

Distribution of ozone, ozone precursors and gaseous components of atmospheric nitrogen deposition in the Lake Tahoe Basin

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Principal Investigators:

Andrzej Bytnerowicz, US Forest Service, Pacific Southwest Research Station, Riverside, CA 92507

Mark Fenn, US Forest Service, Riverside, Pacific Southwest Research Station, Riverside, CA 92507

Alan Gertler, Desert Research Institute, Reno, NV 89512

Haiganoush Preisler, US Forest Service, Pacific Southwest Research Station, Albany, CA

Barbara Zielinska, Desert Research Institute, Reno, NV 89512

Collaborators:

Suraj Ahuja, US Forest Service, Region 5, McClellan, CA 95652; Ricardo Cisneros, Glenn Shaw and Don Schweizer, US Forest Service, Region 5, Clovis, CA 93611; Trent Procter, US Forest Service, Region 5, Porterville, CA 93257; Joel Burley, St. Mary's College, Moraga, CA 94556; Susan Schilling, US Forest Service, Pacific Southwest Research Station, Riverside, CA 92507; Leora Nanus, San Francisco State University, San Francisco, CA 94132, Mark McDaniel and Sandra Theiss, Desert Research Institute, Reno, NV 89512; James Sickman and Michael Bell, University of California, Riverside, CA 92521; Miriam Rorig, USDA Forest Service, PNW Research Station, Seattle, WA 98103.

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1. Extended Abstract

We organized the Lake Tahoe 2010 Study and characterized spatial and temporal distribution of ozone (O_3), O_3 precursors, O_3 formation, and gaseous pollutants that are important contributors to atmospheric nitrogen (N) deposition in the Lake Tahoe Basin. The air quality measurements phase focused on the summer of 2010 while the N deposition measurements extended to the summer of 2011. We used passive samplers for monitoring O_3 , nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), nitric acid (HNO_3) and volatile organic compounds (VOCs) on a network of 34 sites inside and outside of the Basin. Using statistical and geostatistical models, we created distribution maps of the measured compounds for the entire Basin. On a subset of 10 monitoring sites, we also measured real-time O_3 concentrations with UV absorption monitors. At these sites, we also measured N deposition with ion exchange resin (IER) collectors placed in forest clearings (bulk precipitation) and under tree canopies (throughfall). In the bulk and throughfall samples from the IER collectors, we measured the stable isotope composition ($\delta^{15}N$ and $\delta^{18}O$) of NO_3 to evaluate the origin of N deposition in the Basin.

Summertime average O_3 concentrations above the typical North American “background” levels (35-50 ppbv) were determined on the western slope of the Sierra Nevada Mountains range and seemed to have been affected by emissions from the Central Valley of California. In this area, Toluene/Benzene (Tol/Bz) ratios were generally low, indicating aged air masses and thus regional transport. High O_3 concentrations were found above the center of Lake Tahoe, accompanied by high Tol/Bz and NO/ NO_2 ratios, as well as high anthropogenic VOC concentrations (especially the higher molecular weight hydrocarbons n-decane and n-undecane). These measurements may indicate the influence of local spark ignition and diesel engine emissions, such as large boats. High solar radiation over the Lake may promote photochemical reactions and increased production of secondary pollutants such as O_3 and HNO_3 . Enhanced O_3 measured on the eastern side of the Basin at high elevation sites was characterized by low Tol/Bz ratios, which may indicate long range transport of pollutants aloft from the Central Valley of California. However, higher NO/ NO_2 ratios can also indicate additional effects of local emissions from the South Lake Tahoe area. While all sites had similar O_3 concentrations in a range of 55-60 ppb during the daytime, at night, the low elevation sites showed much lower concentrations. Most likely that was caused by combination of various factors including a lack of the long-range transport of O_3 from distant areas, dry deposition to plants and other landscape surfaces, and O_3 titration by NO emitted from local traffic and local campground wood fires. With increasing elevation of the monitoring site, the nighttime O_3 concentrations also increased. Eight-hour mean O_3 concentrations exceeding 75 ppb (greater than the federal primary O_3 standard) only occurred on a few occasions at high elevation locations. Isoprene concentrations, emitted from deciduous species, were comparable to or even higher than α -pinene concentrations, emitted from coniferous species. Both, isoprene and α -pinene have high O_3 forming potential.

Among the N reactive species, NH_3 and NO dominated, comprising 38.2 and 35.4 percent, respectively, of the atmospheric reactive N. However, from the perspective of atmospheric N deposition, NH_3 and HNO_3 were most important due to their high deposition velocities. The highest NH_3 concentrations were measured west of the Lake Tahoe Basin on the western slope

of the Sierra Nevada, indicating the effects of mobile and stationary pollution sources in the Central Valley of California. However, local NH_3 emissions seem to contribute to elevated levels of the pollutant on the southwestern side of the Basin. The highest concentrations of total reactive N gases were measured near the western shore of the Lake indicating effects of local emissions from motor vehicles and other pollution sources.

Nitrogen deposition in throughfall was low (1-2 kg/ha/yr) on the northern and western sides of the Lake, but was moderately elevated (> 5 kg/ha/yr) on the southern and eastern sides of the Lake. Nitrogen concentrations in lichen tissue were above the 'clean-site threshold' at five of the ten megasites and throughfall N deposition at three of the megasites was above the critical load at which epiphytic lichen communities become dominated by eutrophic species. Throughfall deposition of $\text{NH}_4\text{-N}$ was 60% greater than deposition of $\text{NO}_3\text{-N}$ indicating the importance of reduced forms of N in the Tahoe Basin.

2. Introduction

2.1 Local Meteorology of the Lake Tahoe Basin

Lake Breeze: The physical concept of a lake breeze may be stated as a heat transfer problem. During periods of insolation the land surface is heated and its temperature increases, whereas the water surface remains at a relatively constant temperature due to its thermal characteristics. The surface temperature influences the overlying air and as a result there is warmer and less dense air over land while, the air overlying the water is cooler and denser. Near the shore line between the two surfaces, a pressure gradient is established due to the buoyant effects created by the temperature differences. Thus, if the prevailing synoptic conditions are such that the regional wind (pressure gradient driven) is light, the local (buoyancy driven) air flow is the dominant force and a lake breeze is established (Biggs and Graves, 1962).

Lyons and Olsson (1973) showed that the lake breeze favors the occurrence of high air pollution in shoreline areas. This is due to three factors: 1) formation of low-level temperature inversions as cool air over the lake moves onshore, 2) continuous fumigation of elevated plumes from shoreline pollution sources, and 3) recirculation of pollutants (that had moved offshore during the previous night) within the lake breeze. All of these factors are a consequence of the unique features of the lake breeze temperature and wind structure (**Figure 2-1**). A thorough knowledge of the structure is therefore highly desirable.

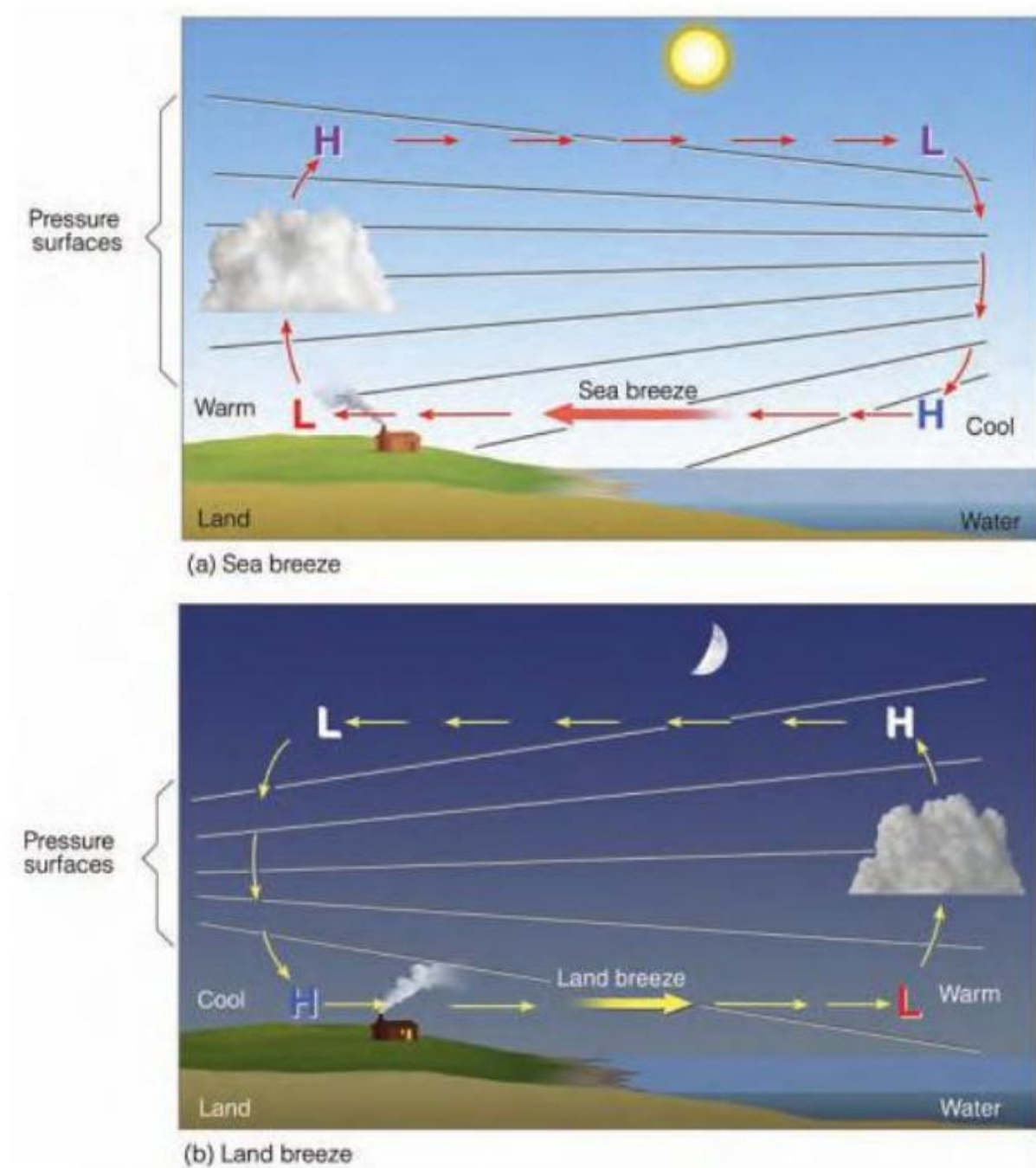


Figure 2-1. Breezes characteristic of the Lake Tahoe Basin.

Upslope/Downslope Flows: This is also a thermal or buoyancy driven circulation that occurs along mountain slopes. During the day, sunlight warms the valley walls, which, in turn, warms the air column above the slope over a depth of a few hundred meters. In a manner similar to the formation of the sea breeze, the warmed air over the sunlit slope expands and becomes less dense than the air of the same altitude above the valley. As the warmer air rises up the slope, the air pressure is decreased near the surface on the slope and increased in the air aloft, causing a pressure gradient that establishes a return airflow drawing air toward the slope near the surface. Consequently, the heated air rises as a gentle upslope wind flow. At night the flow reverses. The mountain slopes cool quickly, chilling the air in contact with them. The cooler, denser air near the slope glides downslope into the valley. This daily cycle of airflow is most developed in clear summer weather when prevailing winds are light (Ahrens, 2007).

Washoe Zephyr: The Washoe Zephyr is a local phenomenon that occurs over the eastern slope of the Sierra Nevada. It is a downslope flow that occurs regularly in the afternoon in opposition to local thermal forcing. The flow usually originates at the mountain crest and is generally strong in magnitude with peak speed occurring in the afternoon or early evening. Zhong et al. (2008) determined that the flow is a result of the pressure difference between a mesoscale thermal low over the elevated desert topography in the interior of Nevada and higher pressure west of the Sierra Nevada. The pressure difference, which usually peaks in the afternoon, draws air from west of the sierra crest down to the eastern slope, possibly bringing more polluted air from the coastal region or from the Central Valley to areas in the Great Basin.

2.2 Present Understanding of the Air Pollution Status in the Lake Tahoe Basin

Understanding the distribution of ozone (O_3) in the Lake Tahoe Basin is important for evaluating the potential effects of this criteria pollutant on human and ecosystem health. Some information on this subject has already been gathered: (a) spatial and temporal patterns of O_3 distribution as 2-week integrated averages were characterized with passive samplers during the 2002 summer season for the entire Lake Tahoe Basin and for upwind areas on the western slopes of the Sierra Nevada (Bytnerowicz et al., 2004); (b) analysis of diurnal O_3 concentrations obtained from active monitors located in several key locations inside and outside of the Basin helped to evaluate the contribution of long-range transport of polluted air masses from the California Central Valley vs. the local generation of O_3 (Dolislager et al., 2012a); (c) modeling of nitric acid (HNO_3) transport from central California (Gertler et al., 2006). These three studies show that the local generation of O_3 and other pollutants in the Basin is more important than long-range transport when it comes to exceedances of the state and national O_3 standards and elevated levels of other pollutants within the Basin. However, very little is known about the spatial and temporal distribution of O_3 precursors (nitrogen oxides, NO_x , and volatile organic compounds, VOCs) in the Basin; this is needed for evaluating the potential for photochemical generation of O_3 in the Basin and developing recommendations for air pollution control strategies. Such information is completely lacking for VOCs. While the concentrations and distribution of NO_x were characterized during the Lake Tahoe Atmospheric Deposition Study (Dolislager et al., 2012b), the spatial coverage of that study was quite limited. In addition to their role in O_3 formation, nitrogen oxides also contribute to atmospheric nitrogen (N) deposition. However, gaseous NH_3 and HNO_3 are much more important drivers of the dry- deposited N in terrestrial ecosystems in California

(Bytnerowicz and Fenn, 1996, Tarnay et al., 2001a; 2001b; 2005). Indeed, NH_3 and to a lesser extent HNO_3 , were found to be the key components of the direct N deposition to Lake Tahoe (Dolislager et al., 2012b; Tarnay et al., 2001a). Improving our knowledge of atmospheric N deposition for the entire Lake Tahoe watershed is essential for understanding the causes of the deteriorating clarity of the Lake as well as the ecological sustainability of forests and other ecosystems in the Tahoe Basin.

Ozone: O_3 is a secondary pollutant, which is not directly emitted from sources. Rather, it is formed by chemical reactions in the atmosphere. In order to control O_3 levels in the Lake Tahoe Basin, it is necessary to understand the underlying chemistry of O_3 formation. The two factors to consider are nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and volatile organic compounds (VOCs). NO reacts with O_3 to produce more NO_2 in a process that is only limited by the availability of O_3 . During the daylight hours NO_2 decomposes photochemically to reproduce NO . The ratio between NO and NO_2 is governed by the photolytic rate $J\{\text{NO}_2\}$. The photolysis of NO_2 leads to the formation of O_3 . Since O_3 is removed by the reaction with NO and is produced via the photochemical reaction, it seems that the net production of O_3 would be limited. However, through a series of reactions involving NO , VOCs, and the hydroxyl radical (OH), additional NO_2 is formed, which can subsequently photolyze to generate O_3 via a chain reaction mechanism. This chain reaction is eventually terminated by a process that yields nitric acid (HNO_3). Thus the chemical processes involving NO_x and VOCs leading to O_3 formation in the Lake Tahoe Basin also result in the formation of HNO_3 , an important contributor to the overall deposition of N.

Ambient O_3 was measured on a spatially dense network during the 2002 summer season in the Lake Tahoe Basin with passive samplers (Bytnerowicz et al., 2004). That study indicated that the Sierra Nevada crest west of the Lake Tahoe Basin (i.e., Desolation Wilderness), poses a barrier that prevents polluted air masses and high O_3 concentrations from the Sacramento Valley and Sierra Nevada foothills from entering the Basin. These results confirm the conclusions for the Lake Tahoe Deposition study (Dolislager et al. 2012b), indicating that the combined effects of day-time upslope westerly winds, evening down-slope air movement and high elevation mountains around the Tahoe Basin inhibit transport into the Basin of polluted air masses from the California Central Valley. Data are not currently available on the spatial distribution of real-time O_3 concentrations at a sufficiently fine resolution to evaluate Basin-wide exceedances of O_3 air pollution standards and its phytotoxic potential. However, according to Dolislager et al, (2012b) the long-range transport of O_3 from out-of-basin sources contributes to elevated O_3 levels on rare occasions and it does add to the regional atmospheric burden. (It should be noted that the data indicated late afternoon elevated O_3 levels at one site, Cave Rock, consistent with the impact of long range transport.)

Volatile Organic Compounds (VOCs): As outlined above, hydrocarbons play a crucial role for the accumulation of ozone in the atmosphere. The rates of O_3 formation and accumulation are nonlinear functions of the mixture of VOC and NO_x in the atmosphere. Depending upon the relative mixing ratios of VOC and NO_x and the specific mix of VOC present, the rate of O_3 formation can be more sensitive to changes in VOC alone or to changes in NO_x alone or to simultaneous changes in both VOC and NO_x (Fujita et al., 2003). One might expect the Tahoe

Basin to be NO_x-limited due to the abundance of natural VOC sources. The Photochemical Assessment Monitoring Stations (PAMS) typically monitor 55 non-methane hydrocarbon compounds (NMHC) that account for 70 – 80% of the total ambient hydrocarbons at most urban locations (<http://www.epa.gov/oar/oaqps/pams/general.html#parameters>). However, no site in the PAMS network is situated in the Lake Tahoe Basin (or even close to this area). Moreover, biogenic hydrocarbons are only represented by one compound (isoprene) on the PAMS list. Since we expected biogenic hydrocarbons to be abundant in the Lake Tahoe Basin, especially those emitted by pines (i.e., α -pinene), we monitored not only anthropogenic, but also biogenic hydrocarbons.

