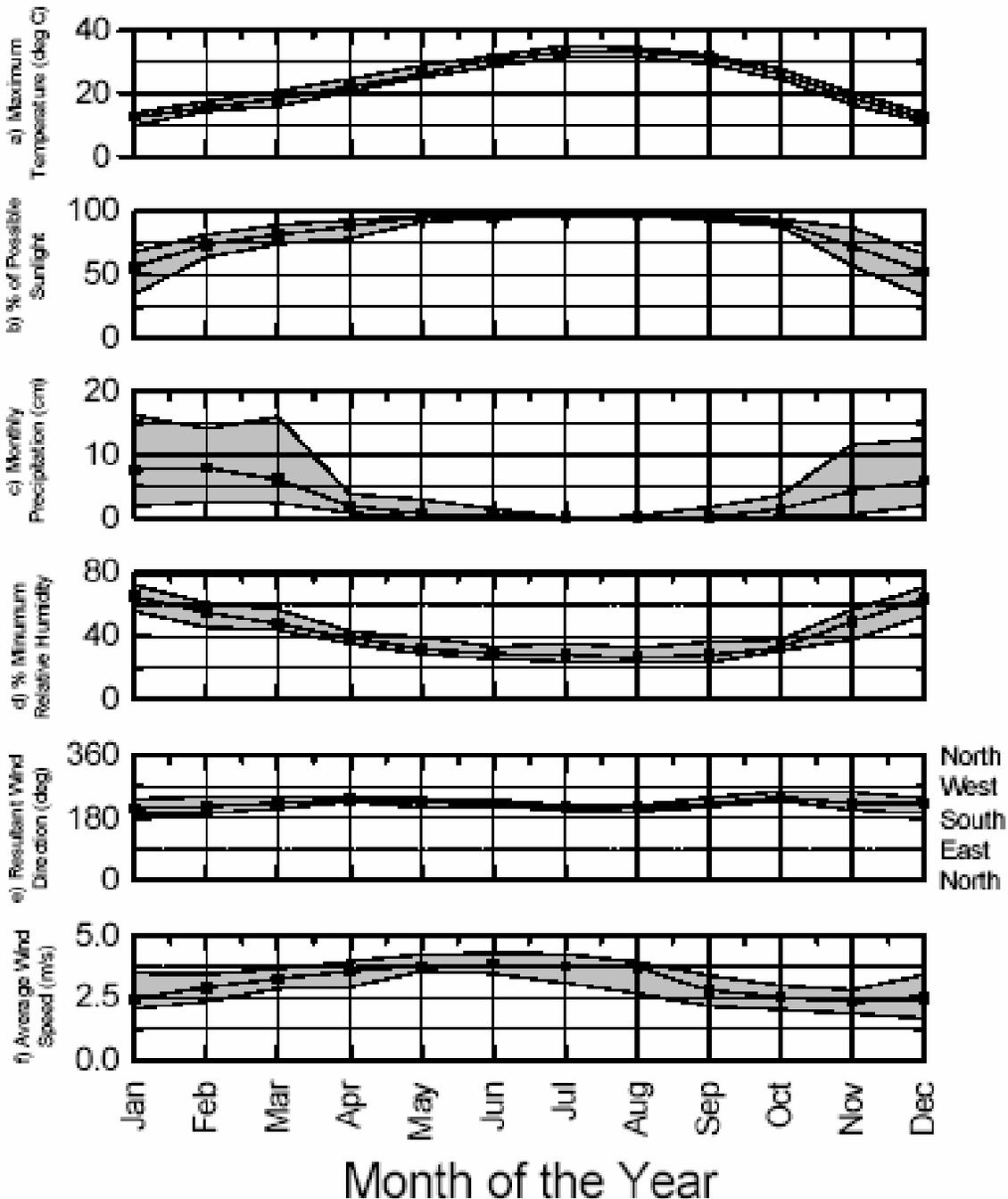
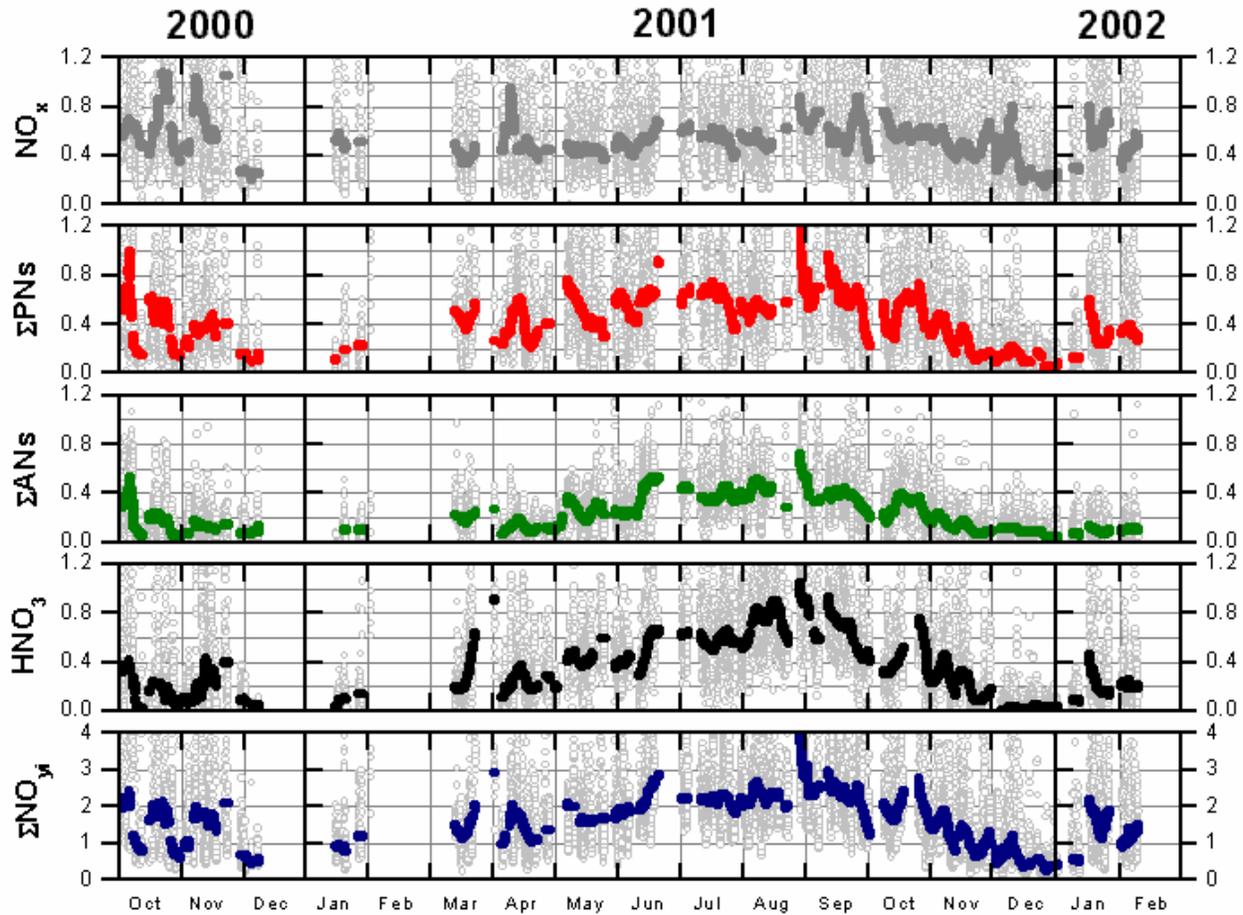


Figure 6-4. Major roads and 1998 California Air Resources Board atmospheric sampling sites upwind of the Blodgett Forest Research Station: Photochemical Assessment Monitoring Station sites (circled P), co-located ozone, nitrogen oxide and non-methane hydrocarbon monitors (+), co-located ozone and nitrogen oxide monitors (star), and ozone monitors (diamond). Most observations used in this study were taken from the Blodgett Forest Research Station, Del Paso Manor, and the Folsom sampling sites.



Figure 6-5. Concentrations (ppb) of nitrogenous air pollutants at UC-BFRS 2000-2002 (30 minute averages and 7-day running medians).



6.5.1 Mixing

Parameters in the model described by Dillon (2002) include mixing of the urban plume with the regional background, chemical processing, emission and deposition. By treating NO_y as a conserved quantity, the calculations represent an upper limit to the contribution of urban NO_x in the Sierra because chemical factors also act to reduce NO_y . Assuming approximately a 25% per hour reduction in concentrations due to mixing with cleaner background air during daytime upslope flow (Dillon, 2002), emissions in the Sacramento area would have been diluted to 28% of their initial concentrations by the time the plume arrived at UC-BFRS (5 hours downwind from the suburbs of Sacramento). If we extrapolate these results to Tahoe, which is another 4 hours downwind, the urban portion of the concentrations would be 10% of their initial values. In summer, the regional background in the area is estimated to be 1.9 ppb and daytime NO_y mixing ratios in the downwind suburbs of Sacramento are 7 ppb; thus, about 5.1 ppb is the direct result of emissions in the Sacramento source area. Based on mixing alone and after five hours of transit, the concentration of NO_y at UC-BFRS

would be 3.4 ppb (1.5 ppb from the plume, and 1.9 from the regional background). Extrapolating another 4 hours to the Tahoe Basin, the concentration of NO_Y would be 2.4 (0.5 ppb from the plume, and 1.9 from the regional background). Observations by *Carroll et al.* (2002) along a transect at 2000 m suggest that the urban plume usually stops before the crest and does not progress across the mountains into the Tahoe Basin, indicating that direct transport of inorganic nitrogen from the Central Valley is likely smaller than this estimate.

6.5.2 HNO_3 Formation and Deposition

Chemical production of HNO_3 followed by rapid deposition removes NO_Y , reducing the urban contribution below the estimate given above for mixing alone. Dillon (2002) determined that the effective OH mixing ratio that acts over the 5 hour transport time to Blodgett Forest is about 1.4×10^7 molecules/ cm^3 or (0.6 ppt). NO_2 reacts rapidly with OH to form HNO_3 ($k \sim 9 \times 10^{-12} \text{ s}^{-1} \text{ cm}^3/\text{molec}$) and in the absence of other reactions of NO_2 , approximately 90% of the suburban NO_2 would be converted to HNO_3 prior to reaching UC-BFRS. HNO_3 is deposited on a time scale set by the ratio of the deposition velocity to the boundary layer height. Using literature estimates for the deposition velocity (0.035 m/s) (Hanson and Lindberg 1991) and the boundary layer height (800 m) (Seaman et al. 1995), results in a lifetime of 6.3 hours. Thus about 50% of the HNO_3 formed during the transit to UC-BFRS is deposited along the way and about 85% is deposited before it gets to the Tahoe Basin. *Day et al.* (2002) provide analysis of the daily cycle of HNO_3 that suggests this estimate of the HNO_3 lifetime is too long (perhaps because the deposition velocity is closer to 0.05 m/s). During the daytime, the HNO_3 concentration is observed to be nearly in a chemical stationary state with a production term characterized by R_3 and loss to deposition. This would not be the case if the time scale for production and deposition were much longer than 3 hours. This result implies that more than 70% of the HNO_3 formed during transit from Sacramento to Tahoe is deposited along the western slope of the Sierra Nevada. This short lifetime suggests that attention be focused on the controls over NO_2 mixing ratios in the Tahoe Basin (or anywhere else where dry HNO_3 deposition is a potential problem).

6.5.3 Organic Nitrate (RO_xNO_2) Formation

Other photochemical byproducts that act as a sink or reservoir for NO_Y include peroxy nitrates and alkyl nitrates formed by the reaction of RO_2 with NO_2 and NO respectively. In the concentration range of NO_Y encountered outside urban areas, organic nitrates can be the major sink of NO_Y radicals. While HNO_3 forms efficiently under high NO_Y conditions, RO_xNO_2 formation becomes more favorable as the NO_Y to hydrocarbon ratio decreases. The lower deposition velocity of organic nitrates lengthens their lifetime in the plume but also makes them less efficient as a source of atmospheric nitrogen to the surface. Hydroxy alkyl nitrates are expected to have comparable deposition velocities to HNO_3 , but it is unclear what fraction of organic nitrates these comprise. Peroxy nitrates are thermally unstable and therefore capable of sequestering NO_Y under cold conditions and releasing it once temperatures rise. This can be an effective mechanism for transporting reactive nitrogen to distant places. Observations by *Day et al.* (Day et

al. 2003) at UC-BFRS show that for many parts of the year, the sum of all organic nitrate species is often the most significant fraction of NO_γ in the plume by the time it reaches the site. More needs to be known about the behavior of these species to assess their potential to deliver reactive nitrogen to Lake Tahoe. Note that atmospheric chemists refer to RONO_2 and RO_2NO_2 collectively as 'organic nitrates'; a term that should not be confused with 'organic nitrogen', which is used to refer to compounds with a C-N bond. Little is known about the aqueous decomposition of peroxy and alkyl nitrates, and whether their NO_3 group would contribute to nitrate measurements in analysis of lake water or precipitation.

6.5.4 Downwind Emissions

The observations and analyses of nitrogen oxides at UC-BFRS indicate that emissions into the urban plume continue after it passes over Folsom. These emissions are large ~ 0.44 ppb/hr. After the five hours of travel on the way to UC-BFRS the total emissions are 2.2 ppb, an amount in excess of the background concentration observed at the site and fully 2/3 of the amount observed at the peak of the urban plume. This result strongly implies that transportation along the 50 and 80 highway corridors, contribution from housing beyond the edge of the Sacramento suburbs and direct emissions from the local ecosystems are significant contributors to NO_γ in the Sierra. Further research is required to quantify the amount contributed by each of these distinct sources.

6.5.5 Summary of Plume Transport and Chemistry

This analysis makes use of a continuous long term dataset that allows for the evaluation of statistics. This comprehensive record of meteorology and chemical composition at UC-BFRS is consistent with other observations from the western slope of the Sierras including aircraft measurements, data from Big Hill (1850 m), and short term ozone studies. Using a model that accounts for the combined effects of emissions, chemistry, deposition and dilution which can be tested against an inclusive set of observations allows us to develop a representation of the mean behavior of NO_γ species in the region. The influence of the urban plume causes an increase in the typical daytime peak mixing ratio of NO_γ at UC-BFRS, which occurs just prior to sunset, to near 3.3 ppb, an amount that is 1.4 ppb above the regional background of 1.9 ppb. For most of the day, the observed mixing ratios are much less than this peak value with a daytime average concentration of about 2.5 ppb (0.6 ppb above the regional background). Thus on an average day at UC-BFRS, the contribution of the urban plume raises the diurnally averaged NO_γ by 32% over the background. Assuming the Lagrangian parameters represent transport beyond UC-BFRS then further dilution and deposition of HNO_3 along the plume's trajectory to the Lake will mean an even lower contribution of NO_γ from the urban plume to the Tahoe Basin.

At least as important as the total amount of NO_γ transported within the plume, is the change in species distribution as the plume evolves. HNO_3 dominates the higher oxides of nitrogen (NO_z) near emission sources of NO_x but is rapidly lost if the air mass remains in contact with the surface. On the other hand, the plume becomes relatively enriched in organic nitrates as it progresses through the day with the sunlight driving

hydrocarbon oxidation, creating RO_2 radicals to combine with the NO_x in the plume. These hydrocarbons have both anthropogenic and biogenic sources. If nitrogen oxides emitted in the Central Valley do reach the Tahoe Basin it is likely they will make it there in the form of organic nitrates. Production of fine particles ($<2.5 \mu\text{m}$ aerodynamic diameter) containing nitrate may be another mechanism for transporting reactive nitrogen, as this size of aerosol has a substantial lifetime (hours-days) in an air mass.

The direct extrapolation of the plume analysis presented above in order to understand inputs to Lake Tahoe is only accurate if the upslope flow is strong enough and persistent enough to deliver air from the Central Valley to the Tahoe Basin in one day. If an average daytime wind speed of 3.5 m/s is used, it would be possible for an air mass to leave Sacramento at 10 am and travel 130 km east to the Tahoe Basin by 8 pm that night. Using appropriately timed NO_2 , NO_x , and NO_y observations from monitoring sites along the Sacramento-Tahoe transect in July enables us to examine the evolution of reactive nitrogen in the plume (**Figure 6-6**). As described above, as the plume moves away from Sacramento and ages, the abundance of reactive nitrogen decreases as the result of dilution, processing and deposition. However, NO_x observations at South Lake Tahoe are substantially higher than one would expect from an extension of the values at UC-BFRS and Big Hill, suggesting a substantial contribution from local in-basin emission sources.