Gaseous nitrogenous pollutants: Studies on O₃, HNO₃, and NH₃ levels and/or formation in the Lake Tahoe Basin are limited. To date, the major investigation of N deposition and O₃ transport, the Lake Tahoe Atmospheric Deposition Study (LTADS, Dolislager et al., 2012b), observed that three-fourths of the deposited N directly to the lake surface is due to NH₃ with a smaller contribution from HNO₃. As part of a series of summer measurements, Tarnay et al (2001a; 2005) quantified HNO₃, NH₃, and particulate NH₄⁺ & NO₃⁻ levels at a number of locations in the Basin and obtained NO_x data collected by CARB at Echo Summit. Higher N-HNO₃ than N-NH₃ concentrations were determined in a daytime, while the opposite was typical at night. However, because the daytime NH₃ compensation points of forest canopies exceeded its ambient concentrations, the authors concluded that forest canopies were the NH₃ source. A final conclusion from that study was that HNO₃ was responsible for most of the N deposition to vegetation, except in areas influenced by high local NH₃ and NO₂ concentrations. Based on those results coupled with geo-spatial modeling (Tarnay 2001b), they concluded that most of the HNO₃ and NH₃ were from the in-basin sources.

To quantify how much HNO₃ is transported from the Central Valley, Sacramento, and San Francisco Bay area to the Tahoe Basin, Koracin et al. (2004) used advanced numerical atmospheric models (CALMET/CALPUFF and MM5) and the measurements performed by Tarnay et al. (2001b) to estimate the contributions from both in-basin and out-of-basin N sources. The overall simulation results indicated that pollutant transport from the Sacramento Valley and the San Francisco Bay area to the Lake Tahoe Basin occurs; however, as indicated in previous studies (Bytnerowicz et al. 2004, Carroll and Dixon 2002), pollutant concentrations are significantly diluted on the west slopes of the Sierras at increasing elevations. In short, the results of Koracin et al. (2004) suggest that although daytime pollutant transport from upwind of the Lake Tahoe Basin appears to be likely, the amount of HNO₃ transported into the Basin is much less than that from in-basin sources.

Maps of spatial distribution of HNO₃ developed for the 2002 summer season confirmed the above findings and were very similar to those for O₃ (Bytnerowicz et al., 2004). However, despite the generally low HNO₃ concentrations in the Basin, HNO₃ is an important component of N deposition and current information on its temporal and spatial deposition patterns is needed. Such information is also needed for NH₃, which is the most important component of the dry-deposited N in the Tahoe Basin (Dolislager et al., 2012b).

Atmospheric nitrogen deposition: Atmospheric deposition of N, and possibly of P, are believed to be important drivers of the decades-long decline in lake clarity (Fenn et al., 2003a). It has been

estimated that more than half of the annual N loading to Lake Tahoe comes from atmospheric deposition (Reuter and Miller, 2000), presumably largely as a result of N deposition directly to the Lake. Available data indicate that terrestrial catchments in the Tahoe Basin are N-limited with normal background levels of inorganic N runoff into the lake (Fenn et al., 2003a). Organic N in runoff is typically ten times greater than inorganic N (Coats and Goldman, 2001); but the importance of N deposition as a source of organic N in runoff and the role of this organic N in affecting algal productivity and lake clarity is not clear.

Current levels of N deposition to the terrestrial catchments in the Tahoe Basin (Fenn et al., 2003b, 2008) are not leading to 'N saturation' of the terrestrial watersheds and thus do not induce elevated levels of nitrate runoff to the lake. However, N deposition and gaseous N pollutant exposures within and immediately upwind of the Tahoe Basin are within the range that strong nutrient enrichment-induced changes in epiphytic lichen communities occur in the Sierra Nevada (Fenn et al., 2008). Thus, gaseous N pollutants are of ecological concern to the Basin due to their role as ozone precursors as well as their direct impacts on terrestrial biota and aquatic nutrient enrichment leading to increased aquatic biotic productivity and declining lake clarity.

This Lake Tahoe 2010 study was designed to fill these gaps in our current understanding of the chemical environment of the Lake Tahoe Basin. We used passive samplers for monitoring NO, NO₂, NH₃, O₃ and VOCs on a network of 34 sites inside and outside of the Basin – the same network that was used in the 2002 monitoring of summertime ambient O₃ and HNO₃ concentrations (Bytnerowicz et al., 2002) with addition of two sites (Desolation Wilderness and NOAA Buoy in the center of Lake Tahoe). At a subset of 10 monitoring sites, we also measured real-time O₃ concentrations with active UV absorption monitors. Using statistical and geostatistical models we developed distribution maps of the measured compounds. In addition, at the same 10 sites, we measured N deposition in bulk and throughfall samples using the ion exchange resin collectors and evaluated the origin of atmospherically-deposited NO_x using stable isotope analysis of delta¹⁵N(NO₃) and delta¹⁸O(NO₃). Results of this study were intended to increase our understanding of the present and future potential of O₃ formation and its biological effects, as well as impacts of N air pollutants and N deposition in the Lake Tahoe Basin. These results will also help to develop the science-based management strategies aimed at improving air quality and ecological sustainability of the Basin.

3. Objectives and hypotheses

Main Objectives:

1. Understand the distribution of ozone precursors and their contribution to ground-level ozone formation in the Lake Tahoe Basin.
2. Characterize the distribution of gaseous reactive N species and atmospheric N deposition in the Lake Tahoe Basin.

Specific Objectives:

1. Characterize the distribution of O₃, NO, NO₂, HNO₃, NH₃ and VOCs.

2. Determine real-time concentrations of O₃ with portable UV-B absorption monitors.
3. Develop GIS maps of spatial and temporal distribution of pollutants.
4. Provide information on potential O₃ formation inside vs. outside the Tahoe Basin to improve our knowledge of local vs. long-range origin of O₃ pollution in the Basin.
5. Develop predictions of future (short term) O₃ concentrations using statistical models (including spatially-dense maps of exceedances of air quality standards).
6. Develop maps of Critical Levels for O₃ and Critical Loads for N needed for evaluation of their exceedances and evaluation of future risks.
7. Characterize the origin of N pollutants and N deposition based on analysis of $\delta^{15}\text{N}(\text{NO}_3)$, $\delta^{18}\text{O}(\text{NO}_3)$, and $\delta^{15}\text{NH}_3$.
8. Develop GIS maps of atmospheric N deposition for the Lake Tahoe Basin.

Hypotheses to be tested:

1. While long-range transport from California Central Valley has little effect on air pollution status in the Lake Tahoe Basin, locally emitted VOCs and NO_x significantly contribute to increasing O₃ concentrations and deterioration of air quality.
2. Both naturally-emitted and anthropogenic VOCs contribute to O₃ formation in the Basin, however, pinenes emitted from coniferous trees have the highest O₃-forming potential in the Basin.
3. Ammonia is the most important contributor to dry-deposited N in forest ecosystems of the Lake Tahoe Basin.
4. Deposition of N in the Tahoe Basin is elevated to the levels exceeding critical loads for sensitive receptors.

4. Methodology

Monitoring network: Passive samplers were deployed on a network of 34 sites located inside and outside of the Lake Tahoe Basin, the same as was used in summer 2002 for characterizing O_3 and HNO_3 distribution (Bytnerowicz et al., 2004), with an addition of two sites – one in the Desolation Wilderness (DW) and the second on the NASA buoy (TB2) near the center of Lake Tahoe (**Figure 4-1**). A subset of 10 sites with an optimal spatial distribution was selected for real-time O_3 measurements, N deposition collections, and stable isotope analysis.

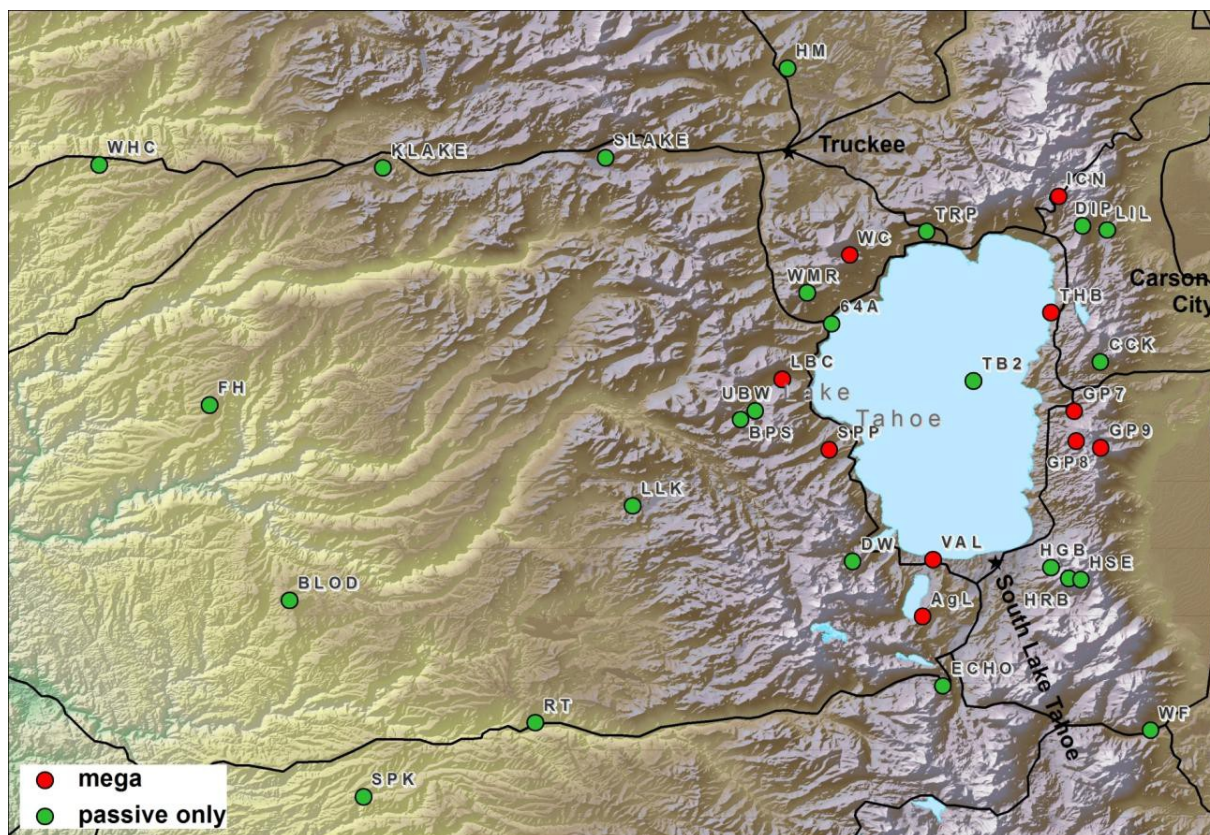


Figure 4-1. Monitoring network used in the Lake Tahoe 2010 study.

Table 4-1. List of 34 monitoring sites in the Lake Tahoe 2010 study network.

SITE Name	Site abbrev.	Elevation (m, ft)	Site Type	SITE Name	Site abbrev.	Elevation (m, ft)	Site Type
Sly Park	SPK	1,067 3,500	Passive	Clear Creek	CCK	2,099 6,886	Passive
Riverton	RT	1,227 4,024	Passive	Upper Blackwood	UBW	2,179 7,149	Passive
Forest Hill	FH	1,252 4,109	Passive	Watson Mtn. Road	WMR	2,187 7,176	Passive
White Cloud	WHC	1,279 4,197	Passive	Angora Lookout	AgL	2,218 7,277	Mega

Blodgett	Blod	1,298 4,260	Passive	Echo Summit	Echo	2,228 7,310	Passive
Hobart Mills	HM	1,806 5,926	Passive	Genoa Peak 7000	GP7	2,232 7,323	Mega
Woodfords	WF	1,811 5,942	Passive	Serene Lake	SLake	2,246 7,370	Passive
Kelly Lake	KLake	1,816 5,958	Passive	Watson Creek	WC	2,293 7,524	Mega
64 Acres	64A	1,900 6,235	Passive	Barker Pass	BPS	2,344 7,690	Passive
TB2 NASA Buoy	TB2	1,905 6,250	Passive	Desolation Wilderness	DW	2,436 7,992	Passive
Valhalla	Val	1,906 6,252	Mega	Genoa Peak 8000	GP8	2,449 8,035	Mega
Thunderbird Lodge	THB	1,915 6,283	Mega	Heavenly Gun Barrel	HGB	2,509 8,232	Passive
Loon Lake	LLk	1,927 6,323	Passive	Upper Incline	ICN	2,523 8,278	Mega
Lower Blackwood	LBC	1,948 6,392	Mega	Diamond Peak	DIP	2,571 8,434	Passive
Sugar Pine Point SP.	SPP	1,951 6,400	Mega	Genoa Summit 9000	GPS	2,734 8,970	Mega
Little Valley	Lil	1,956 6,417	Passive	Heavenly Ridge Bowl	HRB	2,782 9,128	Passive
Tahoe Regional Park	TRP	1,962 6,437	Passive	Heavenly Sky Express	HSE	3,043 9,984	Passive

Duration of the study: The Lake Tahoe 2010 study started in June 2010 and ended in July 2011 (collection of ion exchange resin collectors after the winter/spring exposure). Approximate passive sampler exposure periods are listed in **Table 4-2**. Setting up and changes of samplers were always done within two days. For calculation of air pollutant concentrations, precise time of exposure (minutes) at every site was used.

Table 4-2. Scheduled exposure periods for passive samplers in the Lake Tahoe 2010 study.

Exposure Period	Duration
1	June 15-30, 2010
2	June 30 – July 14, 2010
3	July 14 – 29, 2010
4	July 29 - August 11, 2010
5	August 11 – 25, 2010
6	August 25 – September 8, 2010
7	September 8 – 22, 2010

Selection of study sites: Passive samplers were placed on a wooden pole about 2 m above the ground. The sampler assembly consisted of the O_3 , NO_x , NO_2 , NH_3 , HNO_3 and VOCs samplers (**Figure 4-2**). Samplers were placed in carefully selected sites well-exposed to the incoming air masses. Example of the passive sampler site located at the Desolation Wilderness (**Figure 4-3**). Additional photos of sampling sites are in Appendix A.



Figure 4-2. Passive sampler assembly used at 34 monitoring sites inside and outside of the Lake Tahoe Basin.



Figure 4-3. Passive sampler at the Desolation Wilderness site.

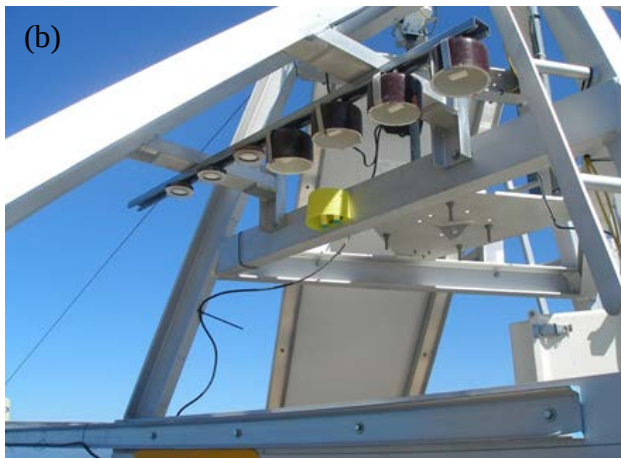


Figure 4-4. The NASA buoy (site 2B2) located in the middle of the Lake Tahoe (a) and a close-up of the passive sampler assembly (b).

Ozone measurements: The basic principle of passive sampling is diffusion of gaseous pollutants across a surface to an adsorbing material on which the pollutant of interest accumulates over time (Krupa and Legge, 2000). Passive Ogawa samplers were used for monitoring ambient O_3 (Koutrakis *et al.*, 1993). Each sampler contains two cellulose filters coated with nitrite (NO_2^-) which is oxidized by O_3 to NO_3^- and analyzed with ion chromatography. The rate of NO_3^- formation (amount of NO_3^- formed on a filter over time of exposure) serves as a measure of O_3 concentration. At the 10 megasites, the two-week averaged O_3 concentrations determined with

passive samplers were compared with real-time O₃ concentrations obtained with portable UV absorption 2B Technologies monitors (Bognar and Birks, 1996; **Figure 4-5**). The empirically derived coefficients were used for calculating O₃ concentrations for passive samplers. Precision of O₃ passive samplers measured as coefficient of variation (CV) of replicate samples for the entire study was 3%. In addition, a comparison between passive samplers and the collocated UV absorption monitors was used to test an ability to investigate the feasibility of generate generating maps of the summer-season hourly O₃ concentrations for the entire Lake Tahoe Basin based on data from the entire passive sampler network.



Figure 4-5. Setting up UV-absorption 2B Tech. monitor at the Angora Lookout site.



Figure 4-6. Installation of equipment at the Lower Blackwood megasite.

Examples of instrumentation set-up at megasites are shown for the Lower Blackwood site (**Figure 4-6**) and the Genoa 9000 site (**Figure 4-7**). **Figure 4-8** presents a close-up of the ion exchange resin collectors for throughfall measurements installed at the Lower Blackwood site.



Figure 4-7. Passive samplers and bulk deposition ion exchange resin collectors at the Genoa 9000 m site.



Figure 4-8. Ion exchange resin throughfall collectors at the Lower Blackwood megasite.

Measurement of inorganic N gases: Ogawa passive samplers were used for monitoring NO_x and NO₂. Each NO₂ sampler contains two filters coated with triethylene amine (TEA) and each NO_x sampler consists of two filters coated with TEA and 2-phenyl-4,4,5,5,-

tetramethylimidazoline-1-oxyl 3-oxide (PTIO) as an oxidizer. Both NO_x and NO₂ are collected as NO₂⁻ which is extracted in water and determined with ion chromatography, and their ambient concentrations were calculated using calibration curves (Alonso et al., 2005). From the difference between NO_x and NO₂ concentrations, NO concentrations were calculated. Passive samplers developed by the US Forest Service (Bytnerowicz et al., 2005) were used for HNO₃ measurements. In the HNO₃ sampler, ambient air passes through a Teflon membrane and gaseous HNO₃ is absorbed on a Nylasorb nylon filter as NO₃⁻. Nitrate concentrations in sample extracts were analyzed by ion chromatography, and concentrations of HNO₃ were calculated using calibration curves (Bytnerowicz et al., 2005). Three replicate HNO₃ samplers were exposed at each site. Ogawa passive samplers (Roadman et al., 2003), with two replicate filters coated with citric acid, were used for NH₃ monitoring. Ammonia reacts with citric acid on the filters producing ammonium citrate. After water extraction, NH₄⁺ concentrations in filter extracts was determined colorimetrically on a TRAACS 2000 Autoanalyzer, and ambient NH₃ concentrations were calculated based on a comparison of passive samplers against the co-located annular denuder systems (Koutrakis et al., 1993). Precision of NO_x, NO₂, NH₃ and HNO₃ passive samplers measured as CV of replicate samples for the entire study was 7, 10, 12 and 9 %, respectively.

Measurements of VOCs: For monitoring selected VOC species we used passive VOC Radiello samplers. After sampling, the collected pollutants were desorbed from the sampling media by thermal desorption method and analyzed quantitatively by gas chromatography-mass spectrometry (GC/MS). The average ambient concentration of pollutants for 2-week long periods was calculated by dividing the mass of pollutant measured analytically by the product of sampling rate and sampling time. Table 3-3 below lists the species we monitored for this project and for which sampling rates have been published (<http://www.radiello.com> or <http://www.sigmaaldrich.com/analytical-chromatography/sample-preparation/radiello/learning-center/applications.html>).

Table 4-3. List of species quantified during the study.

Mnemonic	Compound	MDL (ppbv) ^b	Uncertainty ^b (%) at 2σ	Mnemonic	Compound	MDL (ppbv) ^b	Uncertainty ^b (%) at 2σ
i_prene	Isoprene ^a	0.012	NA ^c	n_non	n-Nonane	0.012	11.8
a_pine	α-Pinene ^a	0.033	29.5	n_dec	n-Decane	0.016	22.4
bud13	1,3-Butadiene	0.012	NA ^c	etbz	Ethylbenzene	0.002	9.1
n_hex	n-Hexane	0.013	10.9	styr	Styrene	0.002	24
benze	Benzene	0.015	8.3	mp_xyl	m/p-Xylene	0.002	11.3
cyhexa	Cyclohexane	0.027	14.7	bz124m	1,2,4-Trimethylbenzene	0.01	9.6
tolue	Toluene	0.002	8.3	n_unde	n-Undecane	0.007	32.7
n_oct	n-Octane	0.014	13.4				

Radiello diffusive samplers consist of stainless steel mesh cylinders (3x8 μm mesh, 4.8 mm diameter x 60 mm length) packed with Carbograph 4 (for all VOC except isoprene and 1,3-butadiene, adsorbing cartridge code R145) and Carbo-pack X (for isoprene and 1,3-butadiene, R141). The cartridges were deployed in the diffusive sampling bodies according to the manufacturer's instruction (<http://www.radiello.com>). After sample collection cartridges were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high-resolution gas chromatographic separation and mass spectrometric detection (GC/MS) of individual compounds. The Gerstel Thermal Desorption System (TDS) unit, equipped with Cooled Injection System (CIS) and 20-position autosampler, attached to the Varian Saturn 2000 GC/MS, was used for the purpose of sample desorption and cryogenic preconcentration. A 60 m (0.32 mm i.d., 0.25 mm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was employed to achieve separation of the target species. For calibration of the GC/MS a set of Radiello passive samplers were prepared by loading the cartridges with a known amount of gaseous calibration standards (purchased from AiR Environmental) that contains the most commonly found hydrocarbons, including those listed in Table 3-3. Four different concentrations (plus one blank) were used to construct calibration curves.

Ion Exchange Resin Deposition Samplers and Isotopic Analysis for Nitrate and Ammonia: At a subset of 10 sites spatially distributed within the monitoring network, ion exchange resin (IER) bulk deposition and throughfall collectors was installed in June and July 2010 to measure annual throughfall and bulk deposition of NO_3^- and NH_4^+ (**Figures 5.4-1 through 5.4-6**). Atmospheric deposition was measured in forest clearings and under canopies as throughfall. The latter includes estimates of dry deposition and cloudwater deposition (Fenn et al., 2009). The IER samplers (Fenn and Poth, 2004) are ideally suited for this work because the collectors accumulate N deposition over time, resulting in samples that only need to be collected approximately every 6 months. These samplers provided data on spatial patterns of N deposition inputs for the summer and winter seasons. To evaluate uncertainty and variability in the deposition data, coefficients of variation were calculated for NH_4 and NO_3 in bulk deposition and throughfall, both for the summer period and winter periods. Open was calculated as the average CV for replicate samplers within a site. For throughfall samplers, CV was calculated for replicate samples within a tree. The CV for throughfall NH_4 summer and winter was 29% and 25%, respectively and for throughfall NO_3 summer and winter was 38% and 28%, respectively. The CV for bulk NH_4 summer and winter was 27% and 17%, respectively and for bulk NO_3 summer and winter was 35% and 28%, respectively. The added benefit of the IER samplers is that dual isotope analysis of the NO_3 samples ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$; Nanus et al., 2008) can also be done to characterize the relative contributions and sources of anthropogenic and biogenic nitrogen to ecosystems. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- vary based on the source and transport pathway of the molecule. Comparing the isotopic signatures of the sites can determine if deposited HNO_3 originates within or outside of the Basin.

The stable isotope data from the IER collectors was used to distinguish precursor sources of atmospheric N in samples collected across the Tahoe Basin monitoring network. The dual isotopic analyses for NO_3 were done using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). These data provide an additional approach for evaluating the relative importance of within-basin versus upwind emissions sources of the NO_x deposited to the Tahoe Basin. Both seasonal and spatial patterns were evaluated to see how N emissions source contributions

may vary spatially and temporally as recently reported for the Colorado Front Range (Nanus et al., 2008) and the Midwestern and NE U.S. (Elliott et al., 2007).

Analysis of diurnal and seasonal ambient ozone patterns from the 10 mega sites and their relationship with weather

Two separate analyses were performed on the hourly ozone data from the 10 mega sites:

- 1) In the first analysis, relationships between diurnal patterns and large scale weather patterns were studied by developing wind roses from archived wind data on a 12-km grid and by comparing graphs of seasonal ozone patterns with synoptic graphs of mean sea level pressure and 500mb geopotential heights from Oakland, Sacramento and Reno. These analyses will show the general flow of the atmosphere at two levels and help identify where the transport is coming from (Section 5.5), if it is in fact occurring.
- 2) In the second analysis, a regression model (Section 5.6) was developed between the hourly ozone values and gridded hourly weather (temperature, relative humidity, wind speed, wind direction), terrain features (elevation, distant to major road, position relative to lake), time of day and week (weekend vs. weekday) and bi-weekly passive sampler values.. The regression model was used to quantify and understand the spatial and temporal sources of variation in the hourly O₃ data (Lee, 2003; Preisler et al., 2002; Preisler et al., 2003). The hourly weather variables for the regression model were obtained from MM5 models produced by CANSAC on a 4-km grid (**Figure 4-9**) (<http://tahoeclim.dri.edu/mm5archive.html>). For each site, we matched hourly weather data from the closest four grid points surrounding the site to the hourly ozone data.

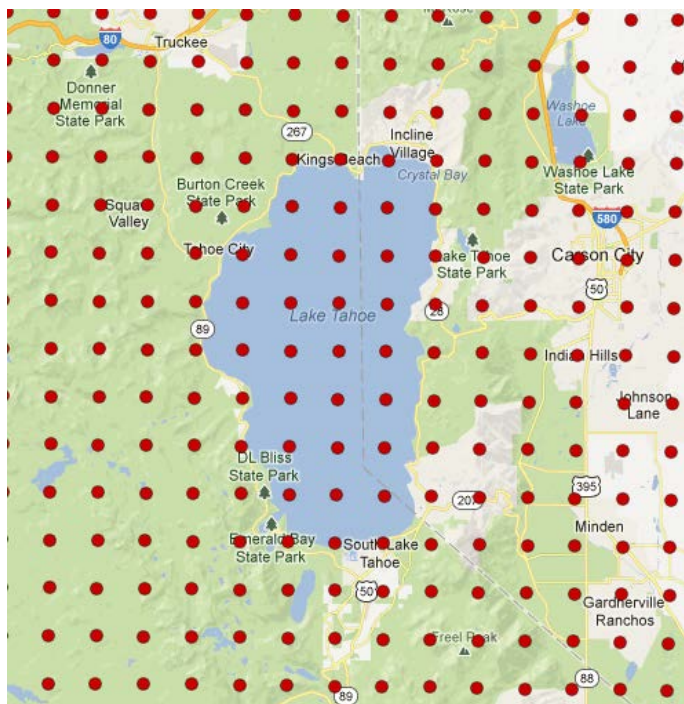


Figure 4-9. Locations of 4-km grid points for the MM5 hourly weather data (red dots).

Details of the regression model are as follows: The following model was fit to each of the 10 mega sites

$$O_3 = \alpha + s(\text{passive}O_3) + s(\text{hr.in.day}) + \sum \text{wkdn}:s(X_k) + \text{error}$$

where:

O_3 is the hourly ozone concentration (ppb per hour);

α is the regression intercept estimating the background (average) ozone concentration at the particular site;

Passive O_3 is the bi-weekly passive O_3 concentration at the site;

wkdn is a four factor variable indicating whether the day is a weekday (Mon-Thur) daytime or night time or weekend daytime or nighttime. In our preliminary exploratory analysis we found differences in relationships between ozone concentrations and wind directions depending on the day-in-week and day or night time hours;

X_k is the k th weather variable (e.g., temperature, wind direction);

$s(X)$ is a nonparametric smooth spline function estimated from the data (e.g., *passive* O_3 , *hr.in.day*);

and

error is an autoregressive error terms to account for the serial correlation in the data in addition to other sources of variation not accounted for by the explanatory variables (Preisler et al. 2009).

Results of regression analysis are presented in Section 5.6.

Development of geostatistical maps. Maps of spatial distribution of O_3 and other measured compounds were developed with Geostatistical Analyst, an extension of Arc GIS software (ESRI, Redlands, CA). The Geostatistical Analyst uses values measured at sample points at different locations in the landscape and interpolates them into a continuous surface. Using a set of pollutant concentration measurements for the study area, a spatial model of pollutant concentrations was constructed using the inversed distance weighted (IDW) method (Johnstone et al., 2001).

5. Results and Discussion

The results of this study improved our understanding of the role of biogenic and anthropogenic VOCs and NO_x O_3 formation within the Tahoe Basin. This improved knowledge helped to formulate science-based recommendations regarding management strategies that could be recommended for effective control of O_3 concentrations within the Basin. All these efforts help to create a knowledge base for future investigations of potential ecological impacts of ambient O_3 and N deposition in the Tahoe Basin under various scenarios of the changing climate for California and Nevada (Cayan et al., 2006). Interpretation of historical data and results from this project will provide very important input to revisions of the Forest Plan for the Sierra Nevada that are planned in the coming years.

The described research was a logical continuation of previous efforts focusing on understanding air quality and its effects on the human health-based national and state air quality standards, and also on potential ecological impacts of air pollution and atmospheric deposition in the Lake

Tahoe Basin (Bytnerowicz et al., 2004; Dolislager et al. 2012a, b; Gertler et al, 2006; Koracin et al., 2004; Tarney et al, 2001a, b; 2005;).

5.1 Ozone spatial and temporal variations – passive samplers and active monitors

Maps of O₃ distribution were developed for exposure periods No. 3 through 7. Such maps were not generated for exposure periods No. 1 and 2 due to a still incomplete sampling network. Ozone distribution patterns for individual periods were very similar (**Figures 5.1-1 through 5.1-3**). High concentrations from the Central Valley of California were observed west of the Lake Tahoe Basin indicating that high elevation mountain ranges (especially those in the Desolation Wilderness) acted as an effective barrier to the polluted air masses. However, we also see evidence of O₃ transport on higher elevations, especially at the Genoa Peak 9000 site. Within the Tahoe Basin, highest 2-week mean O₃ concentrations were determined on the NASA buoy site in the middle of the Lake indicating high potential for photochemical reactions over the Lake surface. This could be due to high levels of O₃ precursors (VOCs and NO_x) from the local traffic around the Lake and motor boat emissions as well as high solar radiation (including light reflection from the lake's surface) and stagnant air masses. The summer season average O₃ concentrations are shown in **Figure 5.1-3**. Generally the distributions and levels of the determined O₃ concentrations are similar to those found in the Lake Tahoe Basin in the 2002 study performed on the same monitoring network (Bytnerowicz et al., 2004; Gertler et al., 2006).

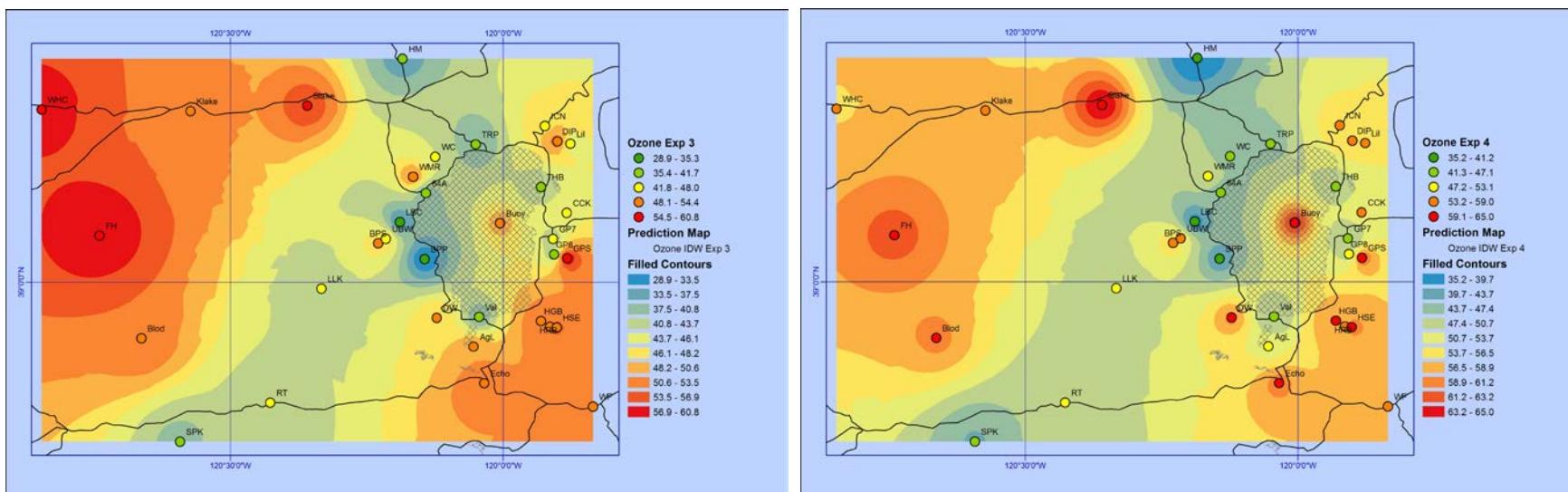


Figure 5.1-1. Ozone distribution (ppb) during exposure 3 (July 14- 29) and exposure 4 (July 29 – Aug. 11).