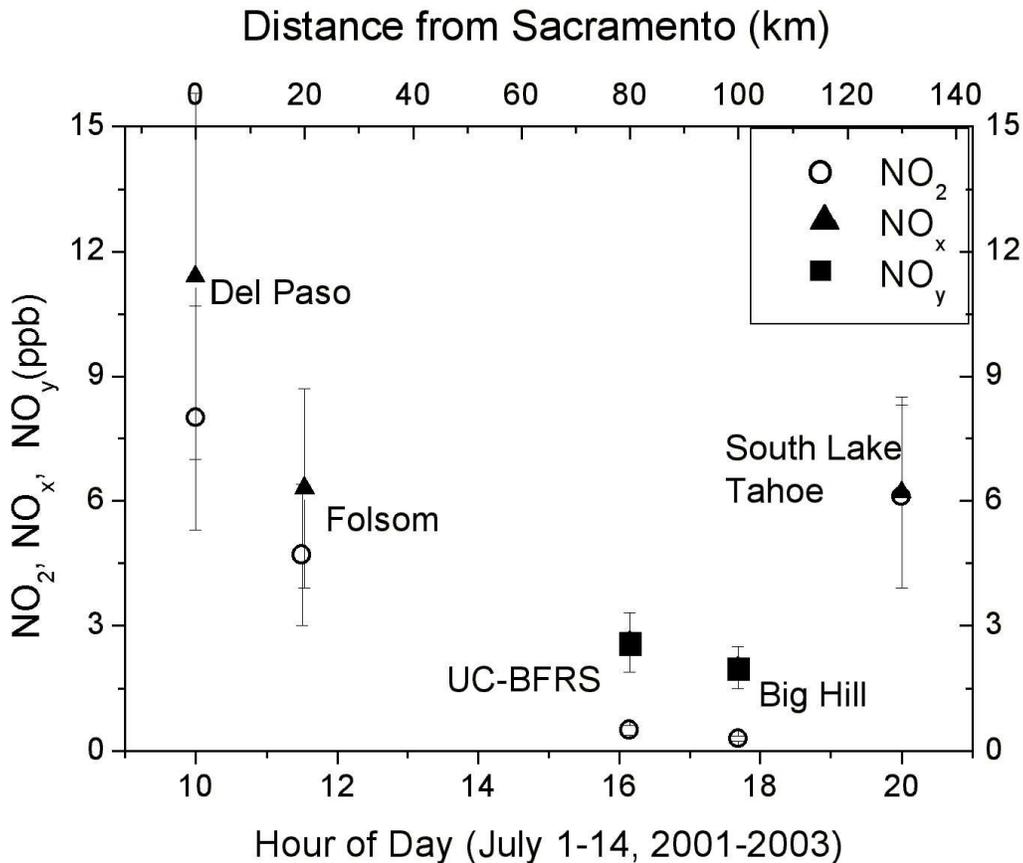
Limited aircraft measurements of $\text{HNO}_3/\text{NO}_3^-$, $\text{NH}_3/\text{NH}_4^+$, and organic nitrogen in the gas and particle phase have been made in the Tahoe Basin and at low and mid-elevation sites along the western slope of the Sierra Nevada (Zhang et al. 2002). While the abundance of these species is significantly lower in the Tahoe Basin than on the western slope of the Sierra Nevada, the distribution between the species was found to be similar in all locations. The authors infer from these observations that under summertime meteorological conditions, Central Valley emissions can be a significant source of nitrogen to the basin. However, because the timescale of photochemistry and deposition of the nitrogen oxides is short, we expect the distribution among different classes of NO_y to have strong variations depending on the time of day and proximity to the source. Further, if the Central Valley were the main source of HNO_3 and NH_3 for all the sites, one might actually expect a very different distribution of nitrogen because the Tahoe Basin is further along (spatially and temporally) the generally west to east air flow transect than are the lower elevation sites. Additionally, there may be some bias resulting from the timing of the measurements: all the western slope measurements occur between noon and 4 pm while half of the Tahoe Basin measurements are in the morning. These intermittent observations are not sufficient to address the issue of transport from the western slope of the Sierra Nevada into the Tahoe Basin.

6.6 Key Research Issues

Measurements made upwind of the basin can be used as a boundary condition on the total amount of reactive nitrogen available in upwind air masses before they enter the Lake Tahoe basin. Data collected at sites on the western slope of the Sierra suggest that the transit time of a boundary layer air mass from Sacramento to Lake Tahoe exceeds the period of upslope flow during a summer day. This implies that if upwind

reactive nitrogen emissions from urban areas have any impact over Lake Tahoe, then it is through an increase in the regional background. The lifetime of reactive nitrogen is largely determined by the deposition rates of its constituent members. Organic nitrates and NH_4NO_3 aerosol (PM 2.5) are longest-lived and therefore most likely to persist in the background, but by this logic they are also the least likely to deposit to the lake surface. Thus it is easy to imagine a scenario in which the majority of reactive nitrogen in an air mass over Lake Tahoe has its origin in aged Sacramento emissions but the recent in-basin emissions of NO_x , quickly oxidized to HNO_3 , are what actually deposits to the lake surface.

Figure 6-6. Reactive nitrogen observations along the Sacramento-Tahoe transect. The distance from Sacramento was multiplied by an average wind speed of 3.5 m/s to estimate the time the air mass would arrive at each site after leaving Del Paso at 10 am. Observations at each site were averaged for an hour around the estimated time. For example, UC-BFRS lies 80 km downwind of Del Paso, and NO_2 and air mass observations between 3 pm and 5 pm were averaged to produce the points reported at 4 pm. The error bars represent the standard deviation of the average.



6.7 Results and Analyses of Big Hill Measurements

Tunable Diode Laser Induced Fluorescence (TDLIF) has a history of successfully providing measurements of NO_y species, NO_2 , peroxy nitrates, alkyl nitrates, and HNO_3 (Cohen and Murphy 2005). Big Hill is located at ~6200' MSL on the western slope of the Sierra to the southwest of the Tahoe Basin. Big Hill is a well-exposed peak on the western slope of the Sierra and perfectly situated to observe air parcel transport above terrain-induced influences (**Figure 6-7**). The orientation of the valleys and river canyons around Big Hill also indicates potential surface layer transport paths roughly parallel to Highway 50 (**Figure 6-8**). Further focusing on the topography, it is clear that Big Hill lookout and helipad are a significant distance from Ice House campgrounds and any potential local source impacts (**Figure 6-9**). The experimental sites and instruments used are described in further detail in *Cohen and Murphy (2005)*.

Figure 6-7. View of Big Hill site from the west.



Measurements of the NO_y species NO_2 , peroxy nitrates, alkyl nitrates and HNO_3 were made between March 2003 and February 2004 at Big Hill, whenever electricity was available to power the instrument. Despite being located in close proximity to the Sacramento Municipal Utilities District tower, power at the site failed frequently during the study, often during times of bad weather. Meteorological variables, ozone, and PM were also measured and are incorporated into the analysis. The corresponding measurements made at Blodgett Forest were included to develop a more complete picture of the factors controlling the distribution of reactive nitrogen within the region.

The annual cycle of measurements will be discussed with reference to seasonal differences and their causes. Then the summertime data (June through October) will be analyzed more fully to examine correlations between trace gas constituents and climate variables.

Figure 6-8. Map of Crystal Springs area showing Union Valley reservoir just to the north of the Big Hill lookout site and Highway 50 at the bottom of the map.



6.7.1 Regional Transport

Due to its position on the western slope of the Sierra Nevada, Big Hill is subjected to regular wind patterns, especially during the summer. Daytime heating causes upslope flow, which draws air from California’s Central Valley eastward into the higher elevations

of the Sierra Nevada range. When the sun sets, the flow reverses and the air drains from higher elevations back toward the valley floor. This flow regime persists along much of the western slope of the Sierra Nevada and strongly influences the seasonal and diurnal patterns observed in primary and secondary pollutants seen in the region.

Figure 6-9. Higher resolution map of topographical features and roads in proximity to the Big Hill monitoring site.

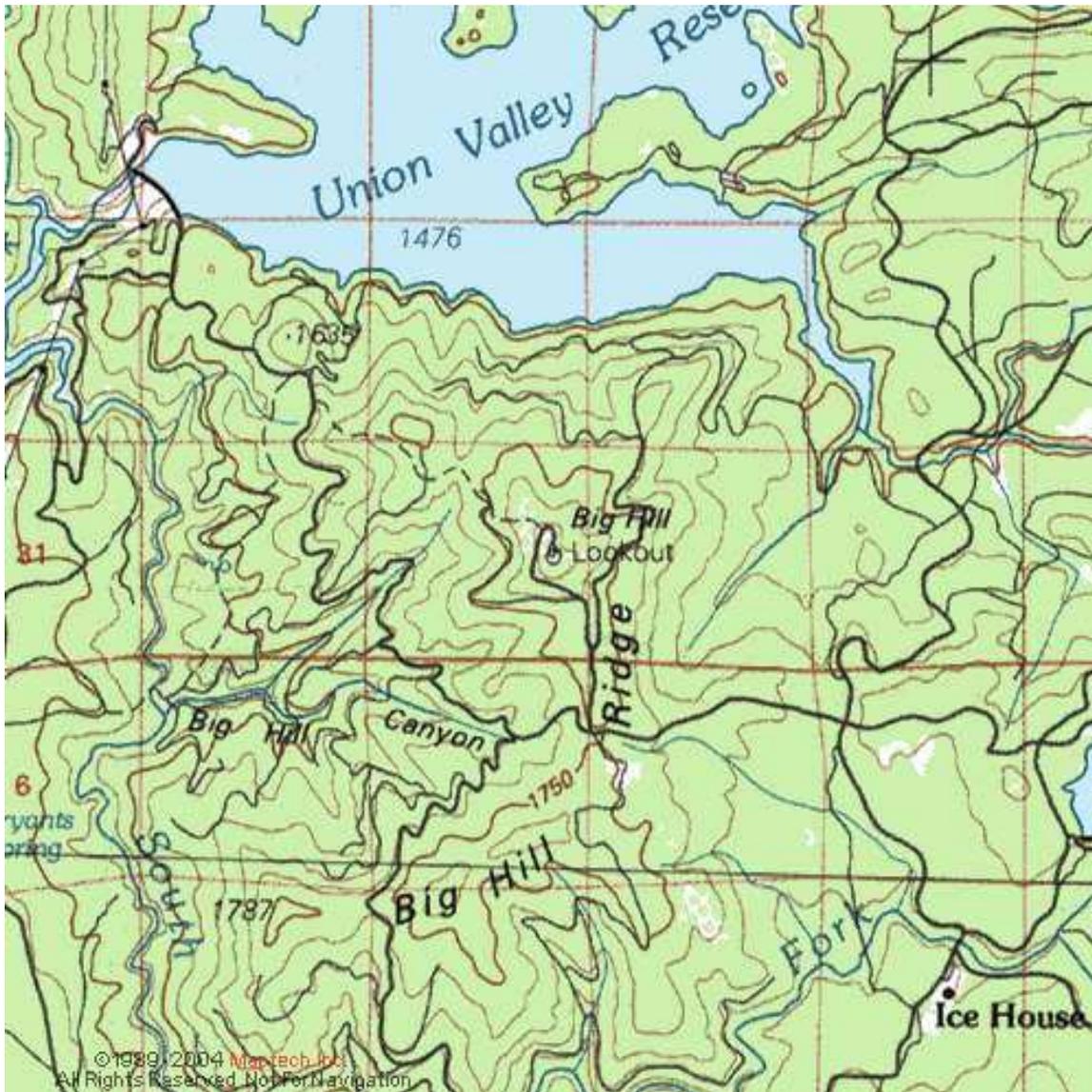


Figure 6-10 shows the location of Big Hill with respect to the nearby city of Sacramento and identifies many other air quality monitoring sites in the region that sample air from the Sacramento urban plume. Wind speed and direction measurements made at Blodgett Forest, Big Hill, and other Air Resources Board sites show that the general

wind direction in the region is from the WSW during the day and the east at night. Blodgett Forest tends to experience winds from the NE at night while flow at Big Hill is from the SE, likely due to topographical differences between the two sites. Big Hill lies roughly 80 km from the eastern edge of the Sacramento suburbs, thus with an average wind speed of 15 km/h, it takes an air mass over 5 hours to reach the monitoring site. During the five hour transit time, the concentration of constituents within the urban plume may be altered by dilution, deposition, photochemical transformations and further emissions. A simple Lagrangian model using measurements made at sites along the Sacramento – Lake Tahoe transect allows us to separate out these parameters and identify the variables constraining nitrogen oxide concentrations in the Sierra Nevada foothills downwind of Sacramento.

As we noted before, observations made at these ground sites reflect the processing of boundary layer air masses during the daytime. Evidence that will be described later shows that at 1850 m elevation, Big Hill frequently experiences nighttime downslope flow, possibly from the free troposphere. **Figure 6-1** is a depiction of the region with the topographical features highlighted. The boundary layer, shown as the dotted line, is expected to be surface-tracking, at least to altitudes of 2000 m in the daytime, and is significantly shallower at night. Flow near the surface follows arrows 1 and 4 with the second arrow dotted and bi-directional to represent the fact that once the sun sets, the flow reverses. Air that is lofted above the Central Valley (arrow 2) will likely be carried eastward with the prevailing winds (arrow 3). Both of these trajectories can bring air masses that have received urban emissions of NO_x toward the Lake Tahoe Air Basin. In the case of surface flow, observations suggests that the wind rarely blows upslope hard enough and for a sufficient number of hours to deliver a species emitted in Sacramento to the Lake Tahoe Air Basin in the same day. Air masses following higher altitude paths may move further to the east in a given day but there must subsequently be a mechanism for that air to mix downwards in order for it to interact with the lake surface.

Figure 6-11 shows calculations of the net weekly east-west airflow for a full year at Camino, based on wind speed and direction measurements at a California Irrigation Management Information Systems (CIMIS) site. Camino is close to Highway 50 between Blodgett Forest and Big Hill. The data suggests the while net airflow between March and October is from west to east, during the winter months long periods of downslope flow result in the net direction of flow at the surface being from Lake Tahoe toward Sacramento. During the winter, daytime upslope flow is generally too short-lived to transport anthropogenic pollutants from the Central Valley significantly further east than Big Hill. This analysis does not take into account the effect of transport aloft or the inclusion of pollutants into storm systems, which tend to move rapidly from west to east during the winter months.

On an average mid-summer day, an air mass originating in the Sacramento area moves roughly 100 km up the western slope of the Sierra Nevada (i.e., west to east) while the sun is up, and then may backtrack 40 km toward the west overnight when the flow is reversed (i.e., east to west). This pattern results in air sloshing back and forth along the

western slopes of the Sierra Nevada and significantly increases the regional background of reactive nitrogen. At lower elevation sites, like Blodgett Forest, air masses measured at night were likely also sampled several hours earlier when they passed by in the opposite direction. At Big Hill, after midnight the lower abundance of H_2O and NO_Y in the air suggests that the site is experiencing descending air.

Figure 6-10. Map of Central California including air quality monitoring sites in portions of the Sacramento Valley and Mountain Counties air basins. Sites marked with stars are State or local monitoring sites, while sites marked with circles are sites where the UC Berkeley TD-LIF instrument has been deployed to make measurements of nitrogen oxide species. The dominant daytime and nighttime wind directions are depicted by the arrows and the inset shows the location of the region within the state of California.