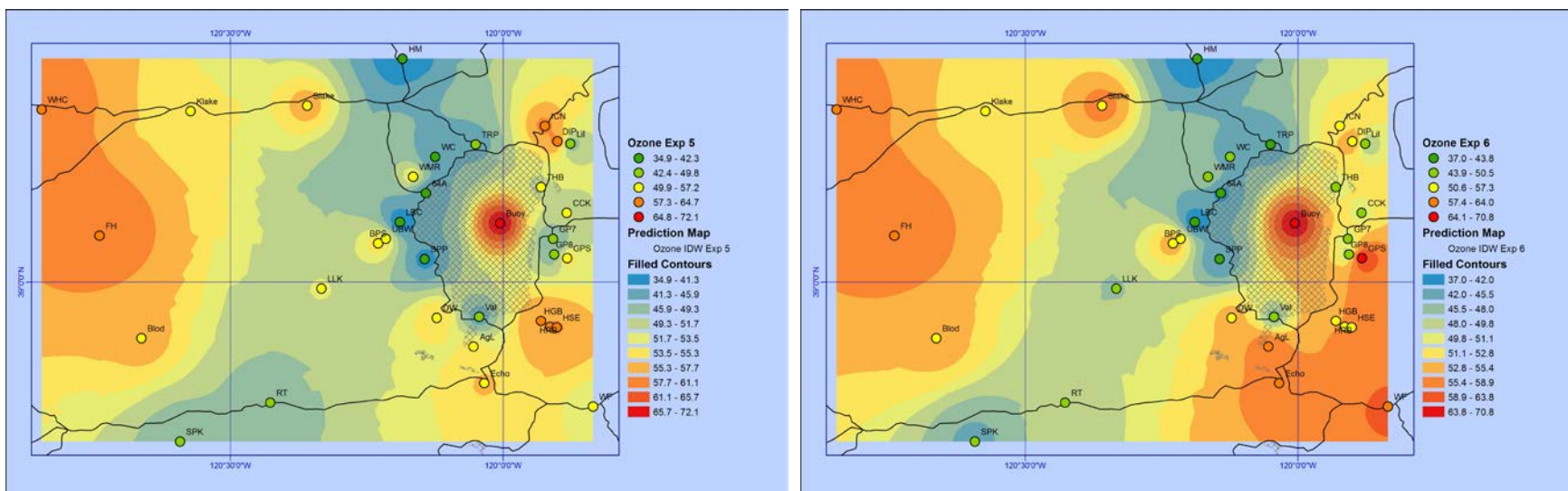


Figure 5.1-2. Ozone distribution (ppb) during exposure 5 (Aug. 11 – 25) and exposure 6 (Aug. 25 – Sept. 8).

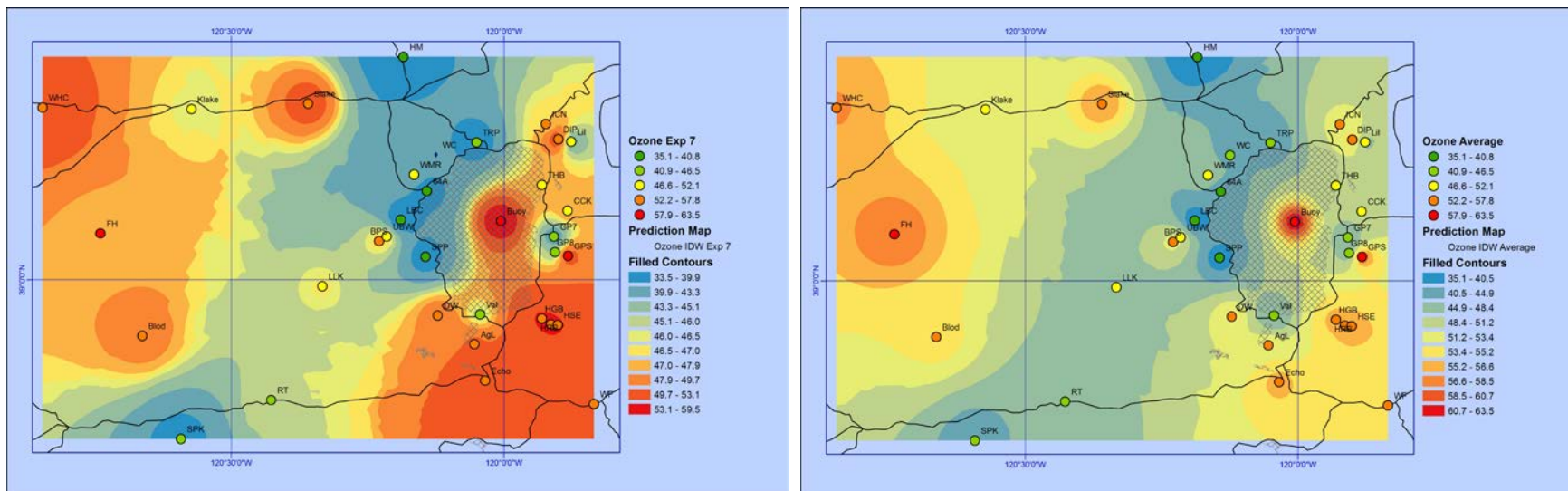


Figure 5.1-3. Ozone distribution (ppb) during exposure 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

Results from the UV-absorption ozone monitors located at the mega sites showed large changes in ozone concentrations, both diurnally and within the summer season (**Figure 5.1-4**).

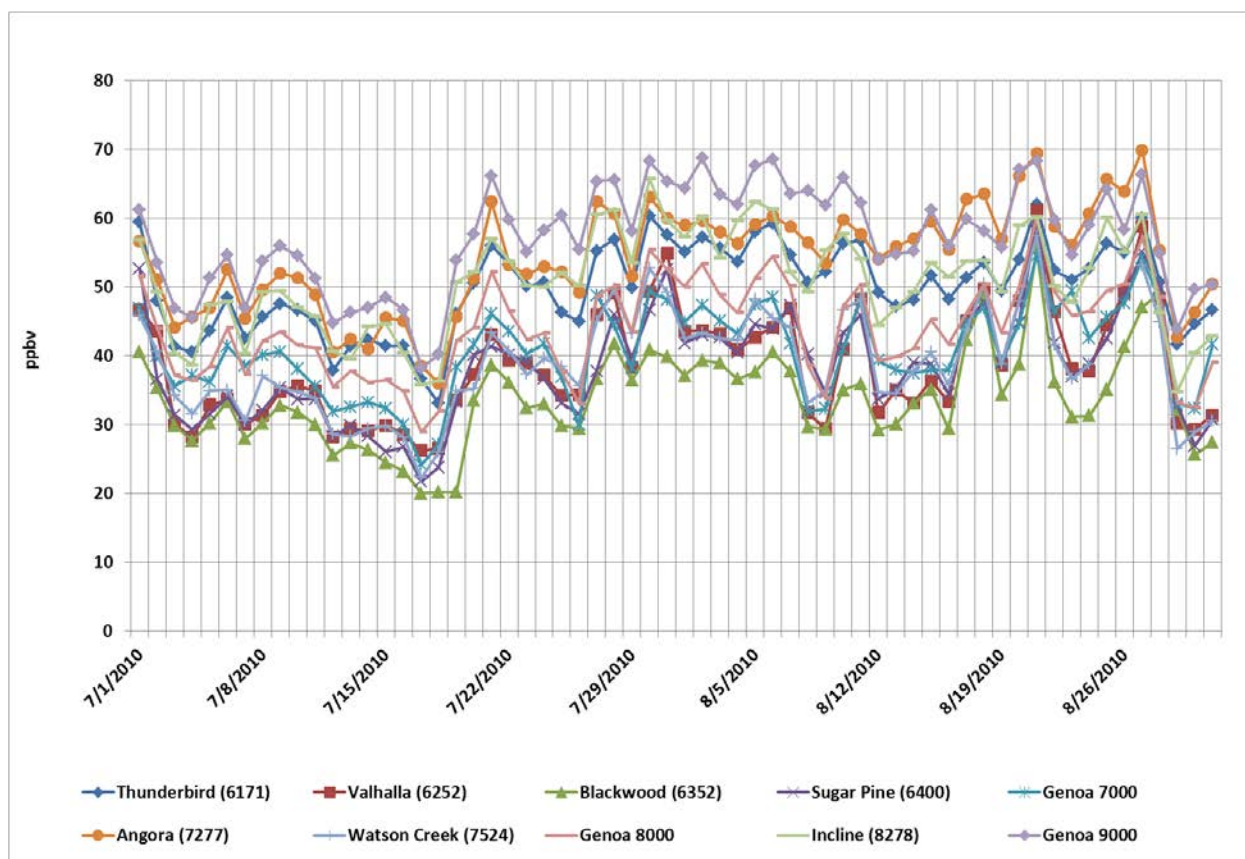


Figure 5.1-4. Changes in O₃ concentrations during the 2010 summer season at various Lake Tahoe Basin locations (mega sites). The numbers behind the site name indicate the site elevation in feet above mean sea level.

Significantly different diurnal O₃ profiles (shown as a summer season averages) were observed among the ten mega sites (**Figure 5.1-5**). While during the daytime, all sites had similar concentrations in a range of 55-60 ppb, at night the low elevation sites showed much lower concentrations (lowest values for the Lower Blackwood site) due to their proximity to major traffic routes and scavenging of ozone by the NO emissions from local traffic and possibly also from local camp fires. As the site elevation increased, the nighttime O₃ concentration also increased. The Genoa 9000 site (the highest elevation site in the study) had the highest nighttime O₃ values which were actually higher than its daytime concentrations. The similar daytime O₃ concentrations indicate good mixing of the air mass over the Tahoe Basin and the limited local influence (<5ppb) during the midday. A thorough discussion of the real-time O₃ data will be provided below in Sections 5.5 and 5.6.

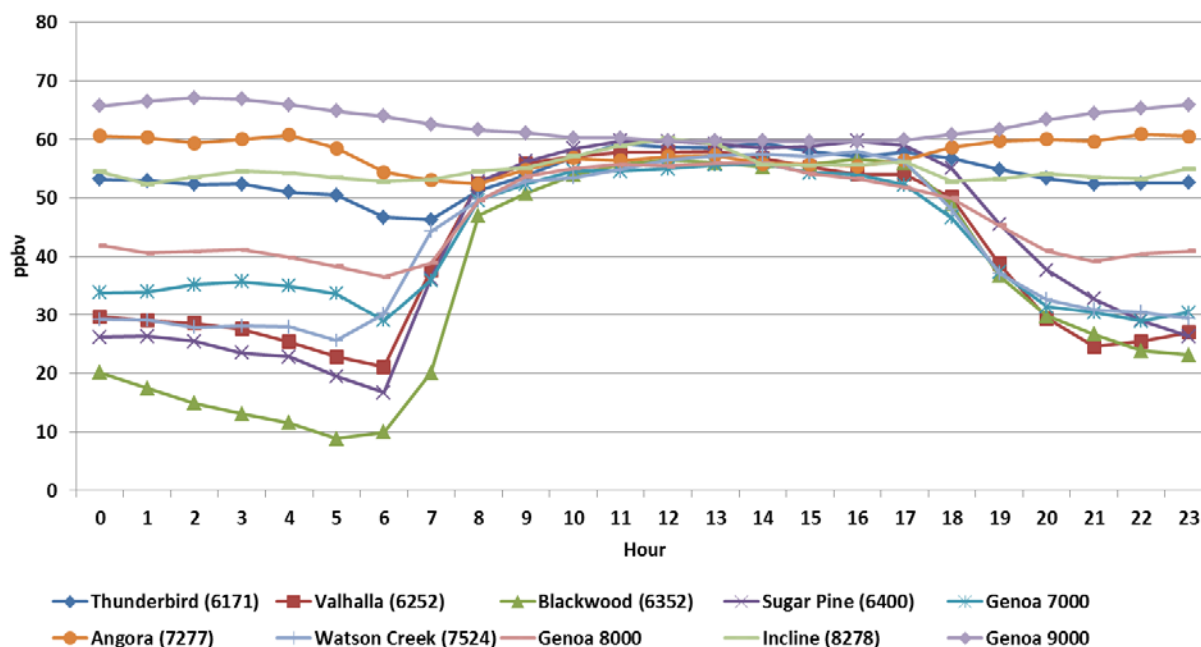


Figure 5.1-5. Diurnal profiles of O_3 concentrations (average values for the summer season) during the 2010 study at the ten mega sites in the Lake Tahoe Basin.). The numbers behind the site name indicate the site elevation in feet above mean sea level.

Our data indicate that O_3 titration by NO plays only a minor role in determining nighttime ozone values. The measured NO concentrations are simply too low, and there is too little inter-site variability in NO , to account for the huge variability that we measured in diurnal O_3 patterns. Given that (i) NO titration of O_3 occurs stoichiometrically (as opposed to catalytically), in a 1:1 ratio, producing NO_2 as a product and (ii) NO and NO_2 levels measured in 2010 were very low, with average $[NO]$ values in the 0 to 3 ppb range, it does not seem plausible that nocturnal titration by NO is playing a significant role in the Tahoe data. The site with the biggest diurnal variability and lowest average ozone (Lower Blackwood Creek, diurnal delta = 40 ppb O_3) experienced average $[NO]$ of 2.80 ppb, while the site with the smallest diurnal variability and highest average ozone (Genoa 9000, diurnal delta = approx. zero ppb O_3) experienced average $[NO]$ of 2.04 ppb. Since these two sites had similar $[NO]$ but ended up with very different behavior for O_3 , NO would not appear to be a significant factor. In a similar vein, the site with the highest average NO and flat topography (Valhalla, 3.15 ppb NO) displayed a diurnal pattern that was actually similar to that from the site with the lowest $[NO]$ (Watson Creek, 1.11 ppb NO). Elevated NO could be giving Valhalla lower O_3 than Watson Creek in the pre-dawn and early morning hours, but the magnitude seems limited to a few ppb. However, higher early morning ozone concentrations at Watson Creek could also be attributed to its higher elevation.

Other factors, especially elevation and local topography – what one might generally call access to the open sky or free troposphere during evening hours – seem to play the dominant role for nighttime O_3 mixing ratios. Therefore we believe that O_3 ambient concentrations are driven

primarily by the combination of elevation and topography, and to a much lesser extent by NO titration and deposition to vegetation and other surfaces. The general trends that emerge from the data are that the higher elevation sites with better exposure have high average O₃ concentrations and small (or negative) diurnal variability. Local topography also appears to be very important, given that flat terrain is required in order to form a stable temperature inversion during evening hours. For example, Watson Creek (WC) is more than a thousand feet higher than Thunderbird (THB), and with lower NO. Based on these criteria alone one might expect WC to have higher average O₃ and a smaller diurnal variability, but the opposite is actually observed. The key distinction here appears to be that the WC site is a flat open meadow that can better support the formation of a nocturnal temperature inversion. In addition that site contains wet vegetation that can act as an effective O₃ sink, similarly to what has been observed at Tuolumne Meadows in Yosemite NP (Burley and Ray, 2007) or Devils Postpile NM (Bytnerowicz et al., 2013). The THB site, which is near the base of a very steep hill, does not have topography that would promote forming or maintaining nocturnal temperature inversions. Therefore nocturnal O₃ loss was limited at this site.

5.2 Nitrogenous pollutants spatial and temporal variations

A series of maps showing the spatial distribution of concentrations were generated for all gaseous N pollutants measured with the passive samplers. The distribution maps of ammonia concentrations are presented for each sampling period when the full network was operational in **Figures 5.2-1** through **5.2-3**. Generally, the spatial distribution of NH₃ did not vary much between the individual collection periods. There was a clearly pronounced SW to NE decreasing gradient of concentrations associated with the transport of air masses polluted by vehicular, industrial, and agricultural emissions in the Central Valley toward the Desolation Wilderness and the Lake Tahoe Basin. Within the Lake Tahoe Basin, the highest ammonia concentrations typically occurred at the Angora Lookout site, with the lowest concentrations on the east side of the Lake. The summer season pattern is shown in **Figure 5.2-3**. In general, the measured NH₃ concentrations at the south-western portion of the Lake Tahoe Basin were slightly elevated, while those at the eastern side of the Basin were low and near background concentrations (Bytnerowicz and Fenn, 1996). These NH₃ concentrations in 2010 were similar to those measured at selected sites in 2006 in the Lake Tahoe Basin (Bytnerowicz, unpublished).

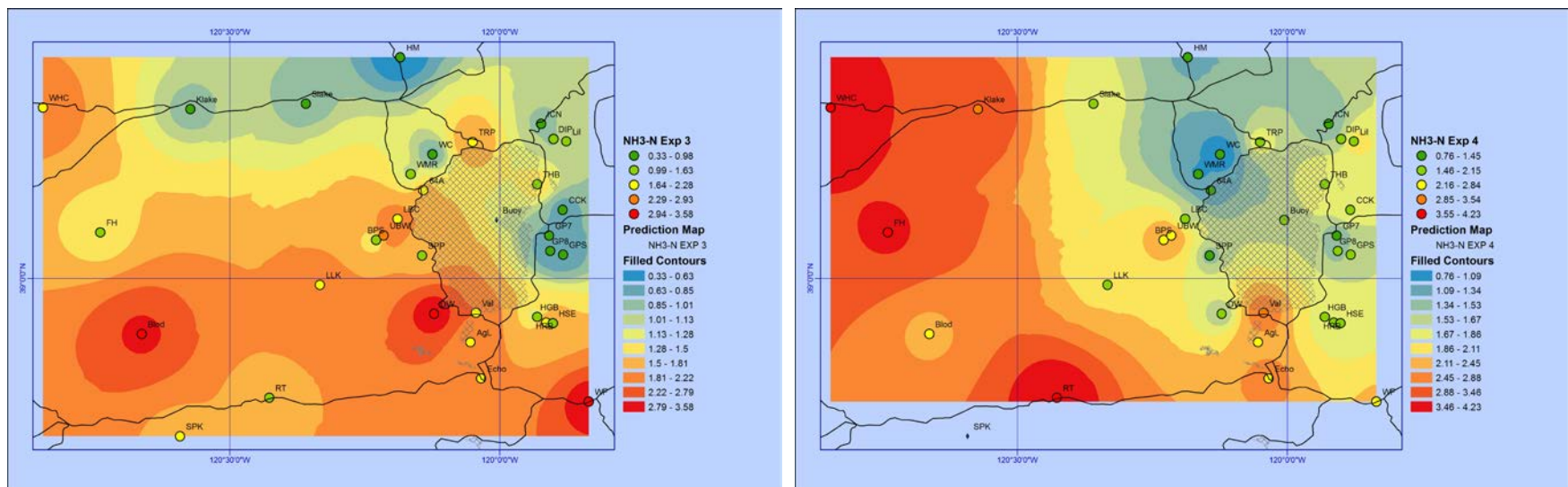


Figure 5.2-1. Ammonia distribution ($\mu\text{g NH}_3\text{-N m}^{-3}$) during exposure 3 (July 14- 29) and exposure 4 (July 29 – Aug. 11).