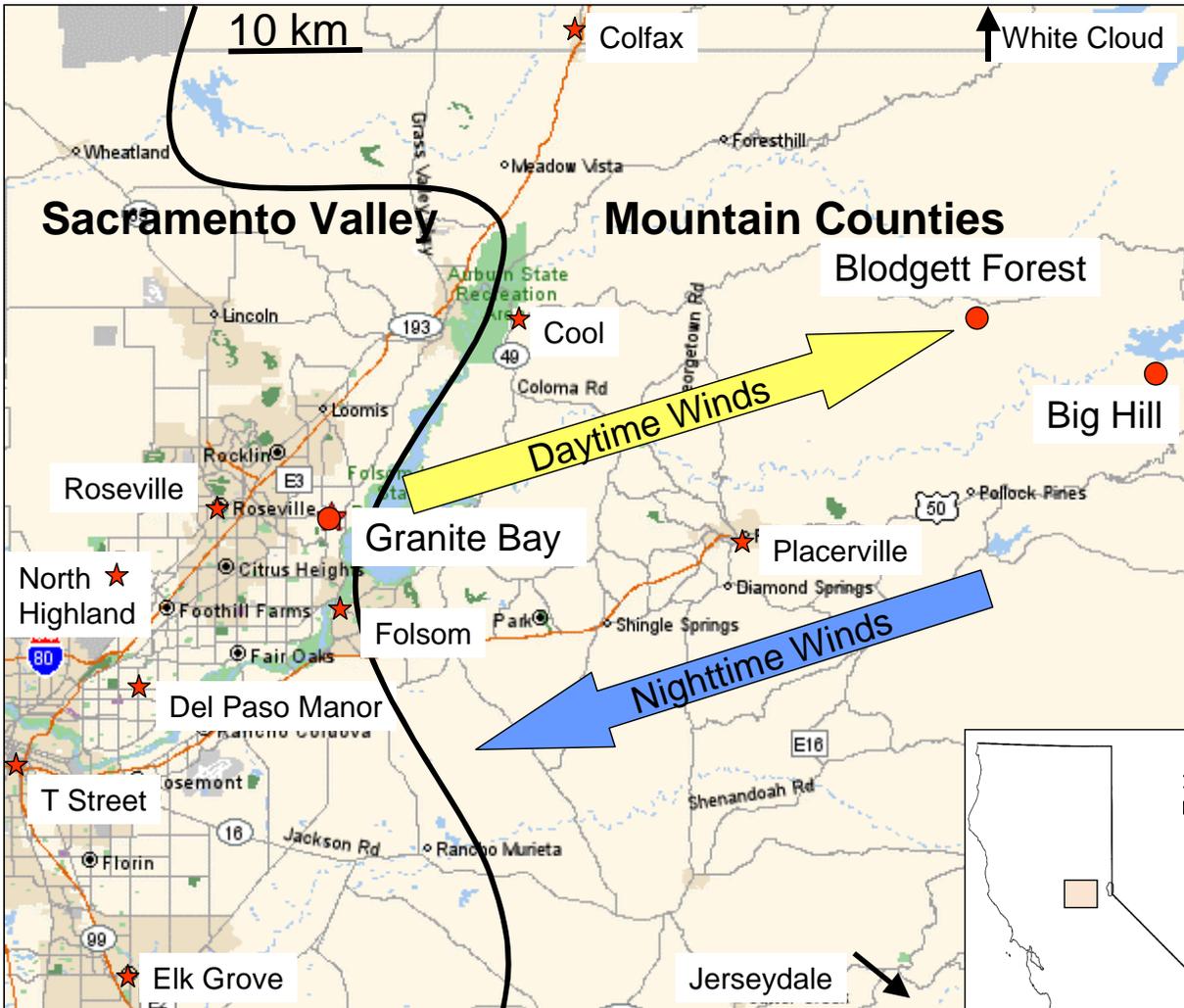
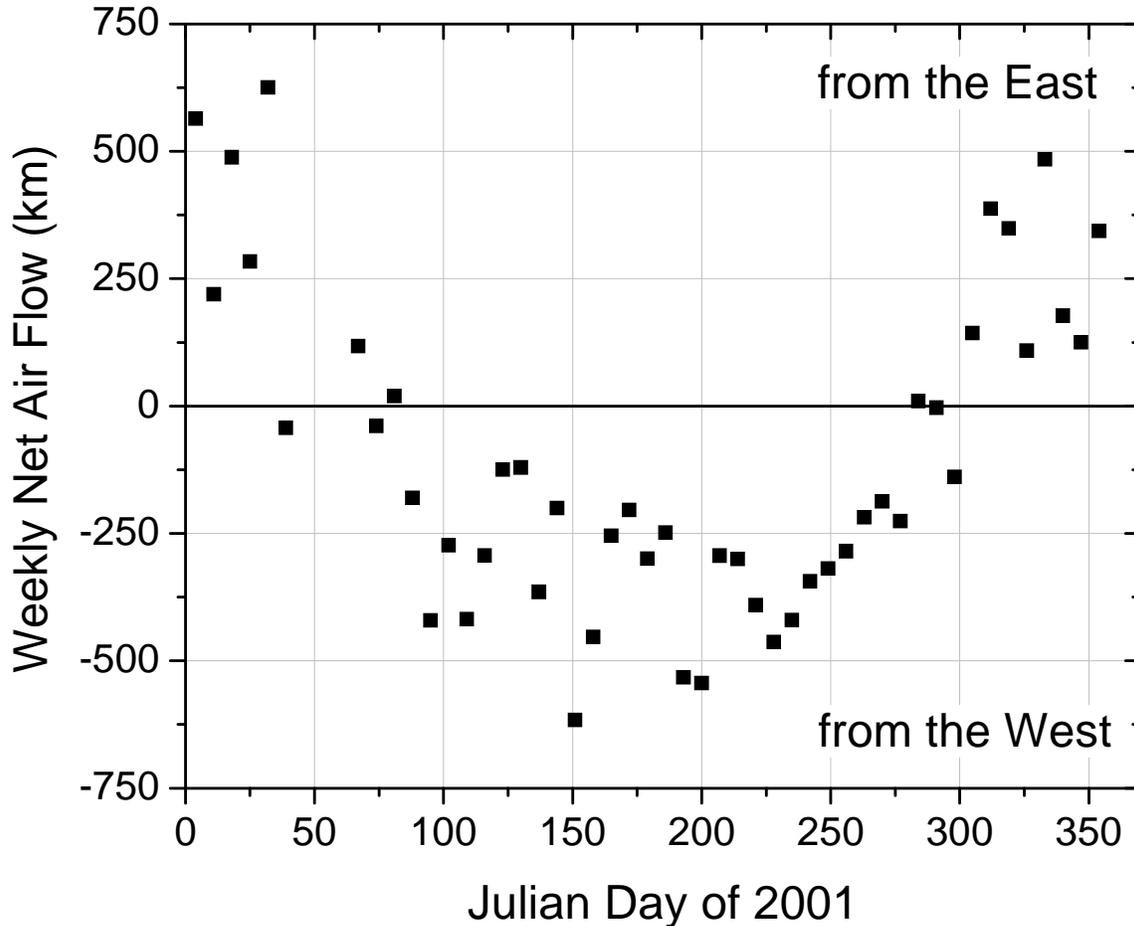


Figure 6-11. Depiction of regional weekly net airflow using meteorological data from the Camino CIMIS site close to Pollock Pines near Highway 50. Between March and October, net flow in the region is from west to east; however, this trend is reversed during the winter months.



6.7.2 Seasonal Cycles in Nitrogen Oxide Species

Data was obtained at Big Hill for a full annual cycle from March 2003 – February 2004, allowing comparison of meteorology and reactive nitrogen for all the seasons. **Figure 6-12** presents observations of temperature, absolute water vapor (calculated as a mole fraction in parts per thousand), and total reactive nitrogen NO_Y (i.e., $\text{NO}_2 + \Sigma\text{PN} + \Sigma\text{AN} + \text{HNO}_3$). From the temperature data, it seems reasonable to consider two different sets of conditions: summer (June through October) and winter (November through April). ΣPN are formed through the association of a peroxy radical and nitrogen dioxide, but only those derived from acyl peroxy radicals are stable enough to survive in the atmosphere. The most common peroxyacyl nitrate is peroxy acetyl nitrate (PAN). ΣAN or alkyl nitrates are formed photochemically through the association of peroxy radicals with nitric oxide. The $\text{RO}_2 + \text{NO}$ reaction can also form ozone; hence, the alkyl nitrate concentrations are generally a good indication of ozone production.

Because of power delivery problems virtually no data were collected during May 2003. While the relative humidity was quite low during the summer months, the water vapor mole fraction is actually higher on average during summer compared to winter. Reactive nitrogen is higher during the summer months at the site though there is substantial day-to-day variability. Most notable perhaps is that the lower values, generally measured during the early morning, reach down almost to zero during the winter but generally not below 0.5 ppb in the summer. This seasonal cycle is consistent with corresponding measurements carried out at Blodgett Forest from 2001-2003. While emissions of precursor NO_x are not known to change substantially in the region by season, what does change is the extent to which these urban emissions are processed and transported to the western slope of the Sierra. As discussed above, net surface flow during the winter months is actually from east to west, so reactive nitrogen does not have the same opportunity to build up in the region that it does in the summer. The seasonal cycle in NO_y at Big Hill and Blodgett Forest is very different than that observed at sites that do not have a seasonal cycle in transport patterns. For example, Harvard Forest (a rural setting in north-central Massachusetts) continues to sample air from urban sources to a similar extent throughout the year. During winter, lower rates of oxidation reduce the conversion of NO_2 to HNO_3 , the ultimate sink of NO_y , and therefore maximum NO_y values are measured during the winter months (Munger, Wofsy et al. 1996; Moody, Munger et al. 1998).

Figure 6-13 displays the full annual record for all the individual NO_y compounds measured. The organic nitrate species, RONO_2 and RO_2NO_2 clearly maximize during the summer months, when higher temperatures and photochemical activity result in increased precursor VOC emissions, more rapid photochemistry and more persistent transport. HNO_3 is also generally higher during the summer months, averaging around 0.5 ppb, but higher excursions tend to occur during the winter months. NO_2 has the least clear seasonal cycle, likely because of compensatory effects between transport and chemistry. During the hot summer months, strong transport of urban emissions to remote high-elevation sites is offset by rapid photochemical oxidation of NO_x to NO_y . In the winter, the plume will have barely reached the site before downslope flow will carry the urban influence away but a much greater fraction of the total NO_y will remain as NO_2 due to reduced photochemistry.

Many of the winter season high NO_y events, especially in November 2003, occurred during prescribed burning events carried out by the US Forest Service or Sierra Pacific Industries, who own much of the nearby forests. Smoke plumes could also be seen from apple orchards and vineyards near Pollock Pines. During these nearby burning events, NO_2 and HNO_3 were the most substantial contributions to NO_y and particulate nitrate was likely an important constituent based on data from the BAM and two week samplers. Some of the low values measured during the winter are the result of precipitation events that scrub soluble forms of NO_y , such as HNO_3 , from the atmosphere.

Figure 6-12. Full dataset obtained at the Big Hill monitoring site for NO_y (ppb), absolute water (parts per thousand, ‰), and temperature ($^{\circ}\text{C}$). Data acquisition began March 5, 2003 (day 64) and ended on Feb 23, 2004 (day 54); however, data are plotted on a calendar year basis to aid the interpretation of seasonal patterns.

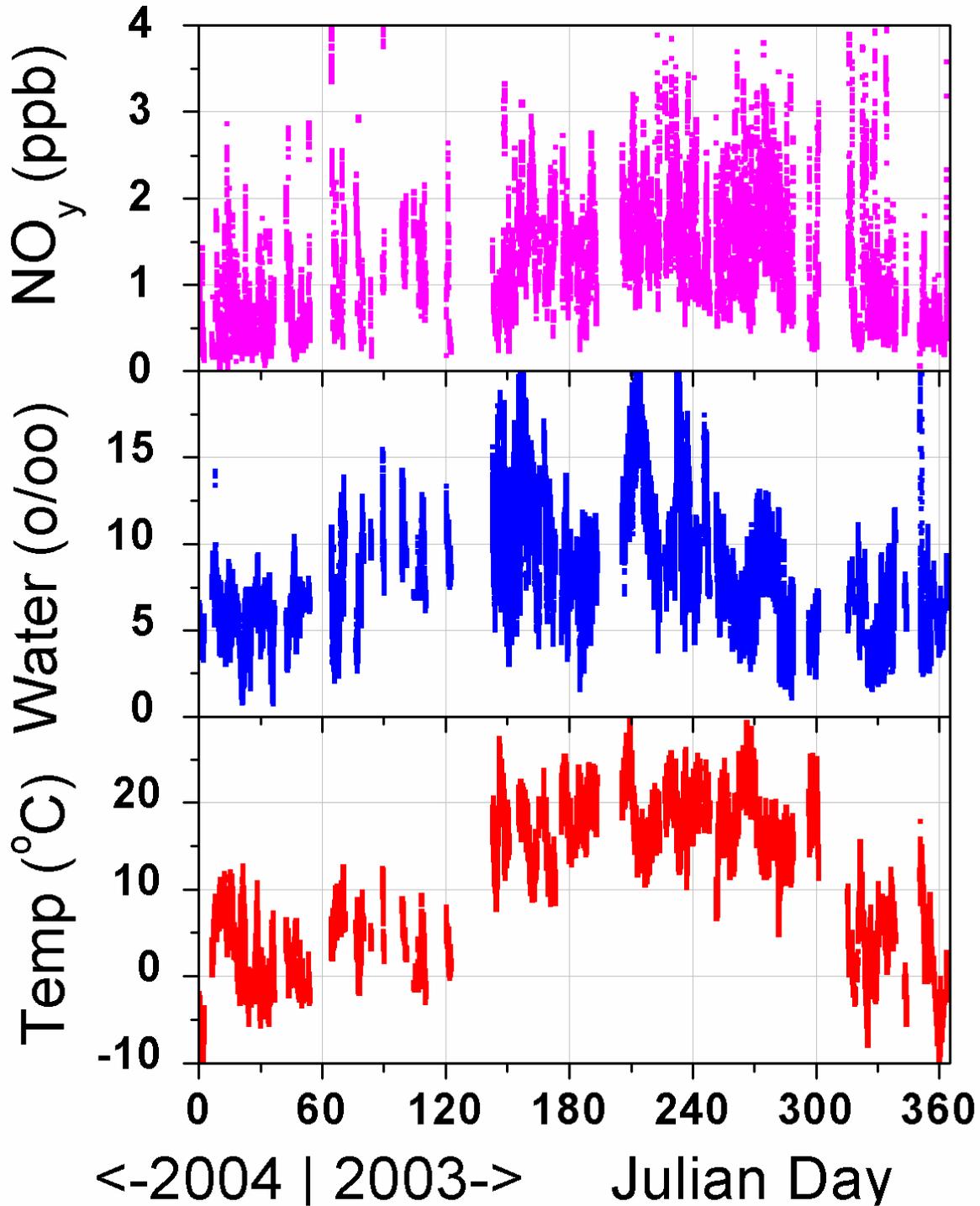
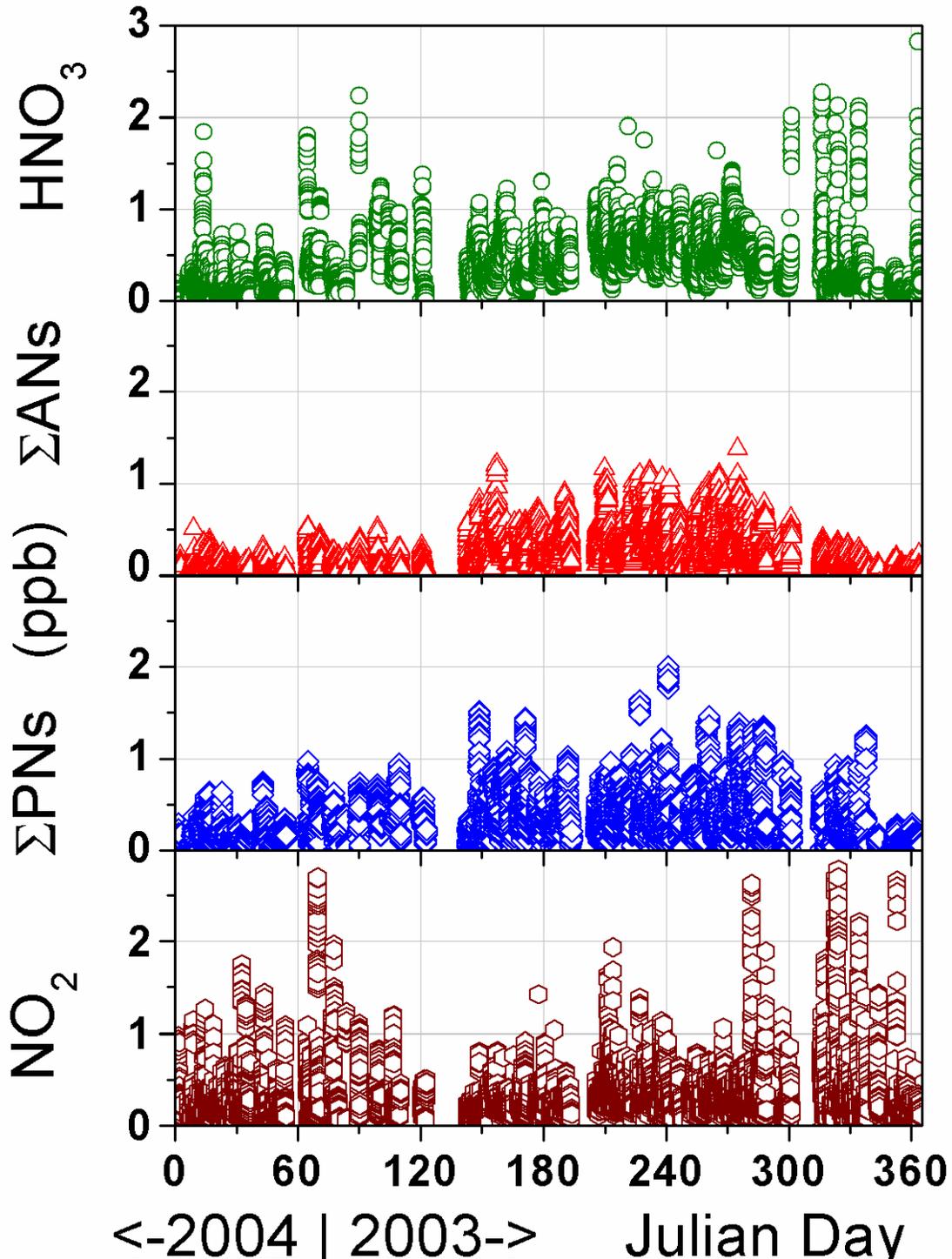


Figure 6-13. Annual record of individual NO_{y_i} species, NO_2 , ΣPNs , ΣANs and HNO_3 , measured at Big Hill. Data points represent a 3-minute average and all concentrations are reported in parts per billion by volume. Data acquisition began March 5, 2003 (day 64) and ended on Feb 23, 2004 (day 54); however, data are plotted on a calendar year basis to aid the interpretation of seasonal patterns.



6.7.3 Summer and Winter Timelines

In this section a summer week and a winter week will be examined in more detail to look at the variability in meteorological conditions and reactive nitrogen and ozone concentrations observed at Big Hill. **Figure 6-14** shows meteorological data from a typical summer week that starts with hot dry conditions, with a cooler wetter weather pattern moving in on day 232. The pattern of upslope – downslope flow is dominant on all days except the day of the weather shift. Daytime winds are close to 4 m/s, while at night wind speeds average around 1 m/s and are more variable in direction.

Figures 6-15 and 6-16 show the observations of ozone, total NO_Y and the individual NO_Y species for the same time period. The late afternoon maximum is consistent with transport of urban pollutants by daytime upslope flow along the western Sierra slopes. Interestingly, while NO_2 and ΣPN exhibit the characteristic afternoon peak on day 230, it is noticeably absent in both O_3 and ΣAN , a co-product of ozone. In general, the patterns of NO_Y and O_3 track each other during the summer months. HNO_3 is the only NO_Y compound which remains as abundant during the cooler, wetter conditions at the end of the week. While total NO_Y values do not decrease significantly at the end of the week, ozone is close to 30 ppb, and there is little apparent photochemical production.

Figure 6-17 shows the same meteorological variables as **Figure 6-14**, but for a week in late November. Winter conditions are less consistent than during the summer, but this data does demonstrate some widespread features in the data collected during the winter at Big Hill. The weather is cooler and the relative humidity is higher during this time period. Several days of strong flow from the southwest are interrupted on day 324 with a return to the more common upslope – downslope pattern but with weaker winds. **Figure 6-18** shows that the diurnal variability in ozone has diminished significantly and values for the week all lie between 45 and 65 ppb. Ozone is no longer correlated with NO_Y , which is likely influenced by burning events during days 322-324. **Figure 6-19** shows that strong flow from the west delivered high concentrations of NO_2 , HNO_3 (and likely particulate nitrate) to the Big Hill site, which is likely due to plumes from upwind burning events. At the end of the weeklong period a diurnal cycle in NO_2 , and especially ΣPN can be seen with the return to the usual flow pattern. Just as ozone concentrations have ceased to rise significantly above background values in the region, ΣAN remains very low throughout most of the winter.

Figure 6-14. Observations of relative humidity (%), temperature (°C), wind direction, and wind speed (m/s) from a typical summer week at Big Hill.

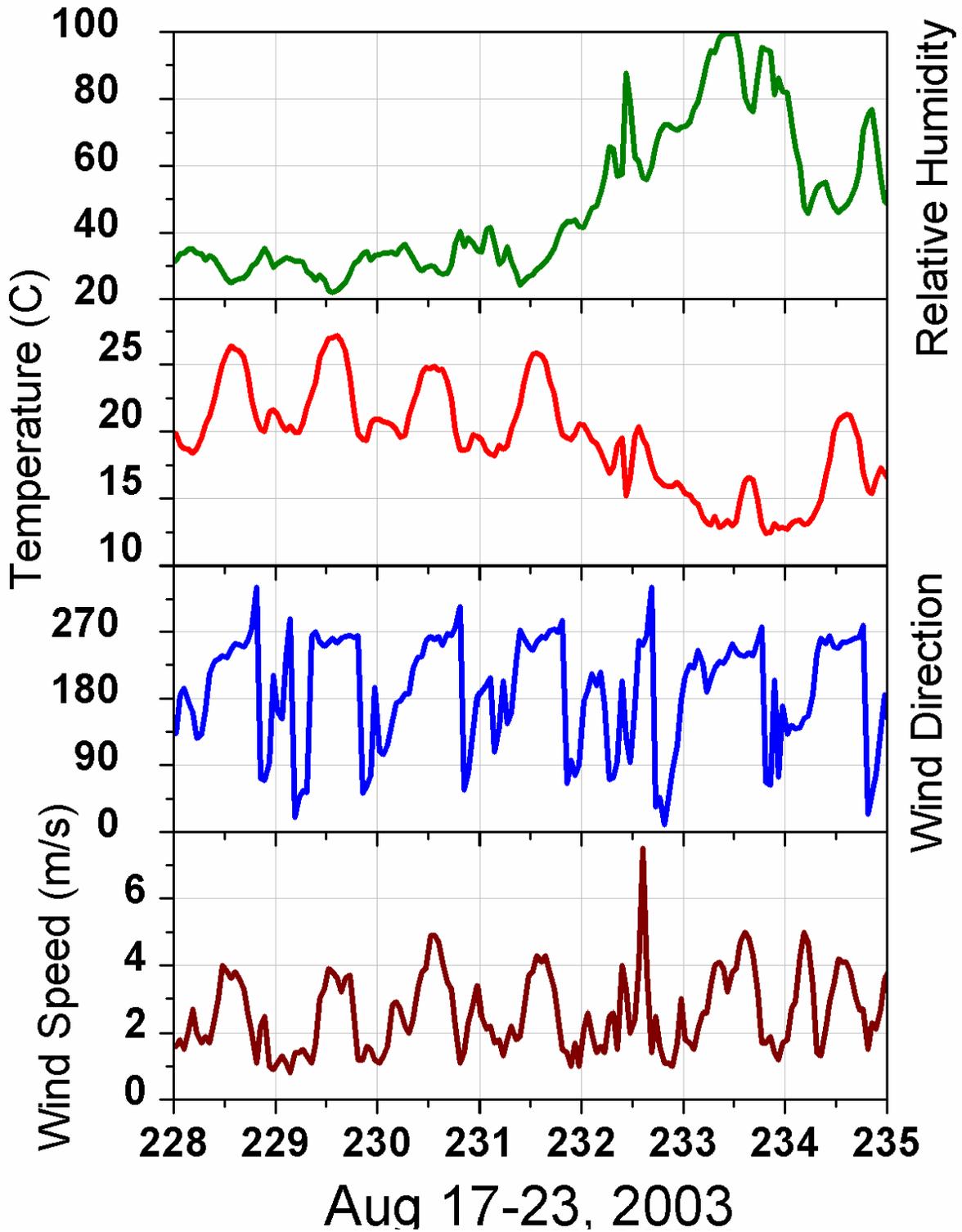


Figure 6-15. Concentrations of NO_y and O_3 (ppb) and PM_{10} ($\mu\text{g}/\text{m}^3$) from a typical summer week at Big Hill.

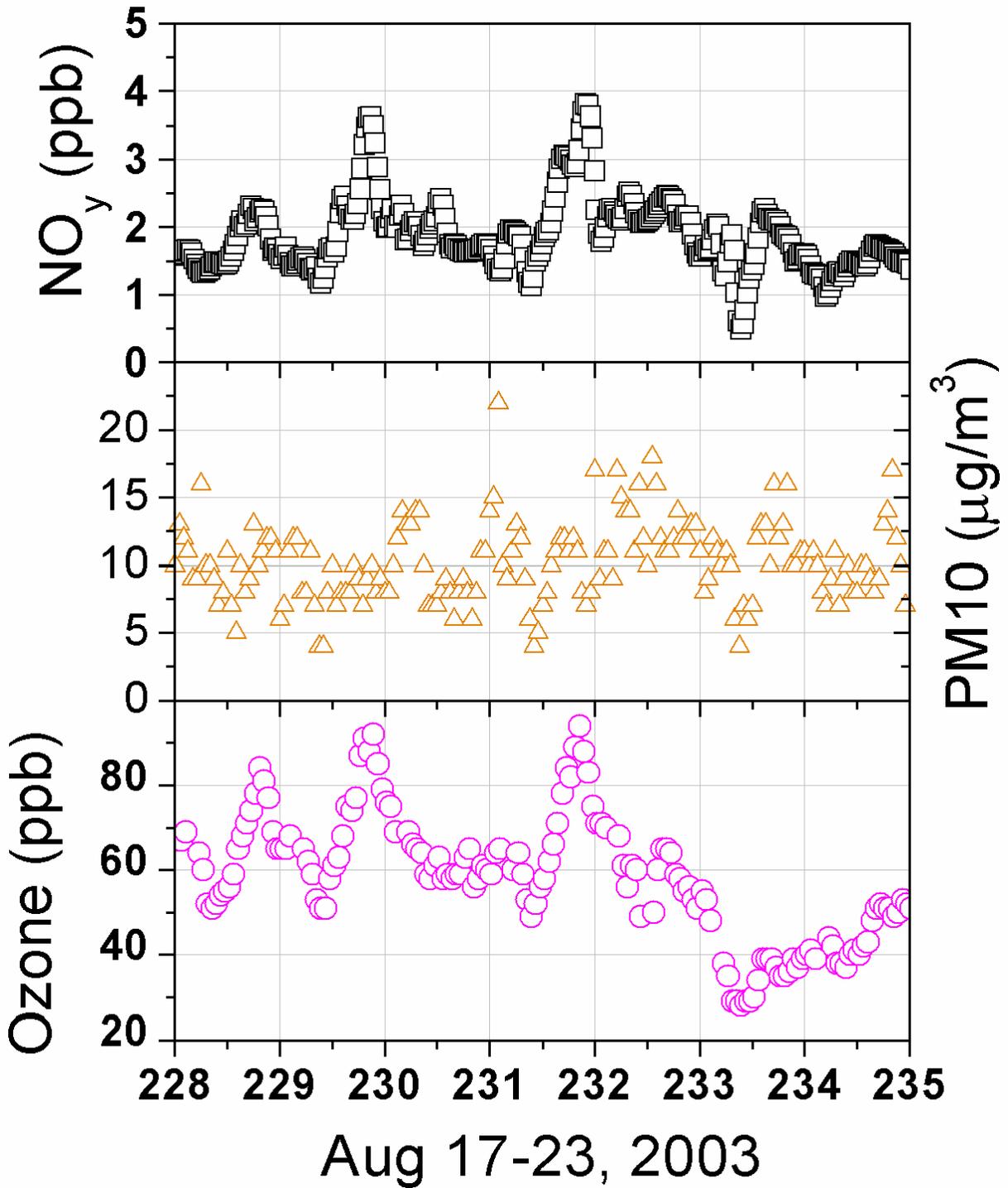


Figure 6-16. Concentrations (ppb) of NO_2 , ΣPNs , ΣANs and HNO_3 from a typical summer week at Big Hill.

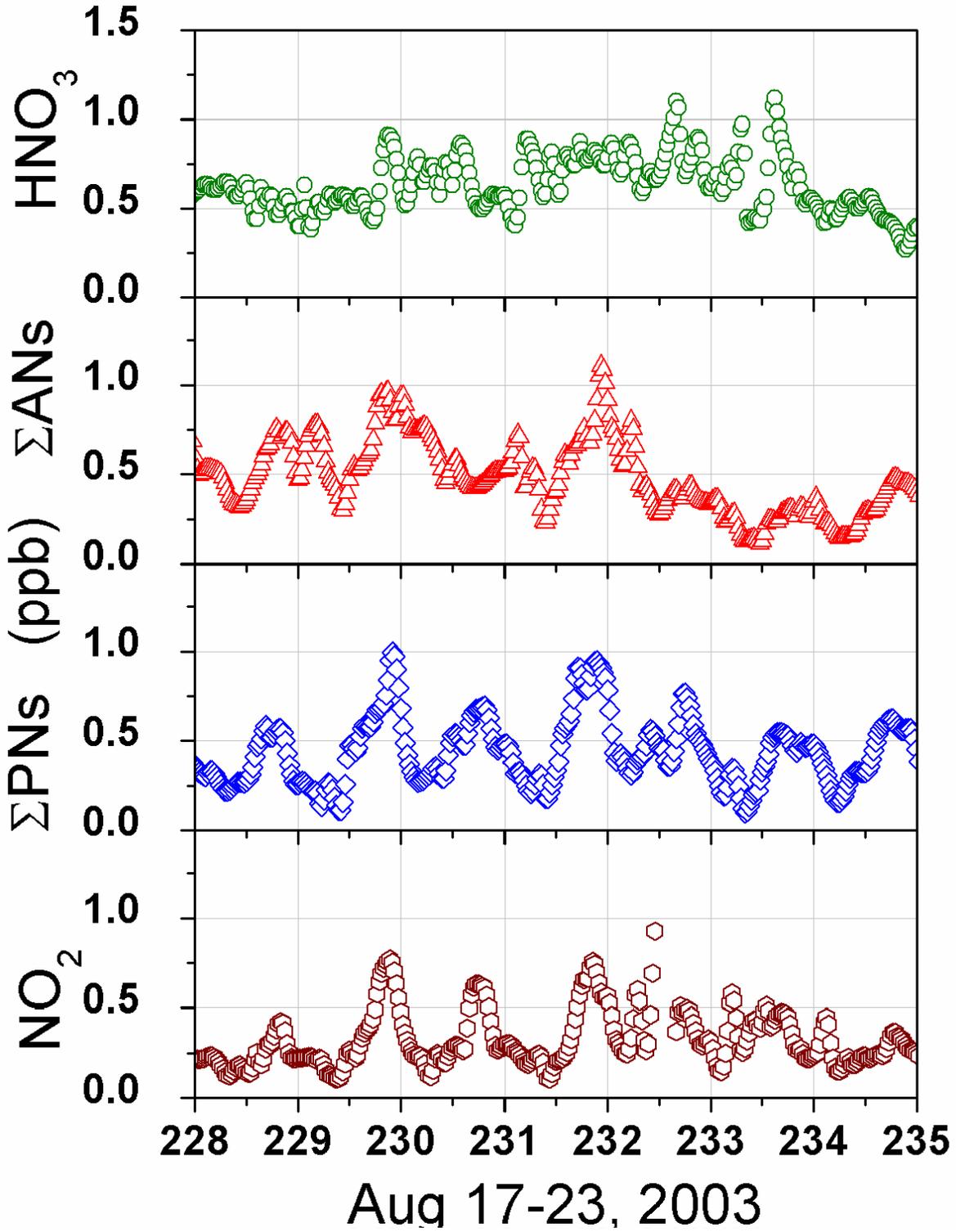


Figure 6-17. Observations of relative humidity (%), temperature (°C), wind direction, and wind speed (m/s) from a typical winter week at Big Hill.