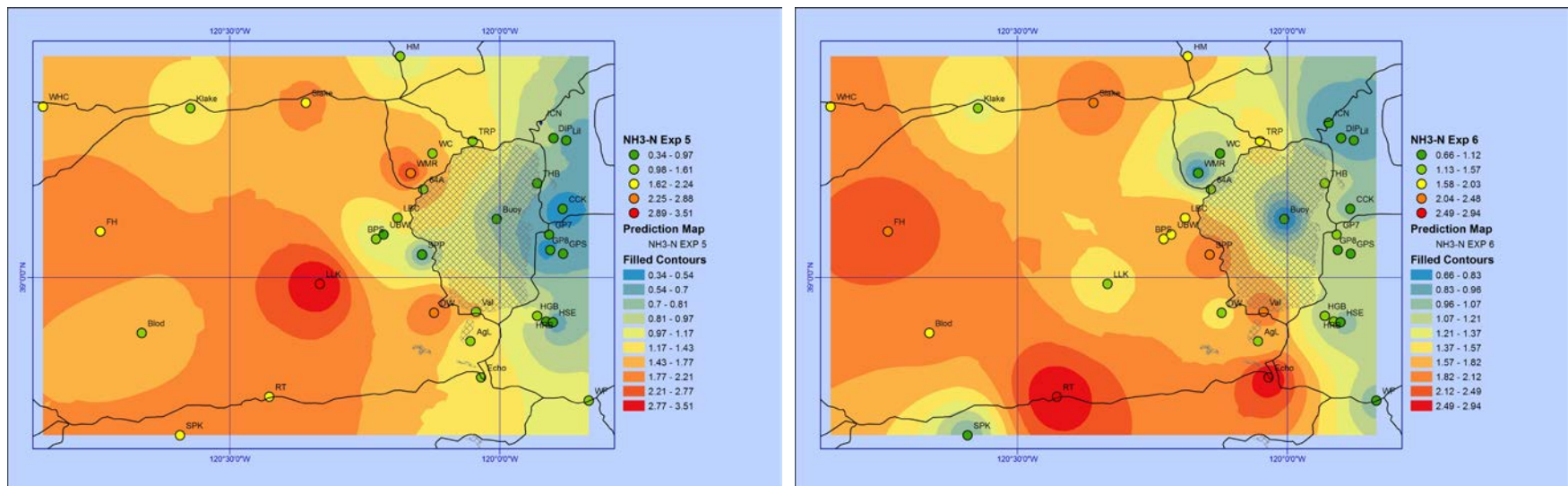


Figure 5.2-2. Ammonia distribution ($\mu\text{g NH}_3\text{-N m}^{-3}$) during exposure 5 (Aug. 11 – 25) and exposure 6 (Aug. 25 – Sept. 8).

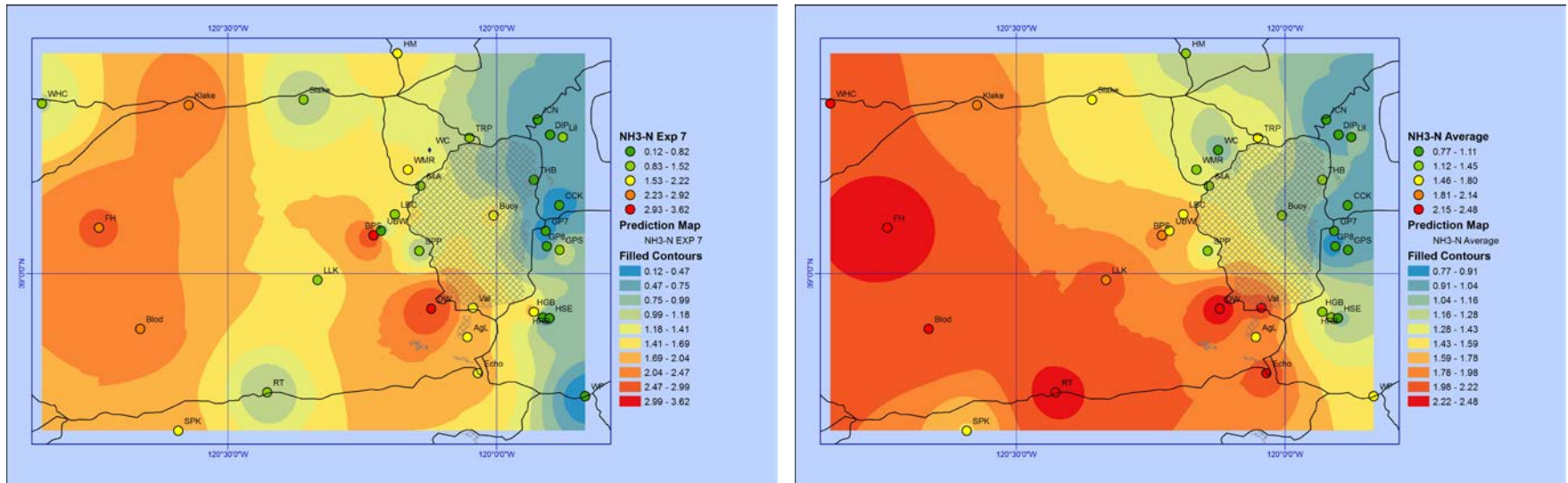


Figure 5.2-3. Ammonia distribution ($\mu\text{g NH}_3\text{-N m}^{-3}$) during exposure 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

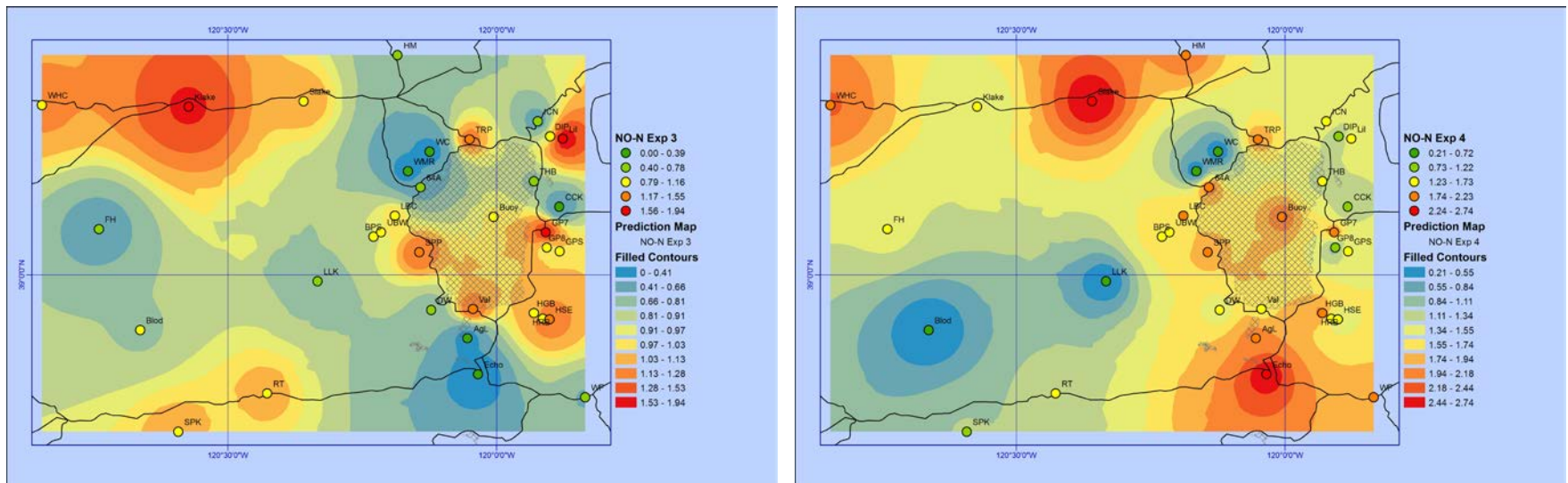


Figure 5.2-4. Nitric oxide distribution ($\mu\text{g NO-N m}^{-3}$) during exposure 3 (July 14- 29) and exposure 4 (July 29 – Aug. 11).

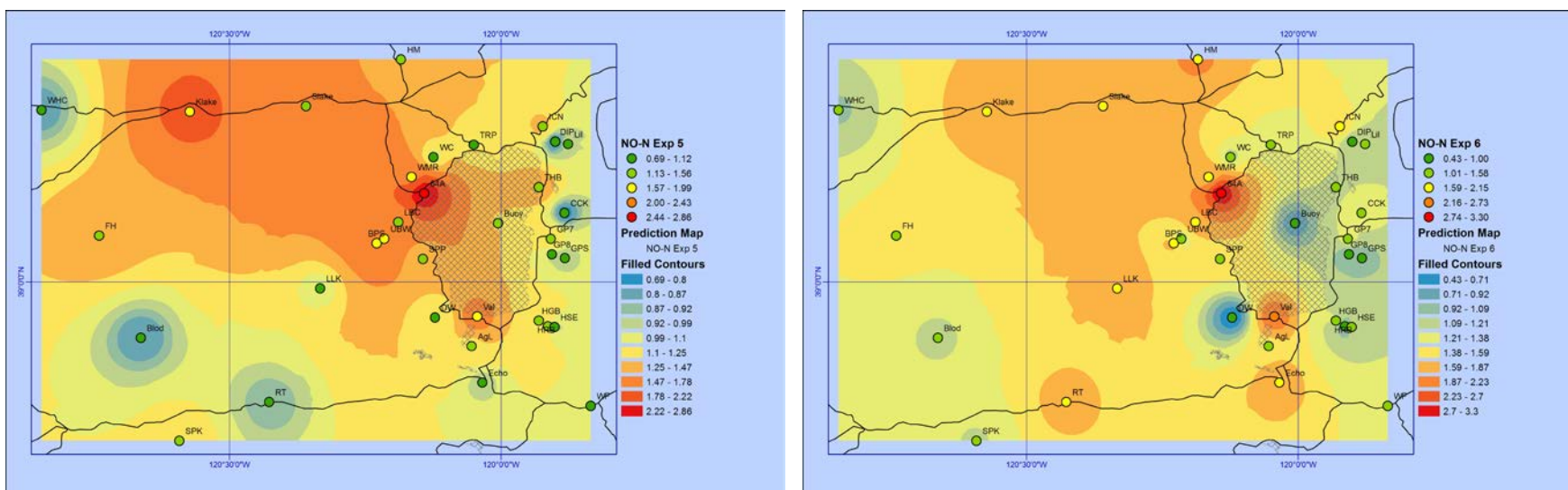


Figure 5.2-5. Nitric oxide distribution ($\mu\text{g NO-N m}^{-3}$) during exposure 5 (Aug. 11 – 25) and exposure 6 (Aug. 25 – Sept. 8).

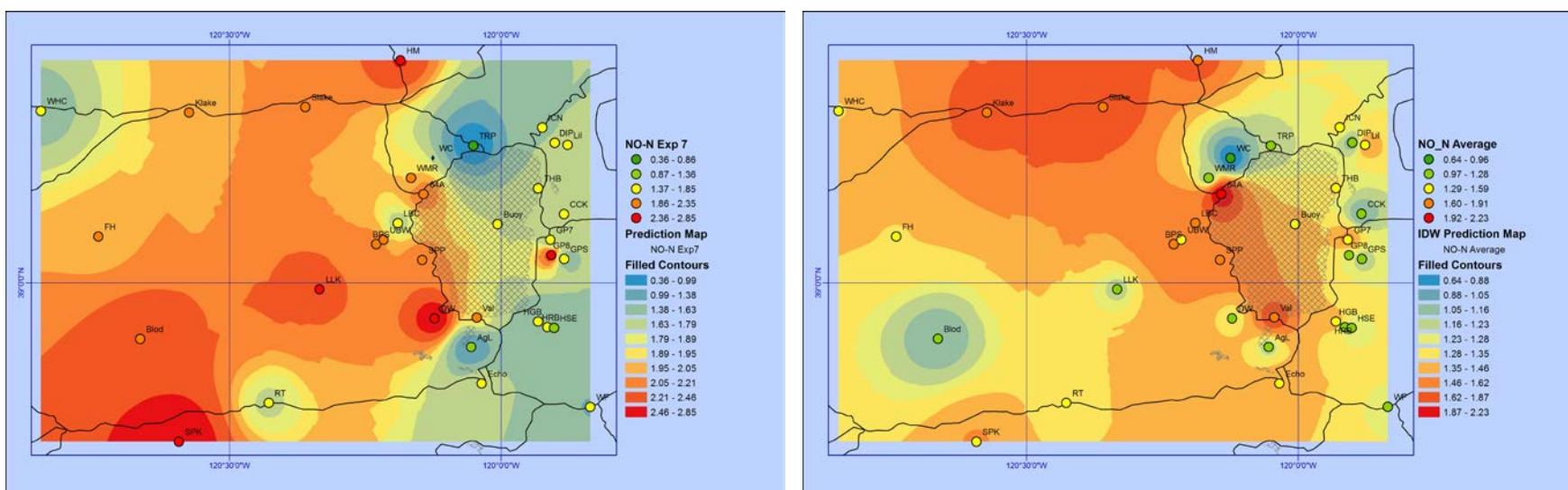


Figure 5.2-6. Nitric oxide distribution ($\mu\text{g NO-N m}^{-3}$) during exposure 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

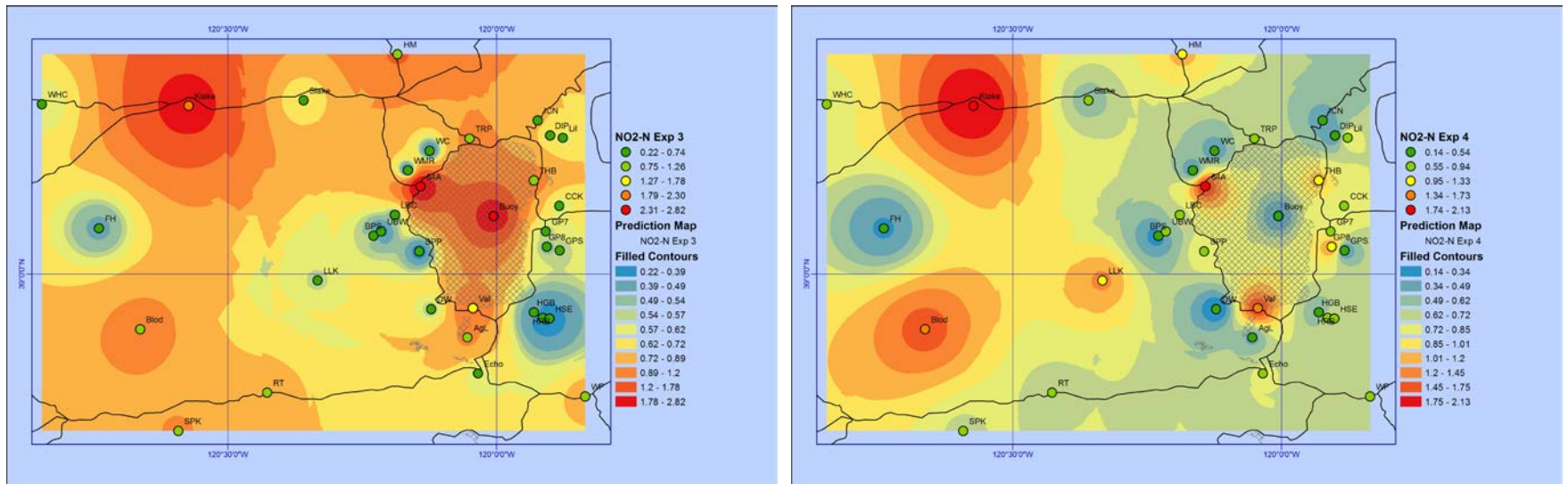


Figure 5.2-7. Nitrogen dioxide distribution ($\mu\text{g NO}_2\text{-N m}^{-3}$) during exposure 3 (July 14- 29) and exposure 4 (July 29 – Aug.11).