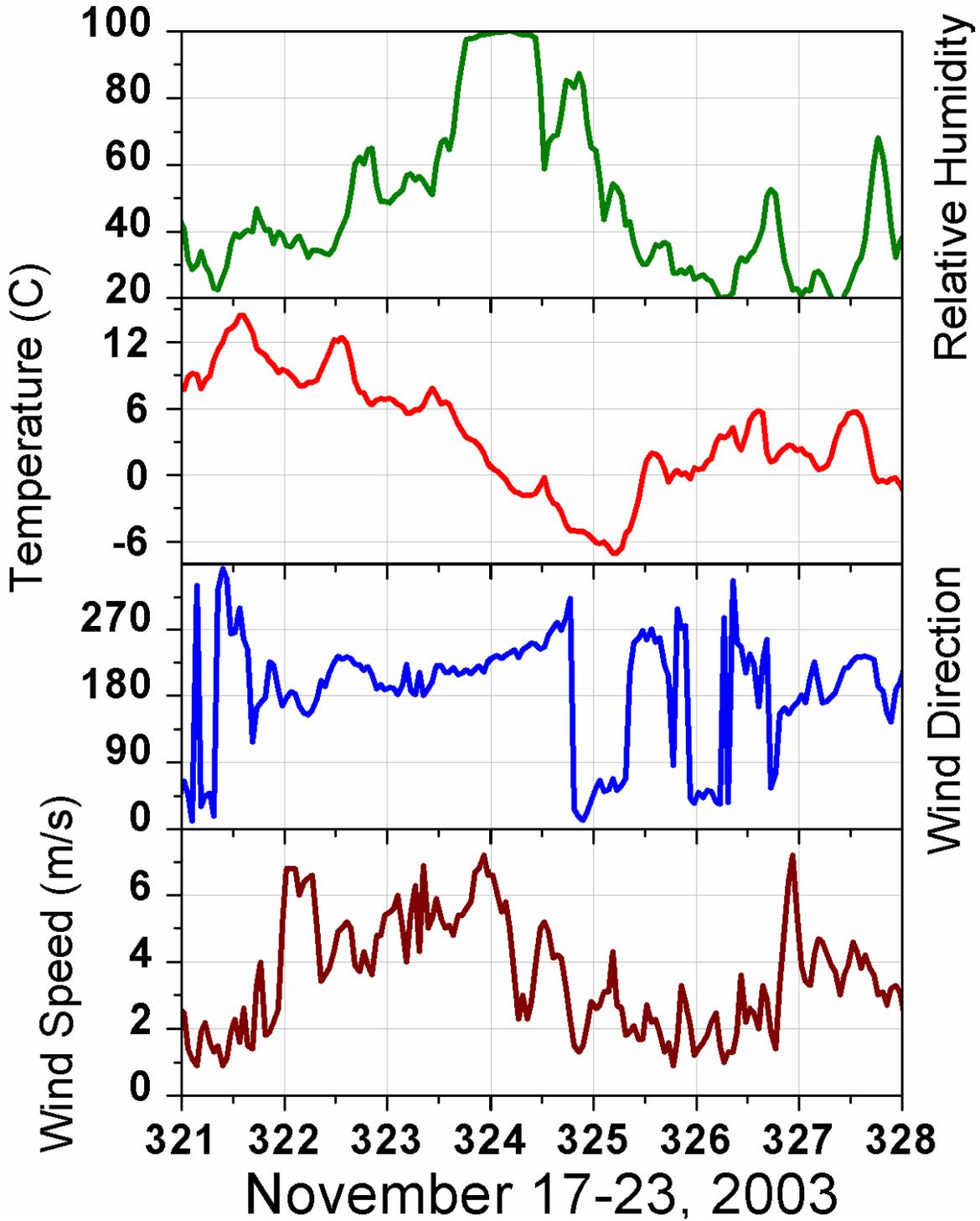


Figure 6-18. Concentrations of NO_y and O_3 (ppb), and PM_{10} ($\mu\text{g}/\text{m}^3$) from a typical winter week at Big Hill.

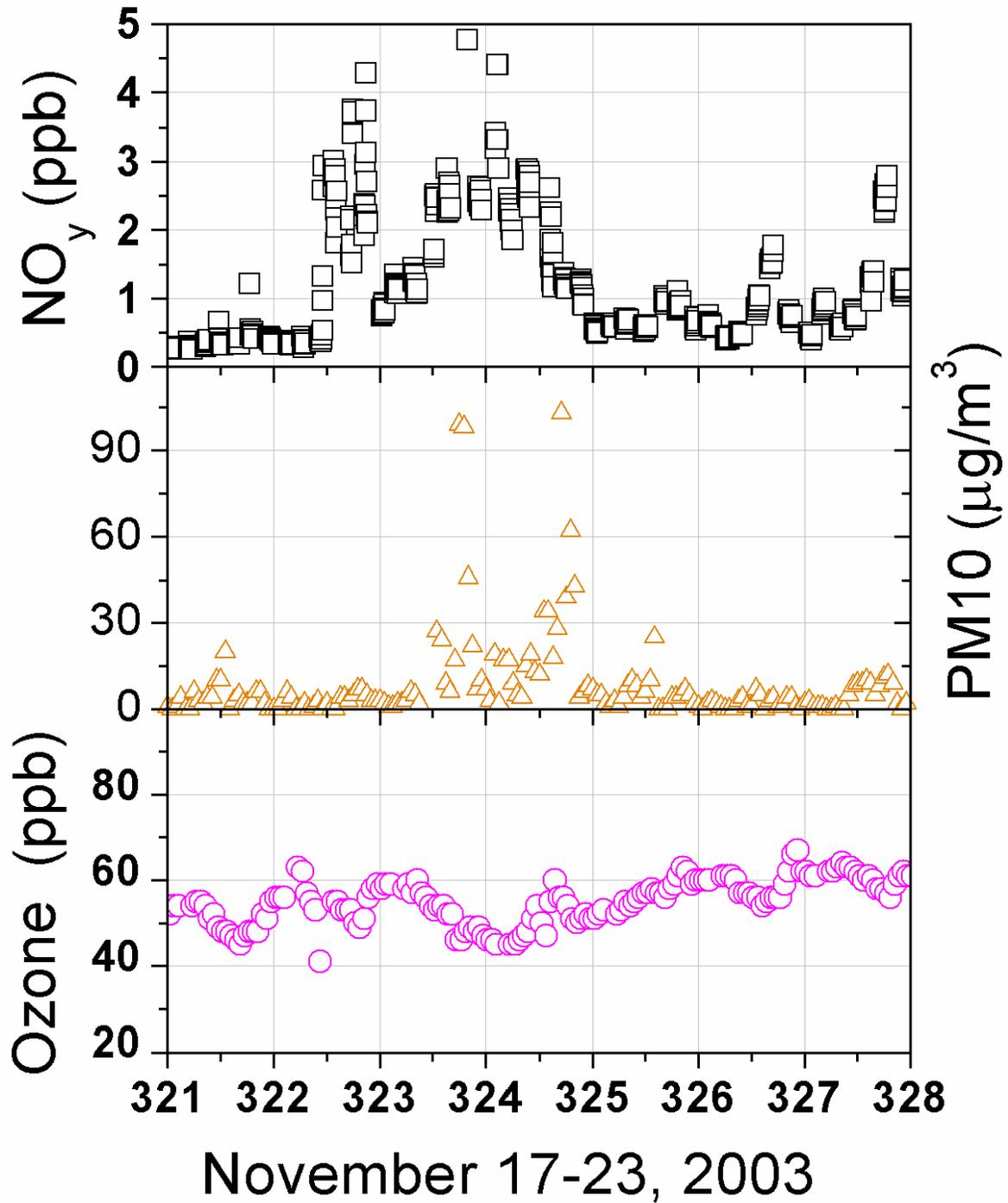
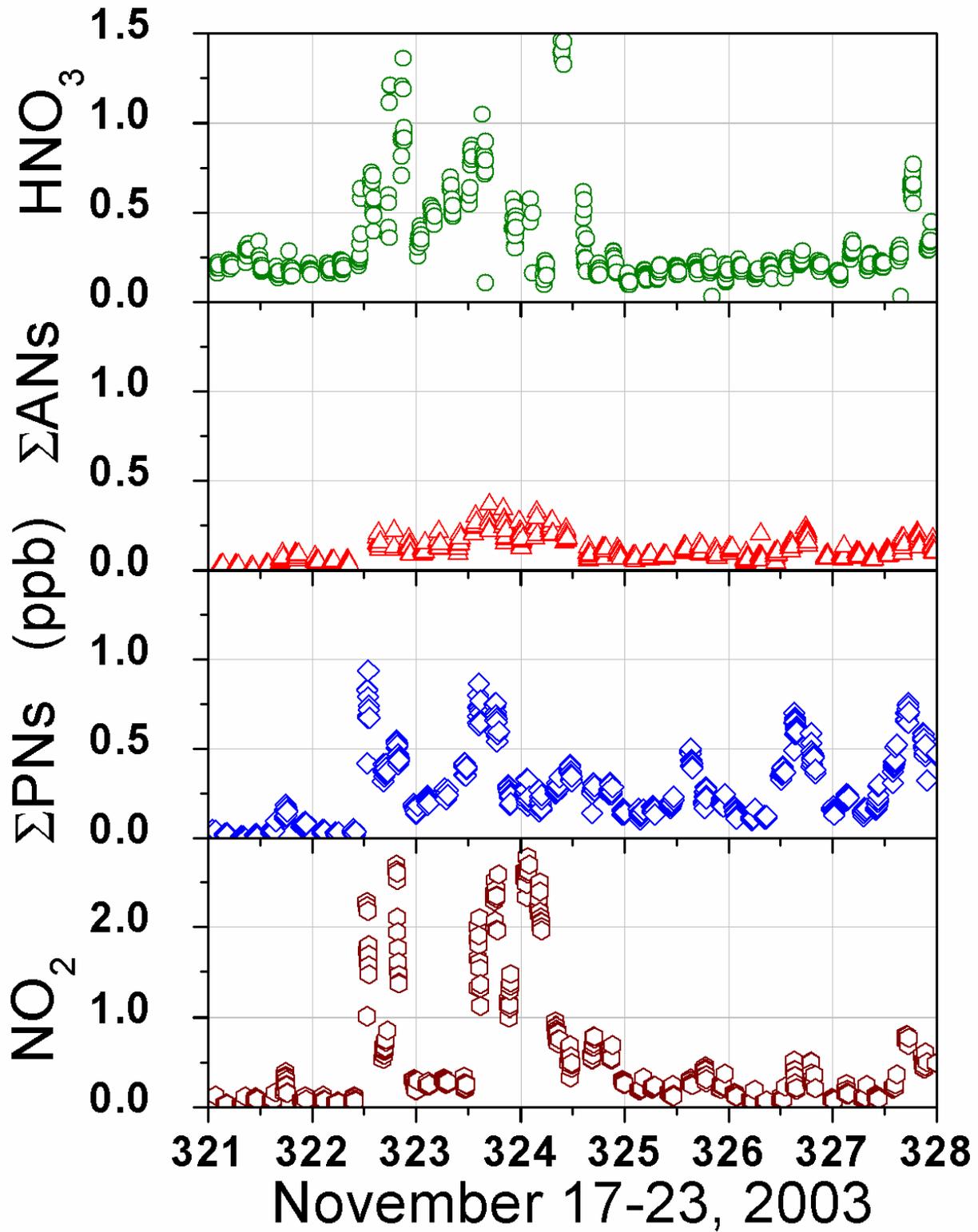


Figure 6-19. Concentrations (ppb) of NO_2 , ΣPNs , ΣANs and HNO_3 from a typical winter week at Big Hill. Note different axes on NO_2 panel.



6.7.4 Summertime Diurnal Profiles of Meteorology, Trace Gases and Particles

Figure 6-20 demonstrates the remarkably consistent meteorology experienced by the Big Hill site during the summer months (June through October in the following analysis). Temperatures were between 10 and 30 °C, with an average swing of approximately 7 °C between night and day. Rain was extremely rare and the relative humidity was generally between 25 and 50 %. With the exception of very few days, between roughly 9 am and 8 pm, the wind blows from the west. Wind direction during the night is more variable but is generally from the east or southeast. Wind speed maximizes during the afternoon at about 4 m/s, and is slowest in the early evening when the predominant flow is changing direction from upslope to downslope. Wind speeds during the night are more variable but are generally slower than during the day. The regularity of transport and climate variables is exploited to analyze the data statistically and increase our understanding of the important parameters involved in determining NO_y distribution in the region.

The summertime diurnal cycles in the individual reactive nitrogen species are shown in **Figure 6-22**. HNO_3 has a remarkably flat diurnal profile at the Big Hill site, in contrast to measurements made by TD-LIF at both Blodgett Forest and Granite Bay, a Sacramento suburb. At those sites, the profile of HNO_3 followed that of the sun, peaking in the middle of the day and decreasing to close to zero at night. The rationale behind the different pattern at Big Hill is two-fold: during the day HNO_3 at Big Hill is lower because the site is further from the NO_x source and the HNO_3 made along the way has had more time to deposit, while at night HNO_3 is higher than other surface sites because it is sampling descending air characteristic of the free troposphere, in which the HNO_3 formed has not had the opportunity to deposit.

Peroxy nitrates have a substantial diurnal profile at Big Hill, peaking between 2 pm and 6 pm at values more than double those observed during early morning hours. As we noted before ΣPN are formed through the association of a peroxy radical and nitrogen dioxide, but only those derived from acyl peroxy radicals are stable enough to survive in the atmosphere. The most common peroxy nitrate, peroxy acetyl nitrate (PAN), is the result of the photochemical oxidation of acetaldehyde in the presence of NO_x . Acyl peroxy nitrates act as a thermally labile reservoir for both RO_2 and NO_2 radicals and therefore on cooler days can sequester these radicals and reduce photochemical ozone production. Peroxy nitrates can also be responsible for transporting reactive nitrogen far from its original source, and act as a radical source upon subsequent decomposition. PAN is known to be acutely toxic to plants at high concentrations, but not much is known about the effects of chronic exposure at the ppb-level. Organic nitrates have relatively low water solubility and their contribution to reactive nitrogen deposition is not well understood.

Figure 6-20. Observations of relative humidity (%), temperature (°C), wind direction, and wind speed (m/s) by hour of day for the entire summer (June through October) at Big Hill. Individual half-hour data points for each day (open symbols) are overlaid by the averages for each half-hour observation (solid symbols).

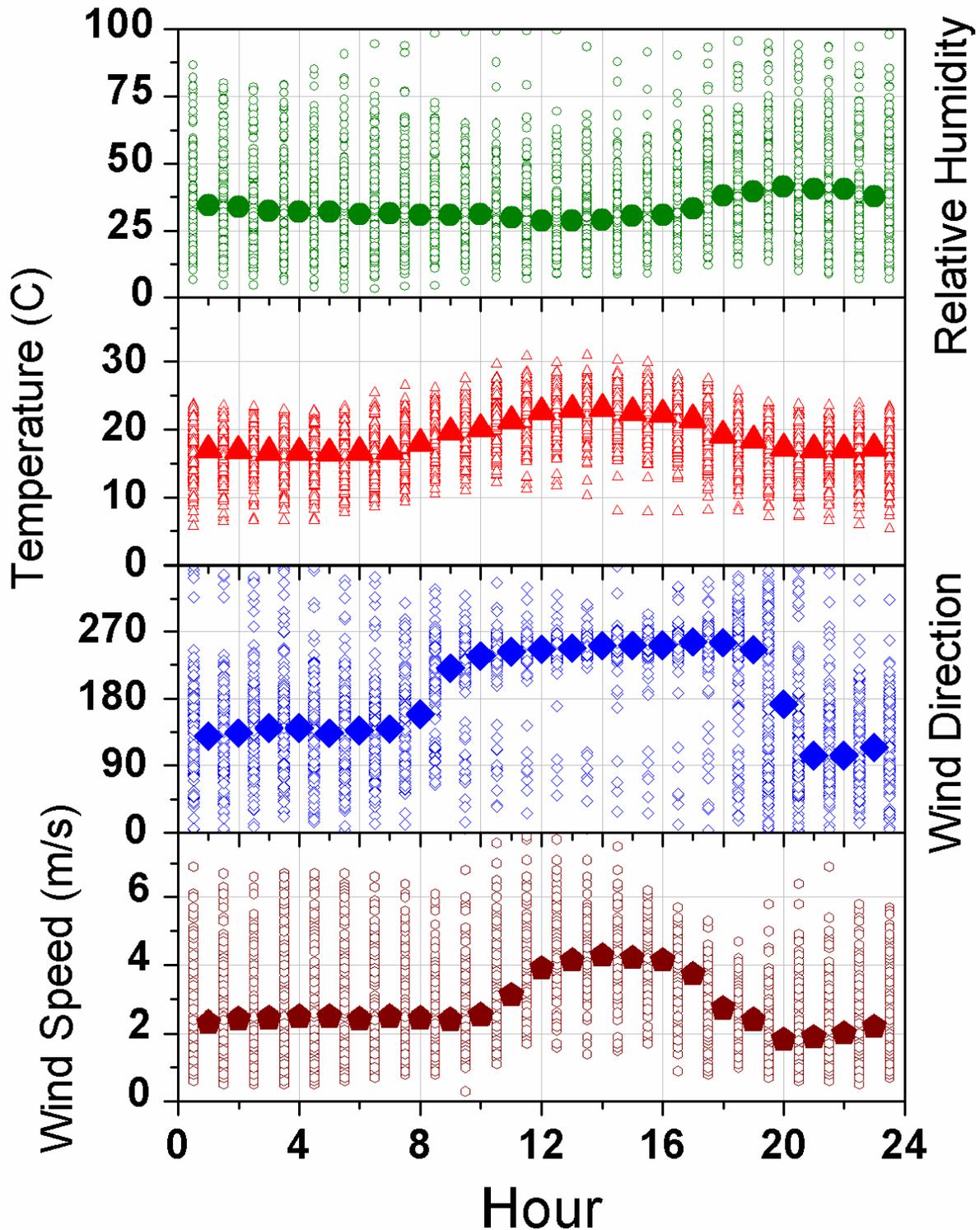


Figure 6-21. Diurnal profile of summertime concentrations of NO_y and O_3 (ppb), and PM_{10} ($\mu\text{g}/\text{m}^3$) at Big Hill. Individual measurements (open shapes) of O_3 and PM_{10} were made every hour at Big Hill, and the NO_y data has been averaged to half-hour points. The average value for every hour or half-hour is overlaid in the solid points.