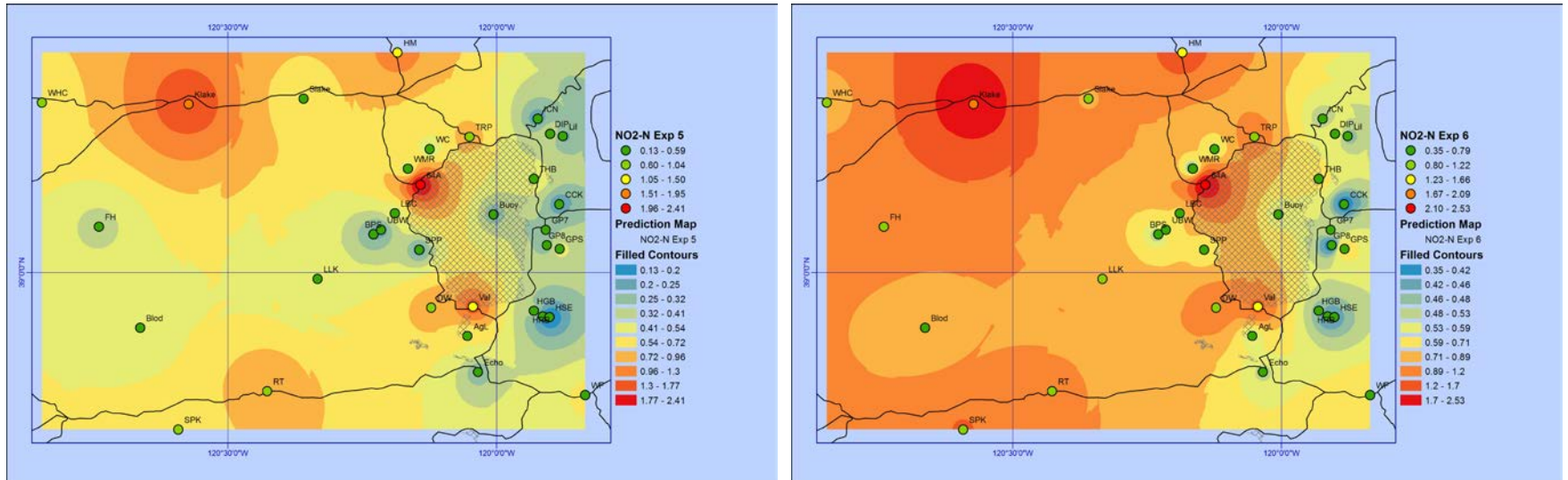


Figure 5.2-8. Nitrogen dioxide distribution ($\mu\text{g NO}_2\text{-N m}^{-3}$) during exposure 5 (Aug. 11 – 25) and exposure 6 (Aug. 25 – Sept. 8).

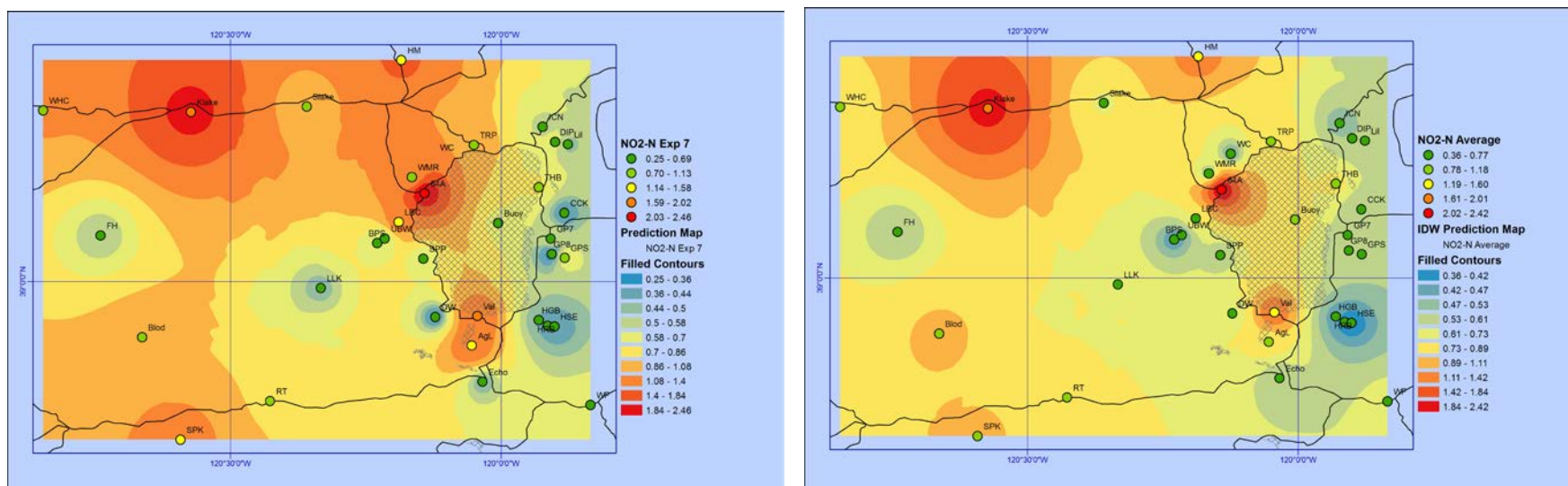


Figure 5.2-9. Nitrogen dioxide distribution ($\mu\text{g NO}_2\text{-N m}^{-3}$) during exp. 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

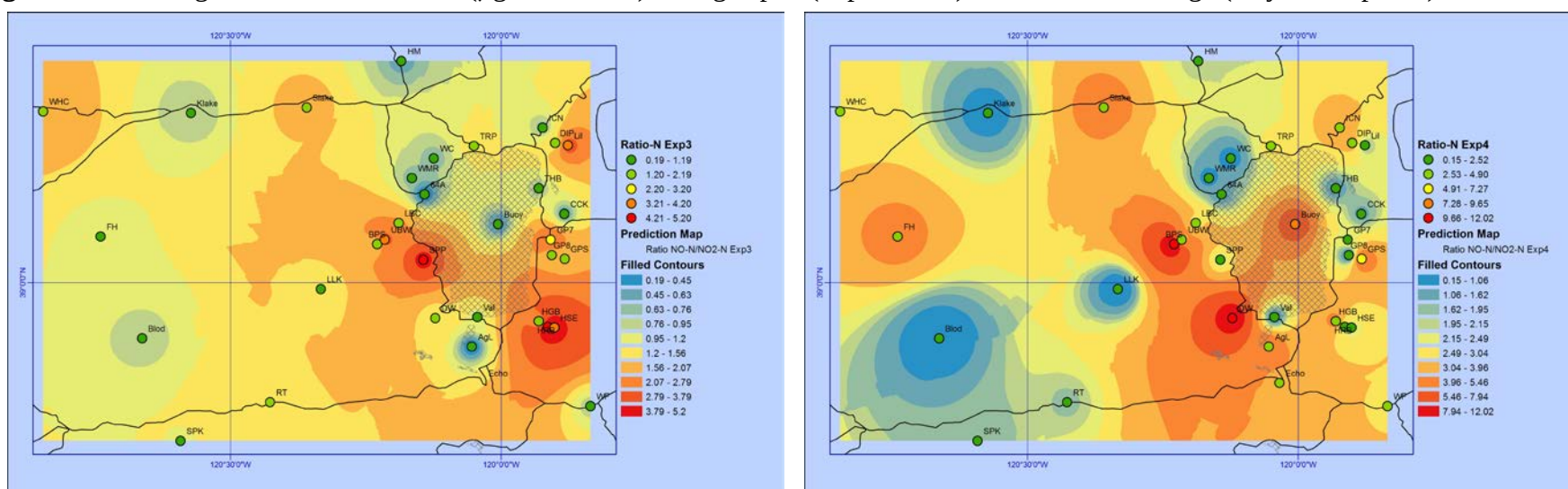


Figure 5.2-10. NO/NO₂ ratio during exposure 3 (July 14- 29) and exposure 4 (July 29 – Aug. 11).

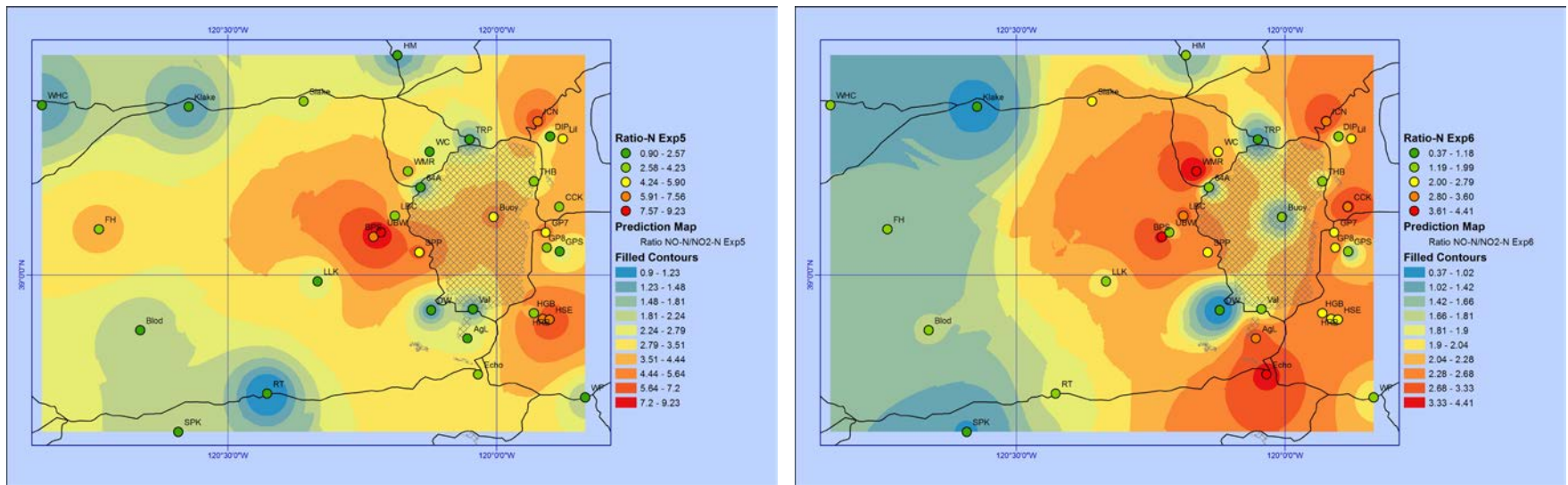


Figure 5.2-11. NO/NO₂ ratio during exposure 5 (Aug. 11 – 25) and exposure 6 (Aug. 25 – Sept. 8).

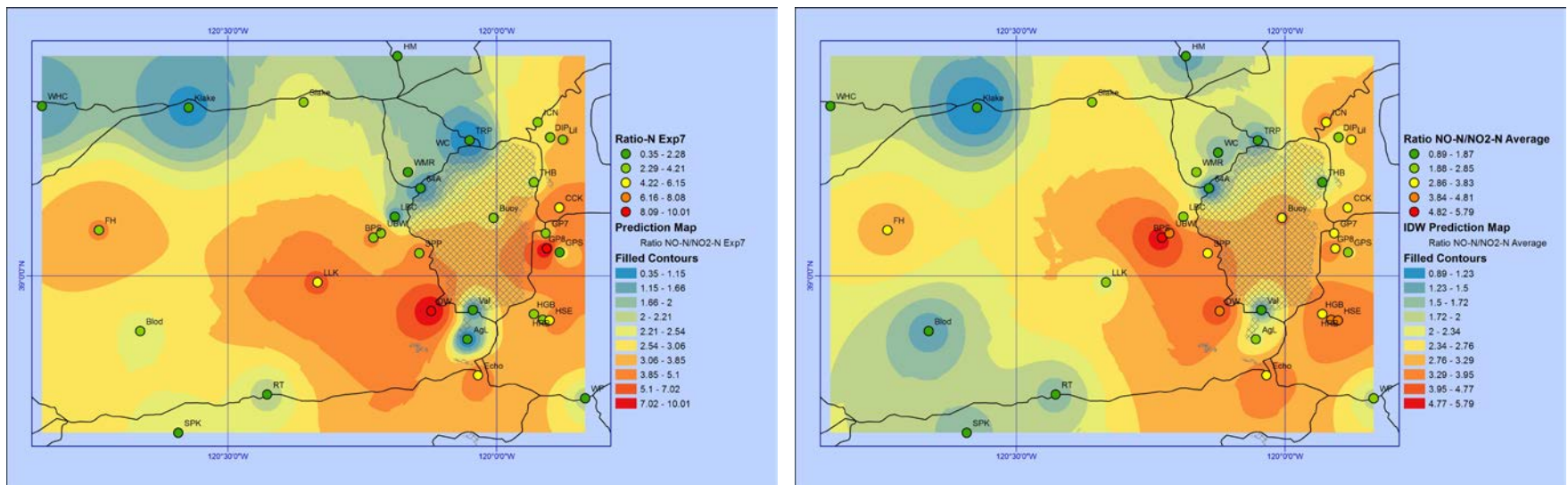


Figure 5.2-12. NO/NO₂ ratio during exposure 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

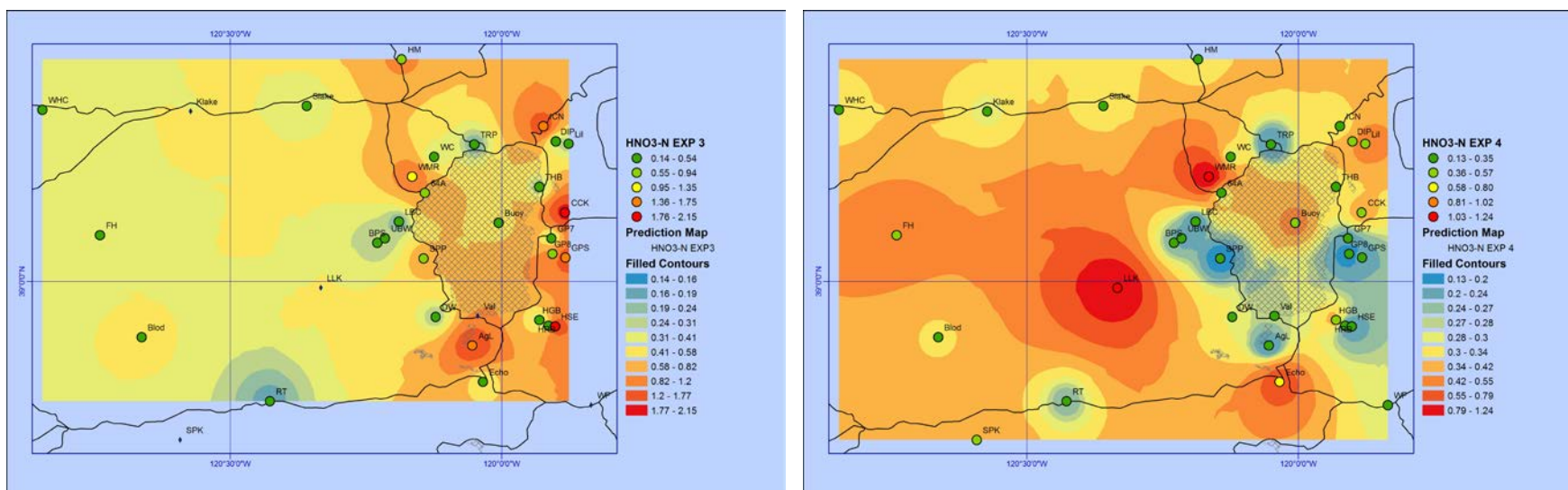


Figure 5.2-13. Nitric acid distribution ($\mu\text{g HNO}_3\text{-N m}^{-3}$) during exposure 3 (July 14- 29) and exposure 4 (July 29 – Aug. 11).

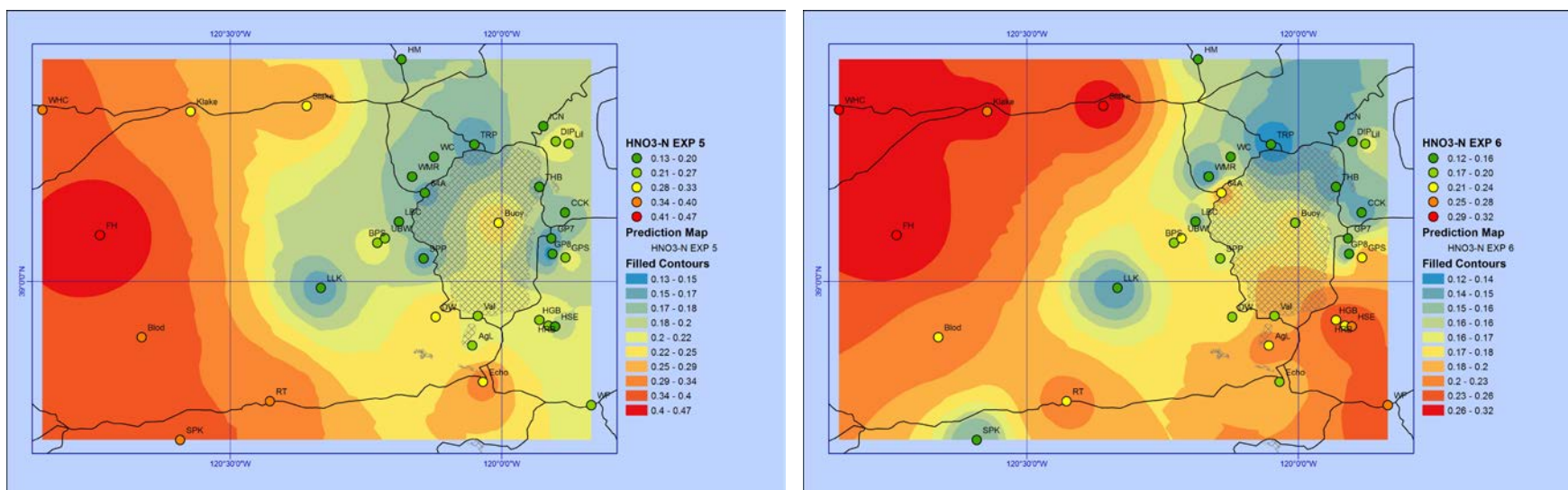


Figure 5.2-14. Nitric acid distribution ($\mu\text{g HNO}_3\text{-N m}^{-3}$) during exposure 5 (Aug. 11 – 25) and exposure 6 (Aug. 25 – Sept. 8).