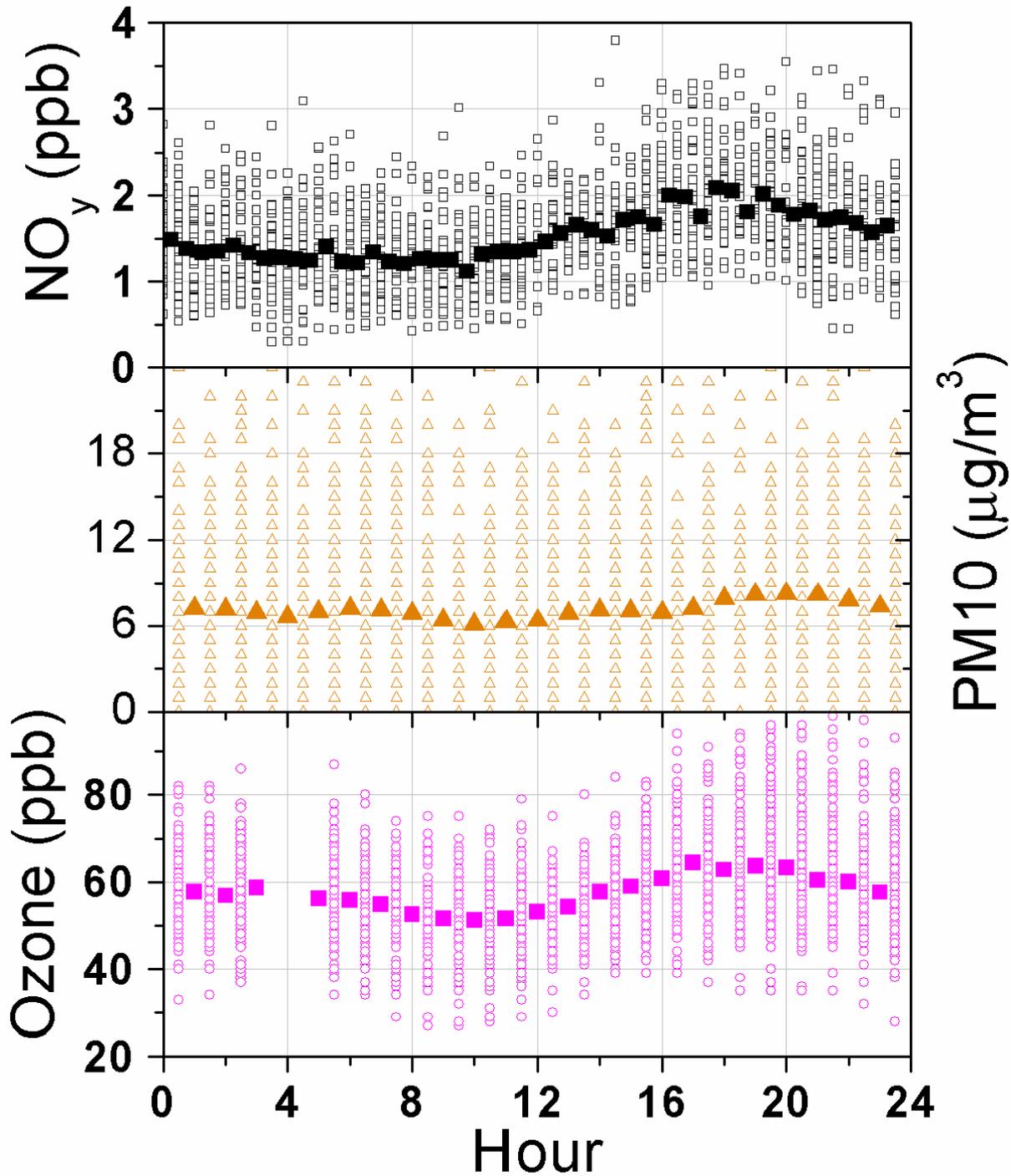
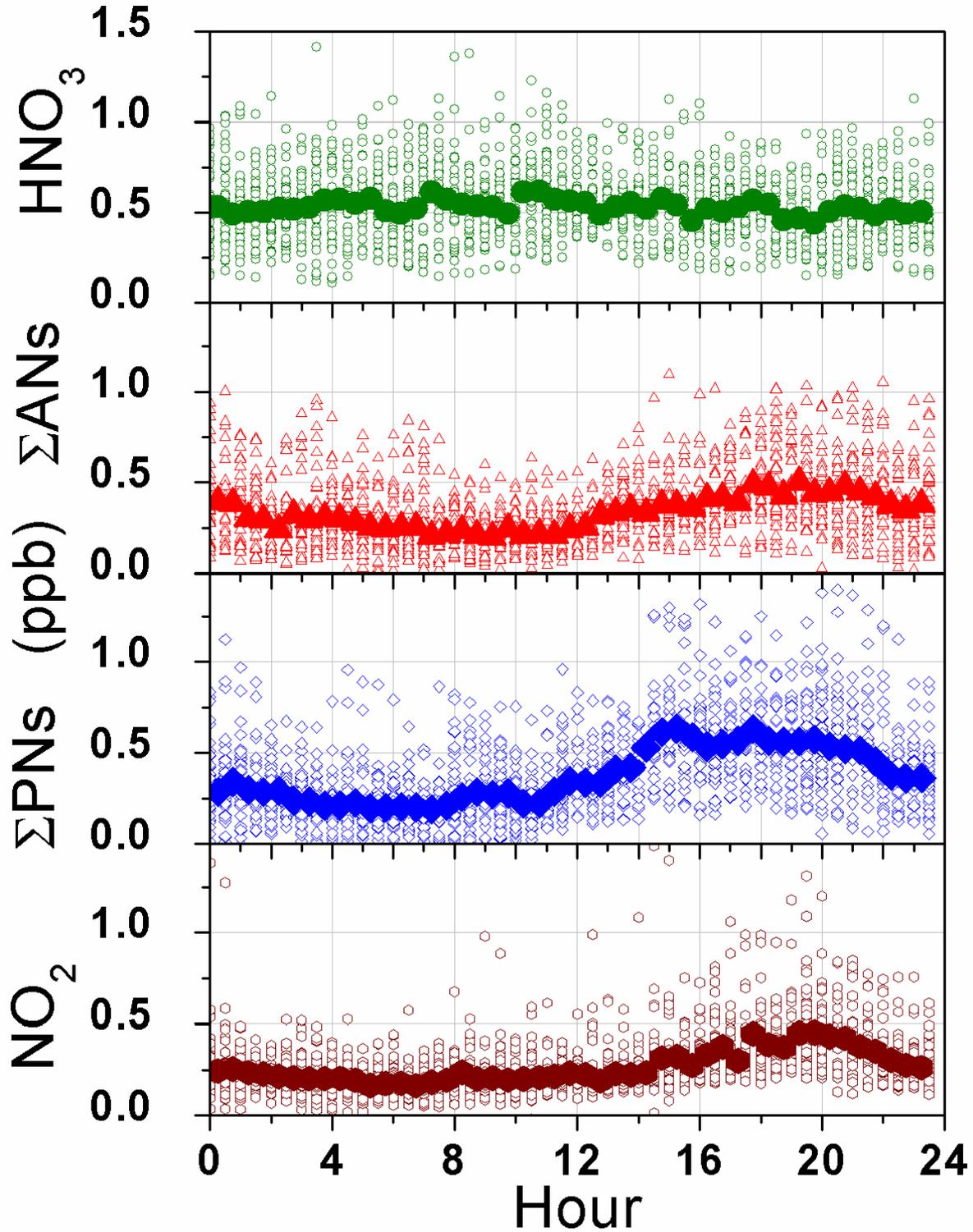


Figure 6-22. Diurnal profile of summertime concentrations (ppb) of NO_2 , ΣPNs , ΣANs and HNO_3 at Big Hill. Individual half-hour data points for each day (open symbols) are overlaid by the averages for each half-hour concentration (solid symbols).



Nitrogen dioxide also has a strong diurnal cycle and has the latest peak of all of the reactive nitrogen compounds at Big Hill. The delayed timing of the peak concentrations can be explained by a combination of transport and photochemistry. The NO_2 emitted into the plume takes around six hours to arrive at the Big Hill site. The air mass containing emissions from the Sacramento area often begin in the late morning to move up the slopes of the Sierra Nevada just when photochemical activity is peaking and the conversion of NO_x to higher NO_y species is maximizing. Air masses leaving Sacramento in the afternoon and arriving at Big Hill in the early evening experience lower levels of actinic radiation and therefore the latter part of the urban plume has a larger fraction of NO_2 remaining. Peak concentrations in this “tail” portion of the plume are roughly double the early morning minimum values.

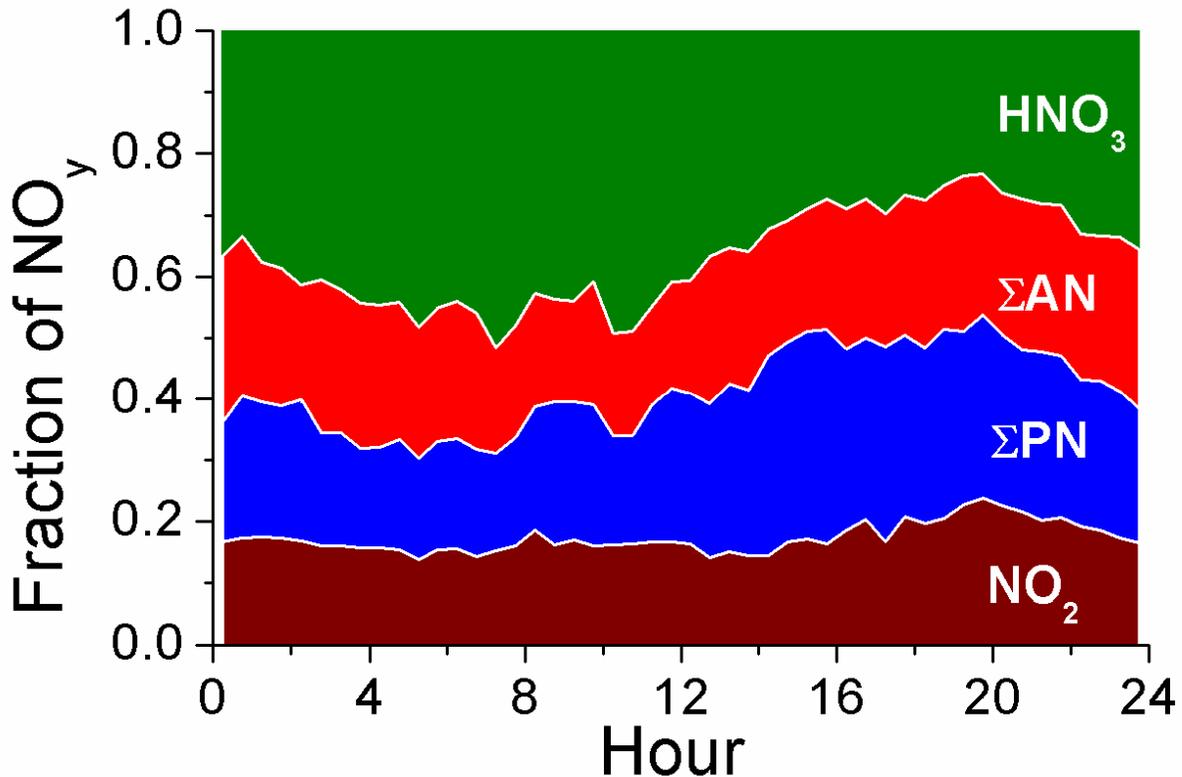
Figure 6-23 shows the partitioning of the NO_y budget at Big Hill by time of day. During the early morning hours, when the site experiences dry, clean air almost 40% of the NO_y is HNO_3 , with the other three classes of compounds contributing about 20% each. At the height of the plume in the late afternoon, the contribution of HNO_3 has shrunk to 25% and ΣPN have become more important. NO_2 never accounts for more than 25% of the NO_y measured at the site and is most important near sun set. The contribution of ΣAN varies from 15% of NO_y during the early morning hours to about 25% in the evening. Peroxy nitrates are most important at the site during mid-afternoon, when they make up almost one third of the reactive nitrogen.

6.7.5 Summertime Distribution of Reactive Nitrogen and Correlation with Other Variables

Changes in climate can be expected to drive differences in both transport and chemistry, affecting the geographical and temporal extent to which the urban plume affects remote sites, and the chemical partitioning with the plume. One of the most important climate variables that govern the distribution of reactive nitrogen oxides is the temperature. The summertime data was divided into two sets of days, half of which had a maximum daytime temperature above 20 °C and half of which did not. The average amount of NO_y in the plume was 1.9 ppb on both of the two sets of days, suggesting that local temperature is not a good indicator of the transport efficiency of the plume. However, the partitioning of reactive nitrogen among its constituent species is strongly influenced by temperature as shown in **Figure 6-24**. The top panel shows the partitioning among NO_y species arriving at the site between 1 pm and 8 pm on days when the maximum temperature exceeded 20 °C. Comparison with cooler temperature data displayed in the bottom panel shows that while NO_2 has undergone similar amounts of photochemical processing under both sets of conditions, lower temperatures favor the accumulation of peroxy nitrates over the production of alkyl nitrates and nitric acid. Peroxy nitrates account for over one third of the reactive nitrogen under the cooler temperatures, sequestering a substantial amount of reactive nitrogen in this reservoir. The reduced contribution of alkyl nitrates at lower temperatures is consistent with fewer RO_2 and NO_x radicals being available to react to form ozone. Indeed, the mean ozone concentration in the plume is 64 ppb on the hot days and 58 ppb on cool days, suggesting that temperature plays a crucial role in determining the availability of alkyl nitrates for ozone production. Another facet of the temperature effect may be the

increased emissions of many biogenic VOC at higher temperatures. A shift in the hydrocarbon composition toward longer chain compounds as opposed to carbonyl compounds could favor the production of alkyl nitrates over peroxy nitrates.

Figure 6-23. Fractional NO_y speciation by time of day during summer months at Big Hill.



In **Figure 6-25**, the correlation between total reactive nitrogen and the mole fraction of water is shown. This relationship is not as clear at Blodgett Forest, where it is likely that the transpiration of nearby vegetation has a strong influence on the water budget at the site. In contrast, water vapor appears to be a good indicator of transport of polluted air masses at a high elevation site such as Big Hill. Observations during the night indicate that the descending air, whether from aloft or mountain slope drainage, tends to be much drier and have reduced total reactive nitrogen. The absolute humidity of the air mass records the degree of mixing that the relatively moist, polluted urban plume has undergone in transit to the high elevation site.

Figure 6-26 depicts the remarkable correlation between reactive nitrogen and ozone at the Big Hill monitoring site throughout the summer. Observations made during afternoon upslope flow are highlighted in orange and show that higher values for ozone and NO_y occur when the urban plume is influencing the site. Other high values are measured shortly after the wind has shifted direction and the air passing back by the site is still characteristic of plume air.

Figure 6-24. Distribution of NO_Y during daytime upslope airflow at Big Hill. The data were separated by temperature such that the top chart includes data from days on which the daytime maximum temperature at the site exceeds 20°C , while the bottom chart shows data from cooler days on which the temperature was never higher than 20°C .

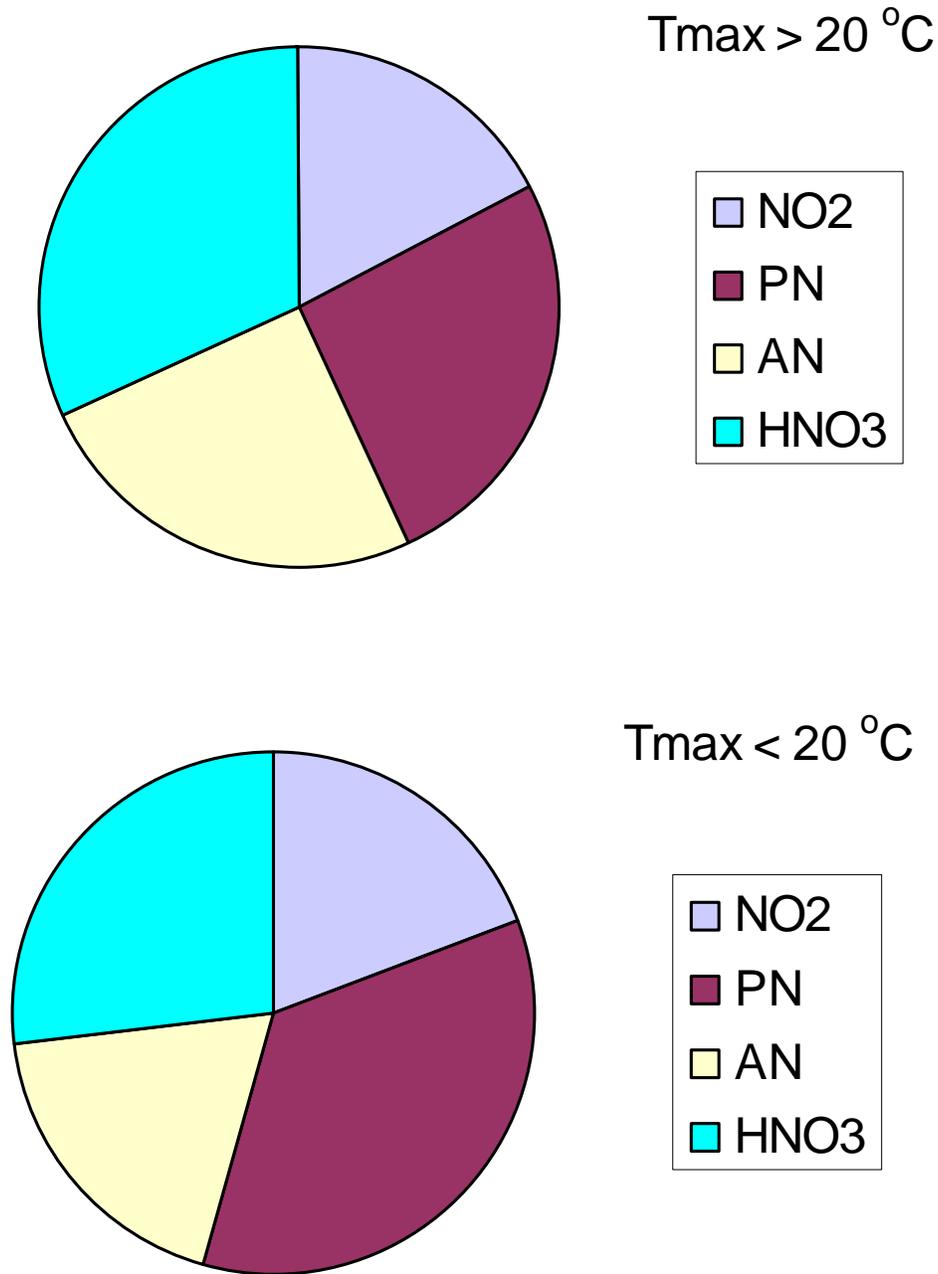
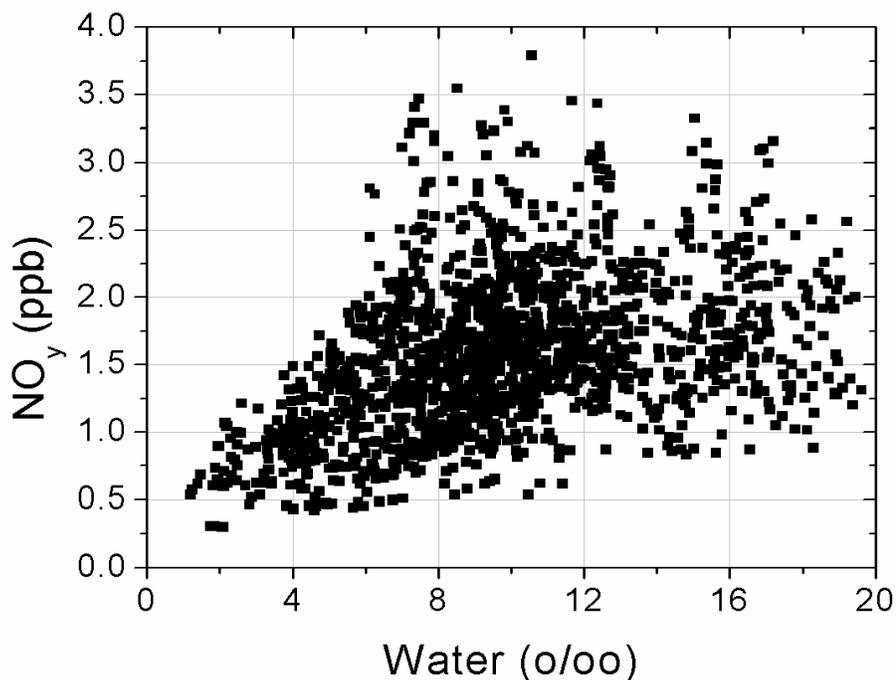


Figure 6-25. Relationship between reactive nitrogen (ppb) and mole fraction water vapor (parts per thousand; ‰) during summer months at Big Hill.

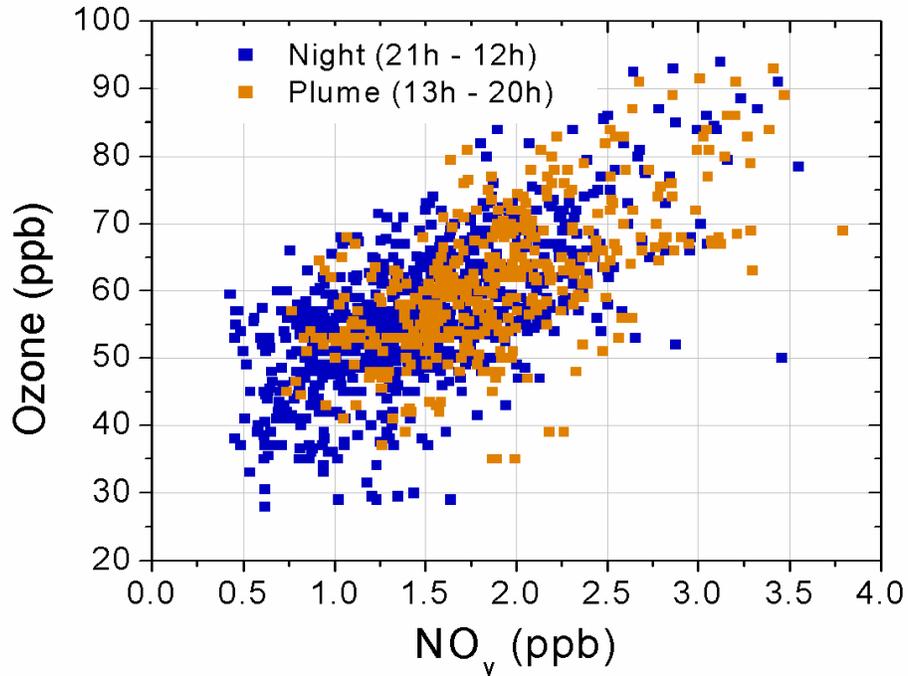


The relationship between NO_Y and ozone is expected because both are derived from precursor emissions of nitrogen oxides. While ozone can be anti-correlated with NO_X in urban areas with high NO concentrations, we expect ozone production to be limited by the availability of nitrogen oxides in remote areas like Big Hill. Minimum values of NO_Y (< 1 ppb), which occur in the early morning hours, are associated with ozone levels between 35 and 60 ppb, while maximum values of NO_Y (> 2.5 ppb) are associated with ozone between 65 and 95 ppb. Clearly, the chemistry and transport patterns responsible for transforming and transporting nitrogen oxides to the western slope of the Sierra Nevada also have similar effects for the reaction products, including ozone and total reactive nitrogen.

A great deal of insight can be gained by comparing observations made at Big Hill to corresponding measurements at the Blodgett Forest site. As mentioned above, both sites lie along the Sacramento – Lake Tahoe transect, but Big Hill is at a higher elevation, a greater distance from the city, and has less vegetation and cooler temperatures. Our analyses of the diurnal cycles at the two sites suggest that they sample similar air masses during upslope flow and we restrict the comparison to the times between 1 pm and 8 pm when both sites are strongly influenced by the Sacramento urban plume. **Figures 6-27 a-f** show the frequency distributions for the individual reactive nitrogen species, total NO_Y and O_3 for both the Big Hill and Blodgett Forest sites. In the case of NO_2 , Big Hill values (median 0.25 ppb) are on average less than half those of Blodgett Forest with significantly fewer half-hour periods with more than 1 ppb. This means that the dilution and photo-oxidation of NO_2 in the plume is

quickly reducing its concentration several hours downwind of Sacramento. In this region, ozone production is expected to be NO_x -limited so it can also be inferred that instantaneous ozone production rates drop off quickly between Blodgett Forest and Big Hill.

Figure 6-26. Relationship between ozone (ppb) and reactive nitrogen (ppb) during summer months at Big Hill. Observations made during upslope flow in the plume are in orange.



Peroxy nitrates have a wider probability distribution at Blodgett Forest than at Big Hill and higher median observations. While absolute ΣPN concentrations are higher on average at UC-BFRS, the ratio of peroxy nitrates to NO_2 is actually higher at Big Hill, likely due to the lower temperatures, stabilizing the reservoir species. This confirms that, as the plume is advected, it is being significantly diluted with air that has less NO_2 and ΣPN , and that the photochemical oxidation of NO_2 to peroxy nitrates acts as a permanent sink of NO_x when temperatures are cool. The probability distributions of alkyl nitrates are extremely similar at the two sites, but for different reasons. The breadth in the distribution at Big Hill derives from a stronger diurnal cycle than at Blodgett Forest, where it appears to result from more day-to-day variability.

Nevertheless, detailed comparison of the observations of alkyl nitrates at the two sites suggests that as a group these compounds are lost very slowly to deposition but are diluted when mixed with air from the free troposphere. Correlations between alkyl nitrates and CO and O_3 show that they are associated with polluted, upslope air and are formed in conjunction with ozone during photochemical activity. The deposition of most

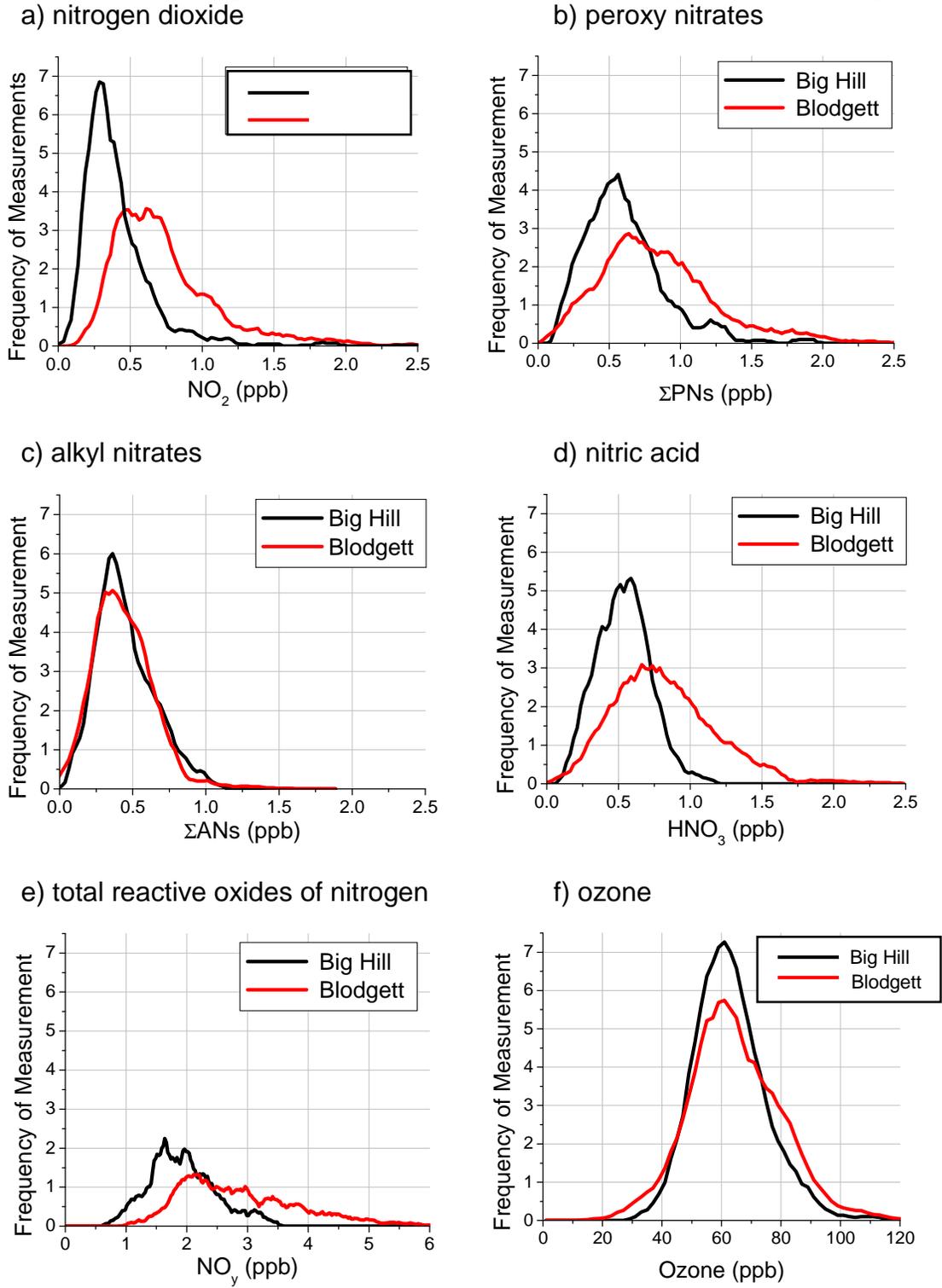
alkyl nitrates appears to be slow enough that a substantial fraction of what is produced in the plume stays in the atmosphere. From the perspective of nitrogen deposition, not enough is known about the behavior of these compounds at the surface.

The fact that HNO_3 concentrations are similar, regardless of the wind direction at Big Hill suggests that there is no significant advection of HNO_3 from Sacramento to the Lake Tahoe Air Basin. HNO_3 concentrations are lower and less variable at Big Hill compared to Blodgett Forest. However, similar to the peroxy nitrates, considered in a relative sense, HNO_3/NO_2 in the plume is higher at Big Hill. The flat diurnal profile for HNO_3 at Big Hill suggests that this site is far enough from fresh NO_x sources that much of the HNO_3 produced during oxidation has already had the chance to deposit before reaching high elevation sites at the surface. Blodgett Forest has high daytime NO_2 concentrations capable of generating strong local production of HNO_3 , but HNO_3 production at Big Hill is less efficient both because the plume is more dilute and because lower temperatures lead to the sequestration of NO_2 by peroxy nitrate formation.

The distribution of total NO_y at the two sites reflects the proximity of Blodgett Forest to Sacramento in both the higher average and the greater variability in concentrations. At Blodgett Forest, the total NO_y in the plume varies between 1-5 ppb, whereas at Big Hill it ranges from 0.5-3.5 ppb. The data used in this analysis was not limited to days on which there was persistent upslope flow, thus some of the lower numbers likely result from days on which the urban plume did not influence the site. The greater variability in total NO_y compared to any of its constituent species shows that the variability in NO_{yi} is not driven by differences in partitioning among the available reactive nitrogen, but more importantly in the extent to which the total urban emissions are influencing these remote sites. It is not clear from the meteorological observations, aside from wind direction, which conditions result in higher concentrations of reactive nitrogen being transported in the boundary layer along the western slope of the Sierra.

Finally, the distribution of ozone with the urban plume is shown for each site in **Figure 6-27f**. Remarkably, the median ozone concentration at each site is very similar, but Blodgett Forest shows both more low values and more high values. The similarity between the two sites results partly from the fact that daytime ozone values are generally not more than a factor of two higher than the regional background, so mixing with the background drives concentrations toward a common value. From a regulatory standpoint, the Blodgett Forest site is much more likely to exceed the federal 8 hour ozone standard because of the significantly higher number of observations above 85 ppb. Comparison of ozone at the two sites suggests that the efficiency of ozone production has slowed considerably by the time the plume has reached Blodgett Forest, and it can no longer match the decreases in ozone due to dilution and deposition as the air moves toward Big Hill. This information can be used to ascertain the extent of influence of the urban plume on ozone in the region.

Figure 6-27 a-f. Frequency distributions of half-hour average NO_{y_i} and O_3 concentrations during summer in the urban plume at Blodgett (red) and Big Hill (black).