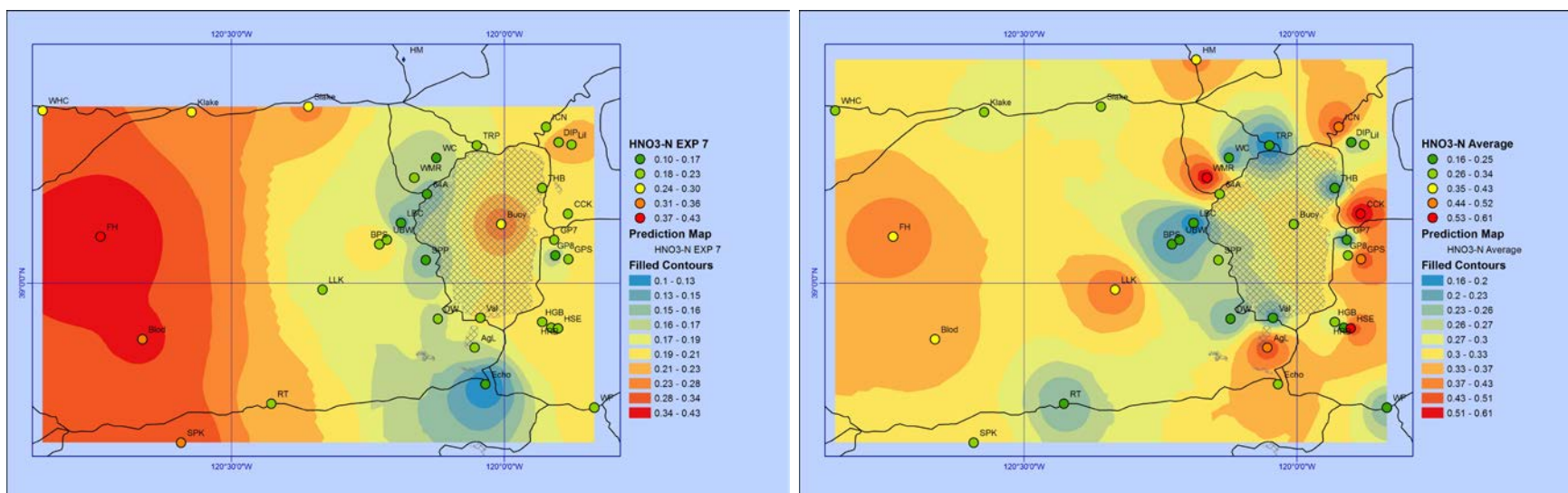


Figure 5.2-15. Nitric acid distribution ($\mu\text{g HNO}_3\text{-N m}^{-3}$) during exposure 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

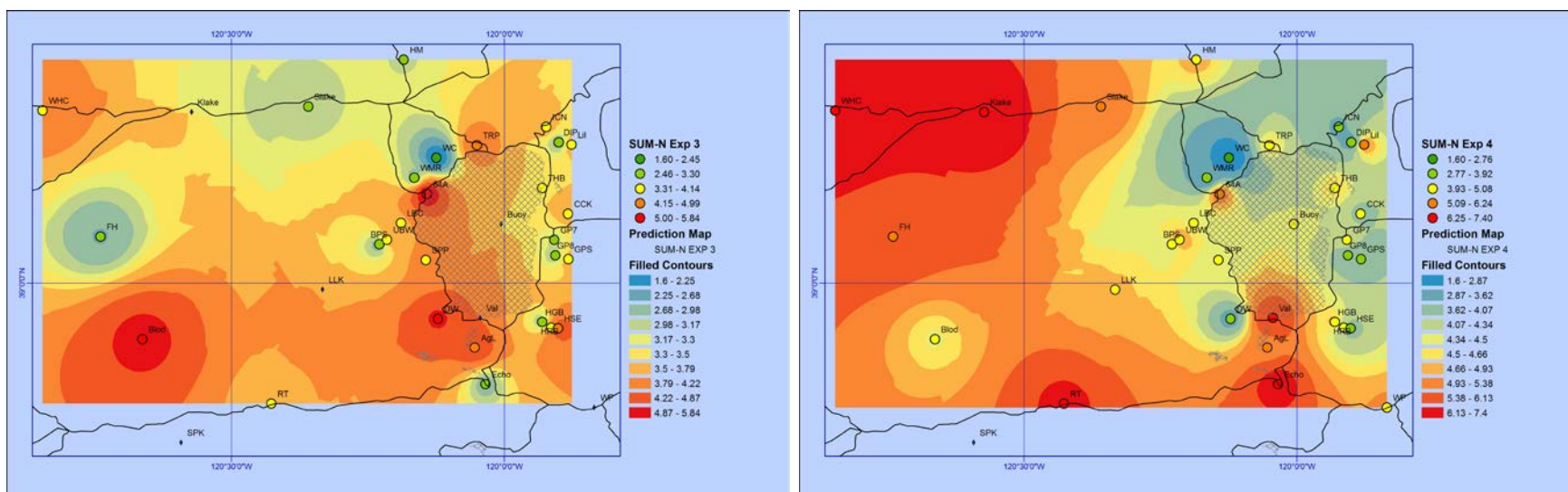


Figure 5.2-16. Total inorganic gaseous reactive nitrogen ($\mu\text{g N m}^{-3}$) during exposure 3 (July 14- 29) and 4 (July 29 – Aug. 11).

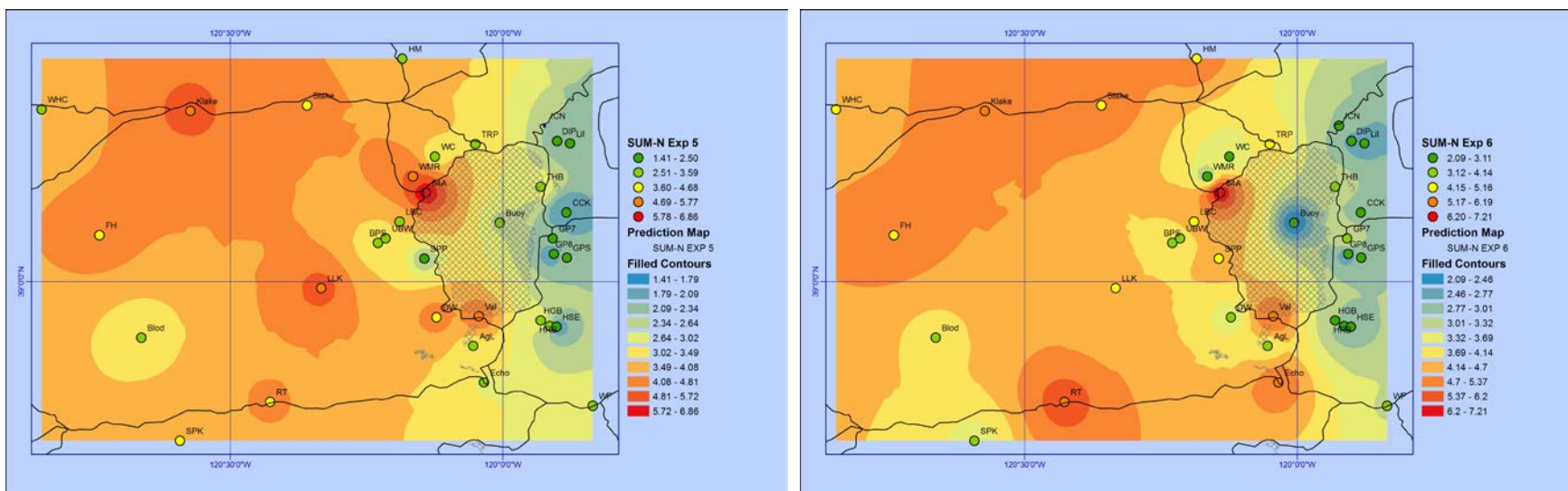


Figure 5.2-17. Total inorganic gaseous reactive nitrogen ($\mu\text{g N m}^{-3}$) during exposure 5 (Aug. 11 – 25) and 6 (Aug. 25 – Sept. 8).

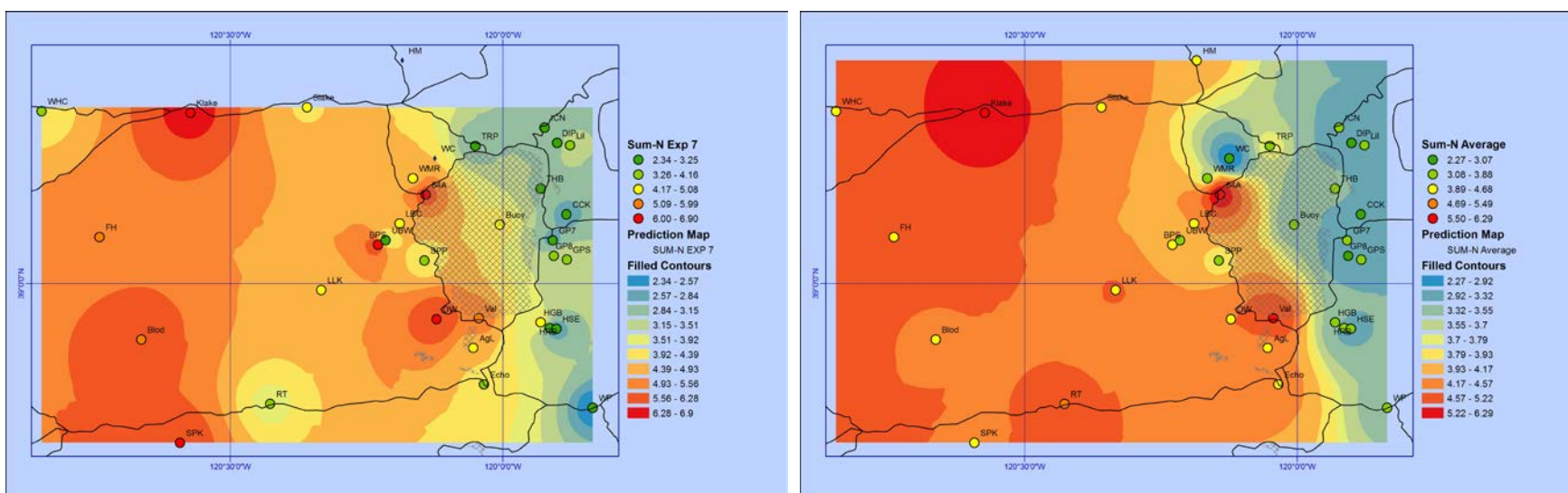


Figure 5.2-18. Total inorganic gaseous reactive N ($\mu\text{g N m}^{-3}$) during exp. 7 (Sept. 8 – 22) and seasonal average (July 14- Sept. 22).

In general, the highest NO concentrations were observed west of Lake Tahoe, and especially in the north-western section of the monitoring area (**Figures 5.2-4** through **5.2-6**). There were significant differences in spatial distribution between the monitoring periods – in periods No. 3, 4 and 7, low nitric oxide concentrations were observed in the north-western area of the Basin, while during periods No. 5 and 6 that area experienced relatively high concentrations of NO. Generally, the highest concentrations of NO occurred near transportation routes, at such sites as Kelly Lake, Serene Lake or 64 Acres. Nitric oxide concentrations at the remote higher elevation sites, such as Watson Creek, were much lower (**Figure 5.2-4**). In general the observed NO concentrations during the study were low.

Generally, the spatial distribution of NO₂ concentrations during individual exposure periods and during the entire summer season (**Figures 5.2-7** through **5.2-9**) were similar to those of NO. The highest concentrations of NO₂ were recorded near the major transportation routes (Kelly Lake and 64 Acres sites), and the lowest at the remote, high elevation sites such as on the Heavenly and Blackwood transects. The measured NO₂ concentrations were generally low indicating no exceedances of the national annual NO₂ air quality standard (annual average of 100 µg/m³).

Molar ratios of NO-N/NO₂-N were calculated for all sites and exposure periods as well as for the entire summer season and are shown in **Figures 5.2-10** through **5.2-12**. This ratio is indicative of air mass aging with the highest values showing a high proportion of the primary pollutant (NO), a situation typical for freshly polluted air masses. Low ratio values indicate well-aged, polluted air masses with a higher proportion of NO already oxidized to the secondary pollutant (NO₂). In general, the lowest values were observed at the high elevation, remote sites. The highest values of NO-N/NO₂-N were occurred at Barker Pass, the highest elevation site on the Blackwood transect. Similarly these ratios also increased with elevation on the Heavenly transect. This is in contrast with the Genoa transect where the ratio declined with elevation – a situation that would be expected in remote areas and oxidation of NO to NO₂ with distance and elevation from the pollution source (mainly transportation routes). Also surprisingly high values of that ratio were determined at the Desolation Wilderness site. This is somewhat surprising because one would expect declining NO-N/NO₂-N ratios with distance from the NO source areas at most of the remote sites of the network.

Compared with other N air pollutants, the distribution of HNO₃ was more variable in time and space. During most of summer (Exposure Periods 4 through 7) the HNO₃ concentrations were high in the western portion of the monitoring area beyond the high elevation Desolation Wilderness site and also on the eastern side of the Basin where they increased with elevation. During those periods, the lowest HNO₃ levels were observed at the low elevation sites in the western portion of the Basin (**Figures 5.2-13** through **5.2-15**). However, during Exposure Period 3, different patterns were seen with the western portion of the monitoring area experiencing much lower HNO₃ than during the rest of the season (**Figure 5.2-13**). The seasonal averages (**Figure 5.2-15**) reflected the patterns seen during most of the monitoring periods - highest concentrations on the eastern side of the Lake increasing with elevation, low HNO₃ levels on the western portion of the Basin, and elevated concentrations in the western portion of the monitoring area likely caused by the photochemical smog from the Central Valley. The HNO₃ concentrations and their distribution were similar to those determined in the 2002 study at the

same study area (Bytnerowicz et al., 2004; Gertler et al., 2006). In general, the distribution of HNO_3 was similar to that of O_3 . This may be explained by their origin as the secondary pollutants generated during photochemical reactions (Finlayson-Pitts and Pitts, 2000).

The spatial distribution of total reactive N (sum of NH_3 , NO , NO_2 and HNO_3) for the individual exposure periods were quite similar as also reflected by the summer season averages (**Figures 5.2-16 through 5.2-18**). Because NH_3 and NO participate most strongly in the total inorganic reactive N, their concentrations mostly affect the observed patterns. Consequently, the seasonal distribution patterns of the total reactive N is very similar to those of NH_3 (**Figure 5.2-3**) and NO (**Figure 5.2-6**). The highest levels of total reactive N are in the western part of the monitoring area, west of the Sierra crest in the Desolation Wilderness, and also on the southwestern side of the Lake near Highway 89 at the Valhalla and 64 Acres sites. The eastern portion of the Tahoe Basin, especially the high elevation remote sites, as well as the Watson Creek site in the NW part of the Basin, have the lowest levels of reactive N species.

Among the measured gases, NO and NH_3 have the highest participation in gaseous inorganic reactive N species (seasonal averages for all sites 35.4 and 38.0%, respectively). However, the contribution of HNO_3 may also be quite high at some of the monitoring sites with a seasonal average for all sites of 8.4%. Due to the high deposition velocities of NH_3 and HNO_3 , these two gases have the highest impact on N dry deposition in arid and semi-arid environments (Hanson and Lindberg, 1990) including California mixed conifer forests (Bytnerowicz and Fenn, 1996). Atmospheric apportionment of the measured gases at all passive sampler sites in the summer season of 2010 is presented in **Figure 5.2-19**.

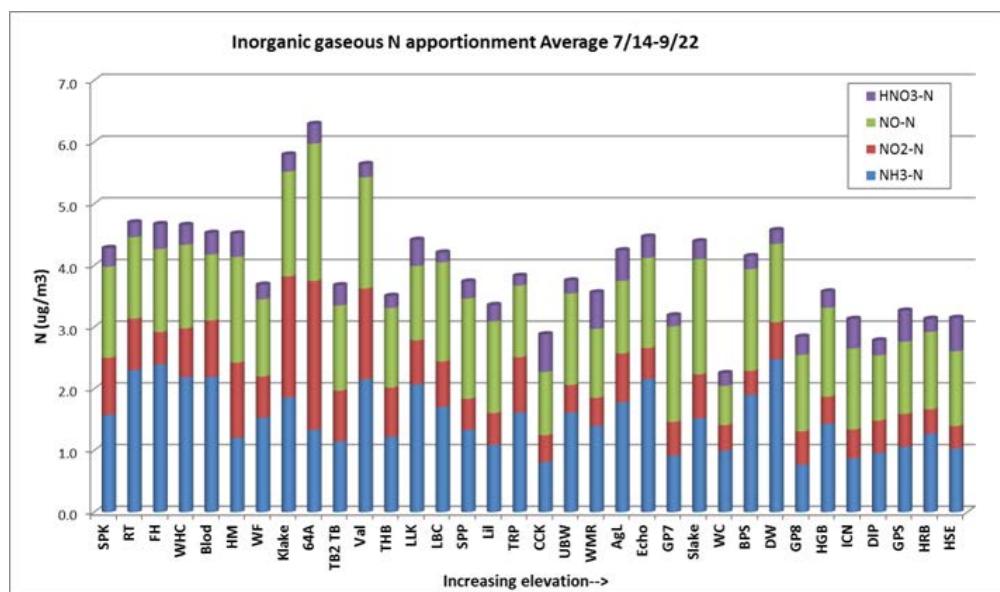


Figure 5.2-19. Apportionment of the measured inorganic gaseous pollutants during the 2010 summer season. The sites are organized from the lowest to the highest elevation.