6.7.6 Observational Constraints on the Transport of Nitrogen Oxides

Table 6-1 compiles data from the frequency distributions shown in **Figure 6-27** for the Blodgett Forest and Big Hill sites. Because the data sets are comprehensive and the meteorological conditions have predictable recurring patterns, it is possible to treat the data statistically. We have combined these data sets, along with observations made in the summer of 2001 at Granite Bay, a suburb of Sacramento near Folsom, to constrain a Lagrangian model of the plume that includes photochemistry, deposition, dilution, and emissions as it is advected eastward from the urban area over the western slopes of the Sierra. **Figure 6-28** shows the concentrations of NO_2 and NO_x (NO_y , which would be $\geq \text{NO}_x$, was monitored at the special study sites) as the air moves along the Sacramento – Tahoe transect. Concentrations were averaged for different time periods depending on the location, reflecting the Lagrangian nature of the analysis, and using observed wind speeds to establish the transit time of the plume.

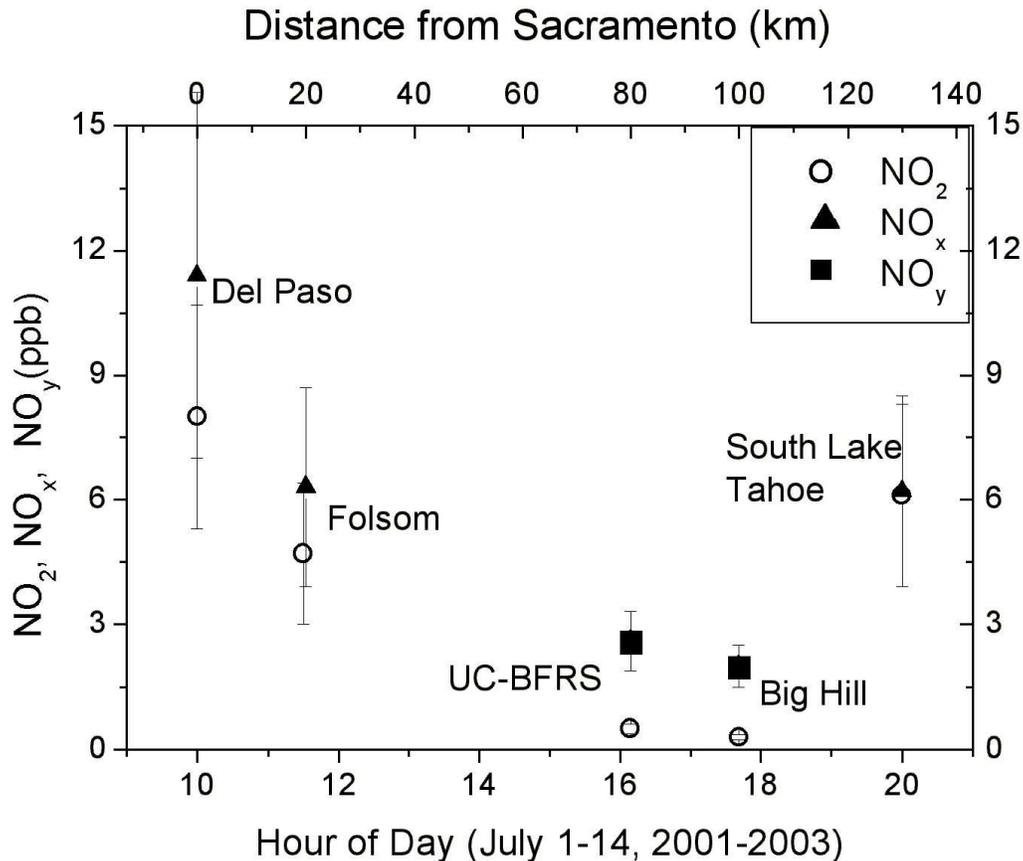
Table 6-1. Concentration statistics for 1 pm – 8 pm, June-October, at Blodgett Forest and Big Hill. For each pollutant listed, the median, 5th and 95th percentile values have been calculated in ppb.

Species	Blodgett Forest			Big Hill		
	Median (ppb)	5 th percentile	95 th percentile	Median (ppb)	5 th percentile	95 th percentile
NO_2	0.63	0.30	1.70	0.33	0.16	0.78
ΣPN	0.79	0.27	1.75	0.55	0.21	1.07
ΣAN	0.41	0.15	0.77	0.39	0.16	0.78
HNO_3	0.79	0.33	1.48	0.53	0.25	0.85
NO_y	2.68	1.57	4.92	1.84	1.05	2.99
O_3	61.5	40.7	88.4	60	45	82

Using observations of anthropogenic VOC from Granite Bay and Blodgett Forest in 2001, we have confirmed the estimate for a dilution rate of approximately 0.25/hour found by Dillon (2002). Analysis of the NO_2 , ΣPN , ΣAN , HNO_3 and O_3 measurements provides constraints on the rates of further NO_x emissions, photochemical oxidation, and deposition within the urban plume as it moves up the western slope of the Sierra Nevada. HNO_3 production is most efficient at the high NO_x concentrations of Sacramento, but as the plume moves eastward and biogenic emissions of VOC are added, the production of organic nitrates begins to compete for NO_x . Between Folsom and Blodgett Forest, there are relatively high production levels of all forms of NO_z ($= \Sigma\text{PN} + \Sigma\text{AN} + \text{HNO}_3$) because of the optimal balance between NO_x and RO_x precursors. Comparison of Blodgett and Big Hill data suggest that the fate of ΣPN depends on the temperature, that ΣAN are well-conserved within the plume, and that deposition of HNO_3 is the most important sink of total reactive nitrogen. The lifetime to

deposition of HNO_3 in the plume is estimated at less than five hours and since most of the production occurs close to the city, a considerable amount of the HNO_3 present in the plume has been lost before it arrives at Big Hill. Our observations suggest that a substantial amount of mixing occurs across the boundary between the surface layer and the free troposphere, which implies that the plume is responsible for exporting substantial amounts of reactive nitrogen that can be transported above the continent at high altitudes. Clearly, local emissions from South Lake Tahoe dominate over the contribution of the processed and diluted reactive nitrogen present in any air masses that may reach the Tahoe Basin. To quantitatively assess the relative importance of upwind transport and local emissions in the Tahoe Basin as a whole would require analysis of measurements from other Tahoe sites further from roads and other intense NO_x sources.

Figure 6-28. Reactive nitrogen observations along the Sacramento-Tahoe transect. The distance from Sacramento was multiplied by an average wind speed of 3.5 m/s to estimate the time the air mass would arrive at each site after leaving Del Paso at 10 am. Observations at each site were averaged for an hour around the estimated time. For example, UC-BFRS lies 80 km downwind of Del Paso, and NO_2 and NO_y observations between 3 pm and 5 pm were averaged to produce the points reported at 4 pm. The error bars represent the standard deviation of the average.



6.8 Ozone

State law (H&SC 39610) directs ARB to assess the role that pollution transport has on violations of the State ozone standard, namely, the contribution of ozone and ozone precursors in upwind regions to the ozone concentrations in downwind regions. Over the last decade, ARB has published a number of assessments describing the transport relationships among California regions. The last such assessment was published in 2001. Past ARB transport assessments have found the Broader Sacramento Area to have an overwhelming transport impact on several counties located within the Mountain County Air Basin, including two that border the Lake Tahoe Air Basin (Nevada County and the eastern portion of Placer County). No assessment has been made of ozone transport into the Tahoe Basin because the 1-hour California Ambient Air Quality Standard for ozone is not being violated. However, with the recent adoption of an 8-hour California Ambient Air Quality Standard (0.070 ppm), ambient data show that ozone concentrations in the Tahoe Basin exceeded this standard multiple times in the last three years. As a result, we expect the Lake Tahoe Air Basin will be designated as non-attainment for ozone when State area designations are reviewed in fall 2006. The designation of the Lake Tahoe Air Basin as non-attainment with respect to the State 8-hour ozone standard will then trigger a formal assessment of the relative contribution of upwind emissions to ozone concentrations in the Lake Tahoe Air Basin that violate State ozone standards.

Historical (Duckworth et al., 1979), routine (Echo Summit), and LTADS (Big Hill) data for ozone in the Sierra Nevada west of Tahoe indicate infrequent ozone concentrations approaching ambient air quality standards and even less evidence of the one-day transport of such concentrations into the Tahoe Basin. Furthermore, the duration of upslope winds when ozone concentrations are high is generally too short to affect the transport of pollutants from the Central Valley to the Tahoe Basin in one day (Duckworth, 1979; Carroll, 1998). This is because high ozone concentrations occur downwind of Sacramento under light wind conditions and the mesoscale meteorological pattern of upslope winds during the afternoon would reverse to downslope winds in the evening before the high concentrations could transport the full distance to Tahoe. The LTADS (2003) ozone data summaries (frequency, timing, and spatial distribution of moderate to high concentrations) presented in Chapter 3 indicate that the transport of ozone concentrations greater than 70 ppb to the Tahoe Basin is likely limited.

6.9 Conclusions and Implications

The motivation for collecting data at Big Hill and the focus for this analysis has been to quantify the distribution of reactive nitrogen oxides at a site upwind of Lake Tahoe and use those measurements to assess the role of transport along the western slope of the Sierra in contributing to nitrogen deposition in Lake Tahoe. By combining the data we obtained at Big Hill with corresponding measurements at Blodgett Forest, we have developed a highly constrained model of the processes that govern reactive nitrogen distribution during the summer months in the region. Data collected during winter months shows that the meteorology does not favor net transport of pollutants from west

to east in the surface layer. Plumes from several prescribed burns were measured, often containing higher concentrations of reactive nitrogen than the urban plume, but likely having significantly reduced geographical influence. Total reactive nitrogen in the region is likely at a maximum during the summer when better upslope transport occurs. Observations from more sites are necessary to quantify the importance of fire events as a source of reactive nitrogen to Lake Tahoe. Based on our analyses of the observations made, we can draw the following conclusions:

- During summer months, the Sacramento region is the dominant source of reactive nitrogen in the urban plume on the western slope of the Sierra Nevada
- HNO_3 deposition is sufficiently fast that very little remains in the urban plume by the time it reaches high elevation sites near the western rim of the Tahoe Basin
- At Big Hill, similar concentrations of HNO_3 are found in air masses coming from the west and the east, suggesting that urban areas to the west of Lake Tahoe cannot be identified as important sources
- Organic nitrates are significantly elevated in the urban plume compared to background conditions but their contribution to nitrogen deposition is poorly understood
- During winter months, total reactive nitrogen is lower, net flow at the surface is downhill, and the Sacramento urban plume rarely reaches the western rim of the Tahoe Basin
- Individual winter episodes of high NO_2 and inorganic nitrates associated with small-scale burning events along the western slope of the Sierra Nevada may generate HNO_3 that can reach Tahoe.

6.10 References

- Cape, J.N. (2003). "Effects of airborne volatile organic compounds on plants [Review]." *Environmental Pollution*, **122**(1), 145-157.
- CARB (1997). "Monitoring in Ozone Transport Corridors." ARB Contract No. 94-316. Final report prepared for California Air Resources Board by Technical & Business Systems, Inc. July.
- Carroll, J.J., Dixon, A.J. (1998), "Tracking the Sacramento Pollutant Plume over the Western Sierra Nevada." Final Report prepared for the California Air Resources Board, Interagency Agreement No. 94-334, March.
- Carroll, J.J., and Dixon, A.J. (2000). "Meteorological and Air Pollution Profiles in the Lake Tahoe Basin." UC Davis.
- Carroll, J.J., and Dixon, A.J. (2002). "Regional scale transport over complex terrain, a case study: tracing the Sacramento plume in the Sierra Nevada of California." *Atmospheric Environment*, **36**(23), 3745-3758.

- Cohen, R. and Murphy, J. (2005), "Keeping Tahoe Blue: Quantifying Atmospheric Nitrogen Oxides in the Lake Tahoe Basin," Final Report prepared for the California Air Resources Board, Interagency Agreement No. 01-327, January.
- Day, D.A., P.J. Wooldridge, et al. (2002). "A Thermal Dissociation-Laser Induced Fluorescence instrument for in situ detection of NO₂, Peroxy(acyl)nitrates, Alkyl nitrates and HNO₃." *J. Geophys. Res.* **107**(D6): 10.1029/2001JD000779.
- Day, D.A., M.B. Dillon, et al. (2003). "On alkyl nitrates, O₃ and the "missing Air mass"." *J. Geophys. Res.* **108** (D16).
- Dillon, M.B. (2002). The chemical evolution of the Sacramento urban plume. *Chemistry*. Berkeley, University of California, Berkeley: 206.
- Duckworth, S. and Crowe D. (1979). "Ozone Patterns on the Western Sierra Slope -- Downwind of Sacramento during the Summer of 1978." *ARB Technical Report*. Technical Services Division. Sacramento. March.
- Flocke, F., A. Volzthomas, et al. (1991). "Measurements of Alkyl Nitrates in Rural and Polluted Air Masses." *Atmospheric Environment Part a-General Topics* **25**(9): 1951-1960.
- Garcia, C., Gouze, S., Wright, J., and Hackney, R. (2001), "Assessment of the Impacts of Transported Pollutants on Ozone Concentrations in California," *ARB Staff Report: Initial Statement of Reasons*, March.
- Hanson, P.J., and Lindberg, S.E. (1991). "Dry deposition of reactive nitrogen compounds: a review of leaf, canopy, and non-foliar measurements." *Atmospheric Environment*, **25A**(8), 1615-1634.
- Keeley, J.E. and C.J. Fotheringham (1997). "Trace gas emissions and smoke-induced seed germination." *Science* **276**(5316): 1248-1250.
- Korontzi, S., S.A. Macko, et al. (2000). "A stable isotopic study to determine carbon and nitrogen cycling in a disturbed southern Californian forest ecosystem." *Global Biogeochemical Cycles* **14**(1): 177-188.
- Lerdau, M.T., L.J. Munger, et al. (2000). "Atmospheric chemistry - The NO₂ flux conundrum." *Science* **289**(5488): 2291-2293.
- Moody, J.L., J.W. Munger, et al. (1998). "Harvard forest regional-scale air mass composition by Patterns in Atmospheric Transport History (PATH)." *Journal of Geophysical Research-Atmospheres* **103**(D11): 13181-13194.
- Munger, J.W., S.C. Wofsy, et al. (1996). "Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland. 1. Measurements and mechanisms." *Journal of Geophysical Research* **101**(D7): 12639-12657.
- Nasholm, T., A. Ekblad, et al. (1998). "Boreal forest plants take up organic nitrogen." *Nature* **392**(6679): 914-916.

- Novelli, P.C., Masarie, K.A., Lang, P.M., Hall, B.D., Myers, R.C., and Elkins, J.W. (2003). "Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires - art. no. 4464." *Journal of Geophysical Research-Atmospheres*, 108(D15), 4464.
- Seaman, N.L., Stauffer, D.R., and Lariogibbs, A.M. (1995). "A Multiscale Four-Dimensional Data Assimilation System Applied in the San Joaquin Valley During Sarmap .1. Modeling Design and Basic Performance Characteristics." *Journal of Applied Meteorology*, 34(8), 1739-1761.
- Seinfeld, J.H., and Pandis, S.N. (1998). *Atmospheric Chemistry and Physics*, John Wiley & Sons, New York.
- Shepson, P.B., K.G. Anlauf, et al. (1993). "Alkyl Nitrates and Their Contribution to Reactive Nitrogen at a Rural Site in Ontario (Vol 27a, Pg 749, 1993)." *Atmospheric Environment Part a - General Topics* **27**(14): 2251-2251.
- Sparks, J.P., R.K. Monson, et al. (2001). "Leaf uptake of nitrogen dioxide (NO₂) in a tropical wet forest: implications for tropospheric chemistry." *Oecologia* **127**(2): 214-221.
- Van Ooy, D.J., and Carroll, J J. (1995). "The Spatial Variation of Ozone Climatology On the Western Slope of the Sierra Nevada." *Atmospheric Environment*, 29(11), 1319-1330.
- Wesely, M.L., and Hicks, B.B. (2000). "A review of the current status of knowledge on dry deposition [Review]." *Atmospheric Environment*, 34(12-14), 2261-2282.
- Zaremba, L.L., and Carroll, J.J. (1999). "Summer wind flow regimes over the Sacramento Valley." *Journal of Applied Meteorology*, 38(10), 1463-1473.
- Zhang, Q., Carroll, J.J., Dixon, A.J., and Anastasio, C. (2002). "Aircraft measurements of nitrogen and phosphorus in and around the Lake Tahoe Basin: Implications for possible sources of atmospheric pollutants to Lake Tahoe." *Environmental Science & Technology*, 36(23), 4981-4989.

THIS PAGE BLANK INTENTIONALLY