5.3 Volatile Organic Compounds spatial and temporal variations

Figure 5.3-1 shows the concentrations of all compounds measured over seven 2-week periods at

all sampling sites (see Table 4-3). However, due to snow cover at higher elevation sites in June, these some sites were established later, (end of June or beginning of July), such that the 1st sampling period is shortened or even absent for these those sites. These sites include Genoa Peak 9000 (sampling started June 30), Upper Incline (June 30), Diamond Peak (July 2), Tahoe Regional Park (July 14), Watson Mountain Road (July 1), Barker Pass (July 8), Upper Blackwood Creek (July 1), all three Heavenly sites (July 1), Desolation Wilderness (July 14), and Thunderbird Lodge (July 1). In addition, due to some logistical problems, sampling at White Cloud, Kelly Lake, Serene Lakes, Hobart Mills, and Forest Hill started on about June 21 – 24 and at Sly Park and Loon Lake on about June 28 – 29. Also, the sampling on the TB2 NASA Buoy on the Lake was initiated on July 22.

The sites on **Figures 5.3-1 a-d** are arranged according to their elevations. **Figure 5.3-1a** shows sites located from 3,500' to 6,000', **Figure 5.3-1b** sites from 6,100' to 6,500', **Figure 5.3-1c** sites from 6,800' to 7,500' and **Figure 5.3-1d** sites from 7,600' to 10,000'. Several samples were lost due to the instrument malfunction during analysis or sampling cartridges missing from the field, as noted in **Figure 5.3-1**. Since the passive cartridges were analyzed by the thermal desorption method (i.e. the whole sample was desorbed from the cartridge for the single GC/MS analysis), there was no possibility of replicate analysis. It can be noticed from this figure that measured VOC concentrations are generally low, in the sub-ppb range. The highest concentrations were usually observed for the sampling period Exp 3 (mid – to end July), followed by the period Exp 2 (the first two weeks of July), Exp 4 (the first two weeks of August) and Exp 5 (mid- to end of August). This is consistent with the average ambient temperatures observed during these time periods. **Figure 5.3-2** shows the average temperatures (in degree C) for Exp 2 – Exp 7 sampling periods and all sampling sites, arranged according to their elevations. Although the ambient temperatures vary between sites, in general the Exp 3 period is the highest and Exp 7 period – the lowest.

Figure 5.3-1 also shows the ratio of measured anthropogenic compounds to biogenic compounds (Anth/Bio) for all valid samples. It is important to note that the absolute Anth/Bio ratios are not meaningful, since only limited number of anthropogenic species was measured (mostly characteristic for fossil fuel combustions). Rather, the changes of these ratios from site to site and between monitoring periods are more important. In general, biogenic species (isoprene and α -pinene) are the more abundant than anthropogenic species (Anth/Bio <1) at all sites and all sampling periods with a few exceptions: the Exp 3 and Exp 6 sampling periods for the TB2 NASA Buoy site, which was situated in the middle of the Lake Tahoe, the Exp 6 period for 64 Acres, the Exp 7 period for Tahoe Regional Park, the Exp 2 period for Upper Blackwood Canyon, the Exp 7 period for Echo Lake, the Exp 3 period for Desolation Wilderness, and the Exp 5 period for Upper Incline site. The concentration data for all measured VOC are provided in Appendix B.

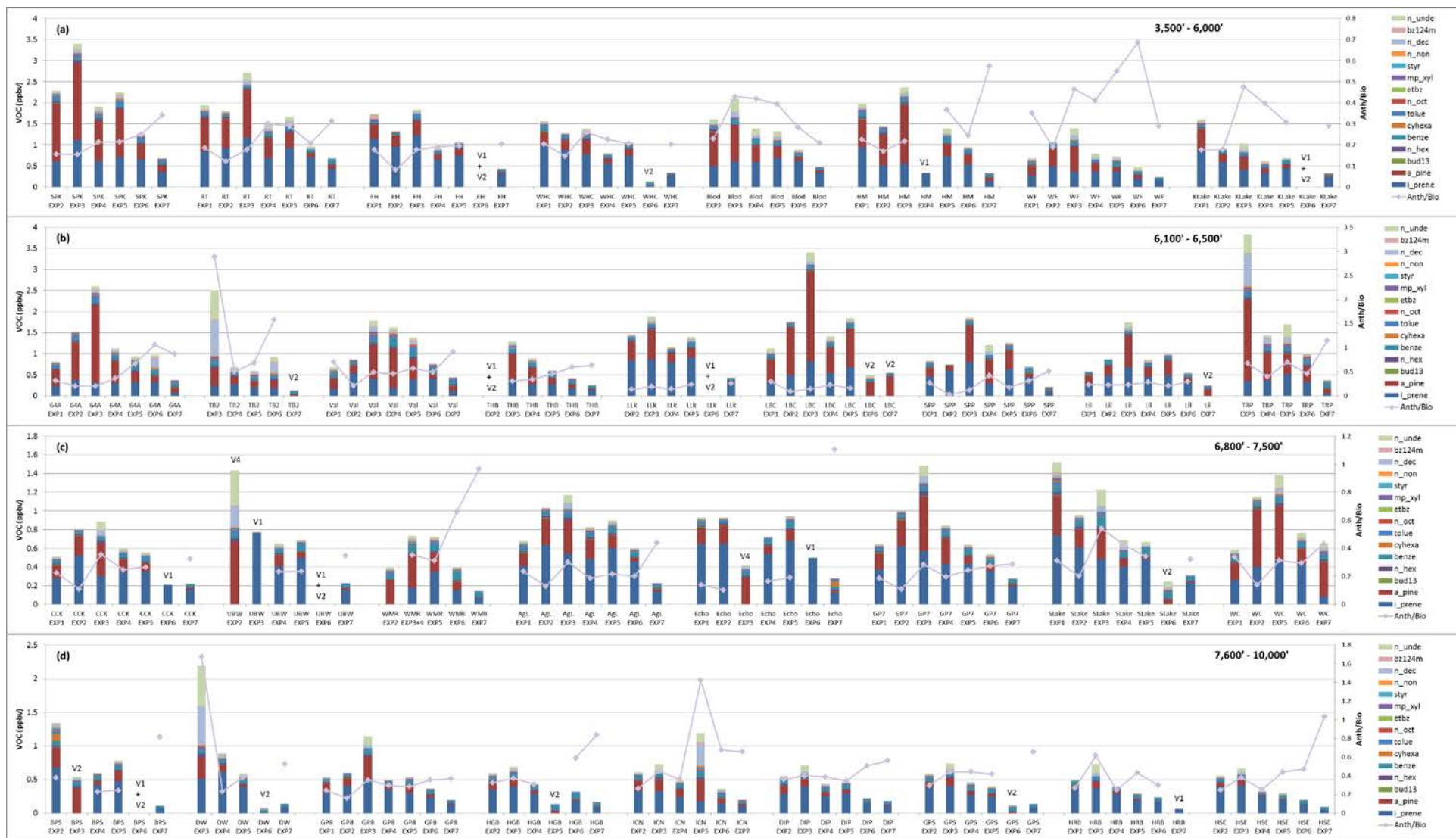


Figure 5.3-1. Concentrations of all monitoring species and Anthropogenic/Biogenic species ratios for all monitoring periods (Exp 1 through Exp 7) and sites, arranged according to their elevations. Panel (a): sites situated at 3,500' to 6,000'; (b) sites at 6,100' to 6,500', (c) sites at 6,800' to 7,500', and (d) sites at 7,600' to 10,000'. See Table 2 for site abbreviations. V1 = data for n-hexane up to n-undecane (including α -pinene) void due to GC/MS instrument malfunction; V2= data for 1,3-butadiene and isoprene void due to GC/MS instrument malfunction; V4= cartridge for 1,3-butadiene and isoprene missing.

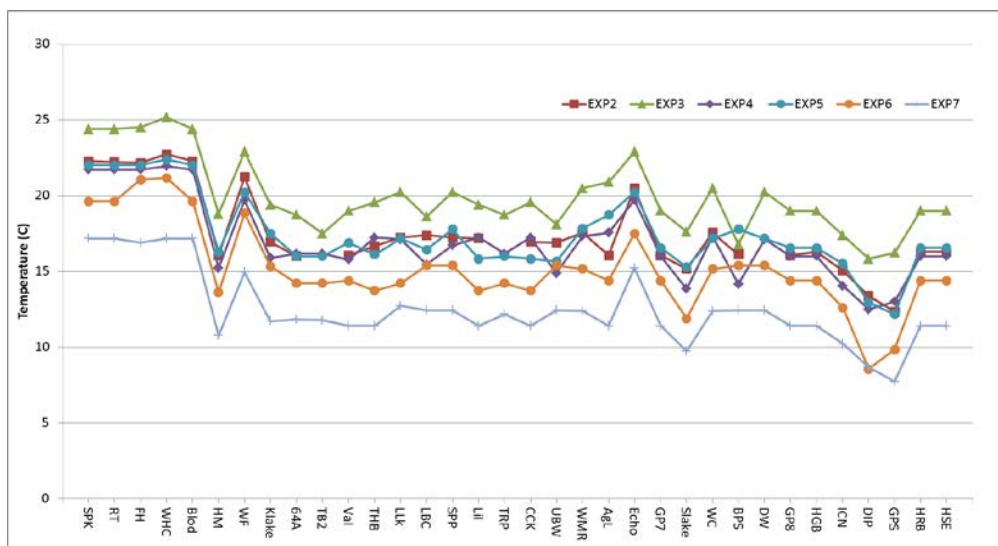


Figure 5.3-2. Average ambient air temperatures (in degrees C) for Exp2 – Exp7 sampling periods for all sampling sites, arranged according to their elevations

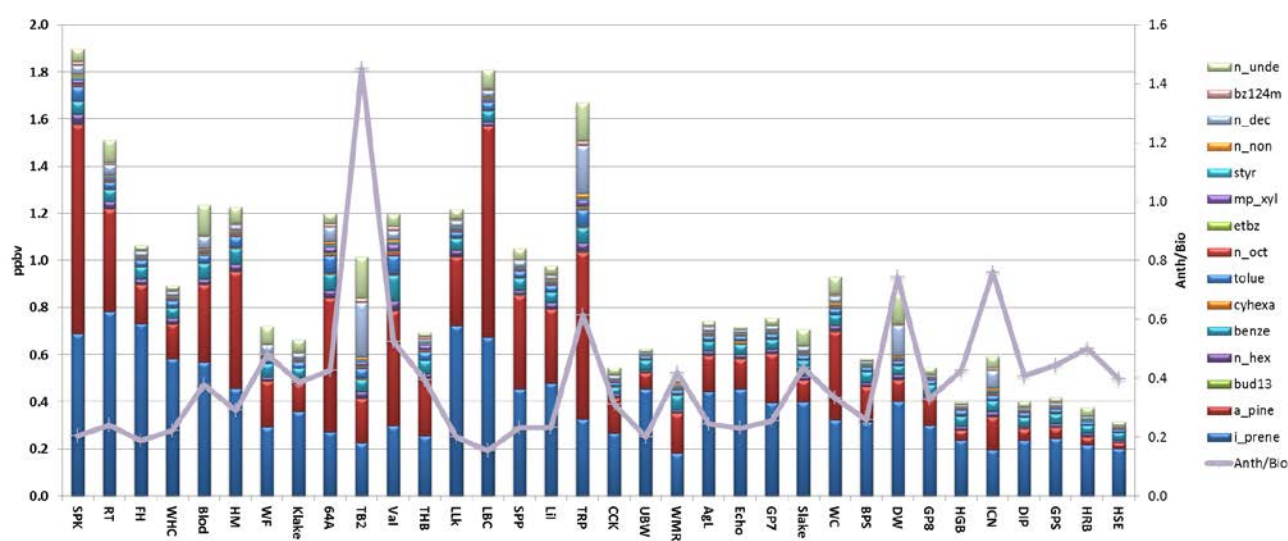


Figure 5.3-3 shows the concentrations of measured VOC compounds averaged over Exp3-Exp7 sampling periods. Sites are arranged according to their elevations. Although the highest VOC concentrations are measured at the lower elevation sites on the western slope of the Sierra-Nevada mountain range (SPK, RT, Blod and HM), they are dominated by isoprene and α -pinene. For sites situated close to the Lake, anthropogenic species are becoming more important (i.e. TRP, 64A, Val), although sites like LBC and SPP are still dominated by biogenic species. The highest Anth/Bio ratios are consistently observed at the middle of the Lake (TB2 NASA Buoy).

Anthropogenic/Biogenic Ratio Maps. The set of maps was developed with Geostatistical Analyst, for the distribution of Anth/Bio ratios. Many sites were not active until Exp3. **Figure 5.3-4** shows Anth/Bio ratios for the Exp1 and Exp2 sampling periods. Sites with missing or invalid data are denoted as white circles. All sampling sites were active by Exp3.

The Exp3 sampling period (**Figure 5.3-5**), was characterized by the highest ambient temperatures (see **Figure 5.3-2**) and high ozone concentrations. The data for Echo Lake, Upper Blackwood and Barker Pass were not valid for Exp3 (see **Figure 5.3-1**). Also, due to the restricted access to the sites out of Watson Mountain Road, passive cartridges for the WMR site were exposed for 4 weeks (Exp3 + Exp4) instead of two weeks and for the Watson Creek site (WC) there are no samples for Exp3 and Exp4 periods. In Exp3 there were high Anth/Bio ratios (in the range of 1.9 - 2.9) observed for TB2 NASA Buoy site and Desolation Wilderness. For the TB2 site, higher molecular weight hydrocarbons n-decane and n-undecane are more abundant (see **Figure 5.3-1**), which may indicate the influence of diesel emissions from large boats. At that site accumulation of these species may occur over time, since they are more resistant to a photochemical degradation as compared with reactive biogenic species or methylated aromatic anthropogenic compounds (i.e. toluene, xylenes or 1,3,5 –trimethylbenzene).

Figure 5.3-6 shows Anth/Bio ratios for the Exp4 sampling period. The data from Hobart Mills (HM) were not valid and Watson Creek (WC) samples were missing (see above). This period was characterized by higher ozone concentrations and average ambient temperature in the normal range, but Anth/Bio ratios were rather low (the highest range 0.4 – 0.5). Again, the Lake area and the sites around and north of the Lake have had the highest Anth/Bio ratios which may indicate the influence of a local traffic. Also, Genoa Peak 9000 (GPS), Woodfords (WF) and Blodgett (Blod) areas had Anth/Bio ratios in the range of 0.41 - 0.45.

Figure 5.3-7 shows Anth/Bio ratios for the Exp5 sampling period. The ratios are higher (the highest range 0.7 – 1.4), but the pattern is similar to Exp4 period. **Figures 5.3-8** and **5.3-9** show Anth/Bio ratios for sampling period Exp6 and Exp7, respectively. Both periods have several missing data points, as indicated by white circles. For these periods the average ambient temperatures were dropping (see **Figure 5.3-2**), which may influence biogenic species emissions. Consequently, Anth/Bio ratios were rising.

Finally, **Figure 5.3-10** shows Anth/Bio ratios averaged over Exp3 – Exp7 (7/14/2010- 9/22/2010) monitoring periods (since all monitoring sites were active by the Exp3 period), with all non-missing values included. The highest ratios are observed for the Lake area and the sites close to the main roadways.

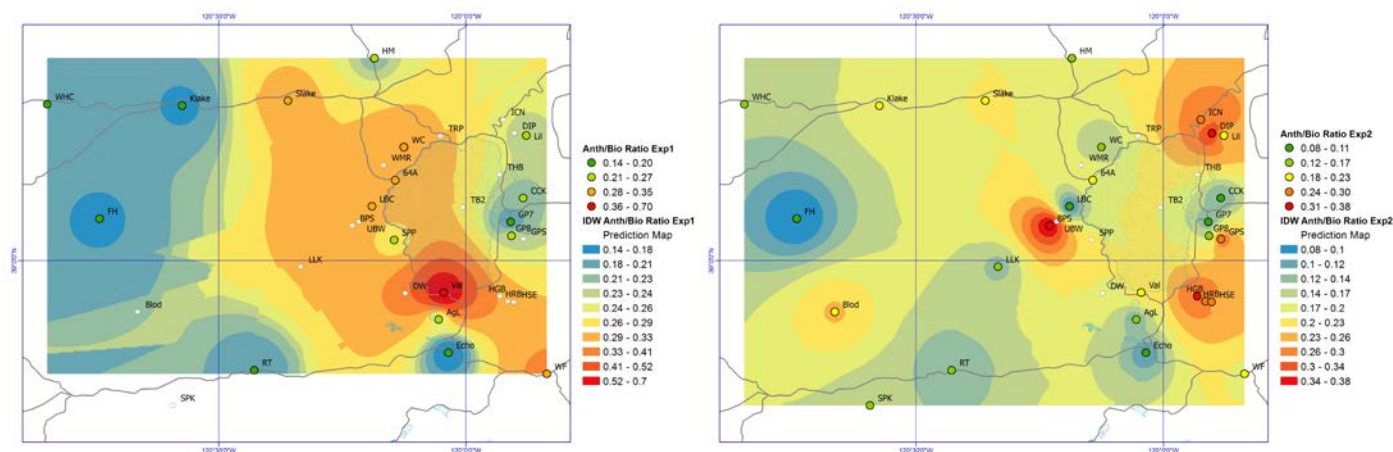


Figure 5.3-4. Anth/Bio Ratio prediction map for Exp1 (6/15-6/29) and Exp2 (6/29-7/14). Sites with missing or invalid data are denoted as hollow circles.

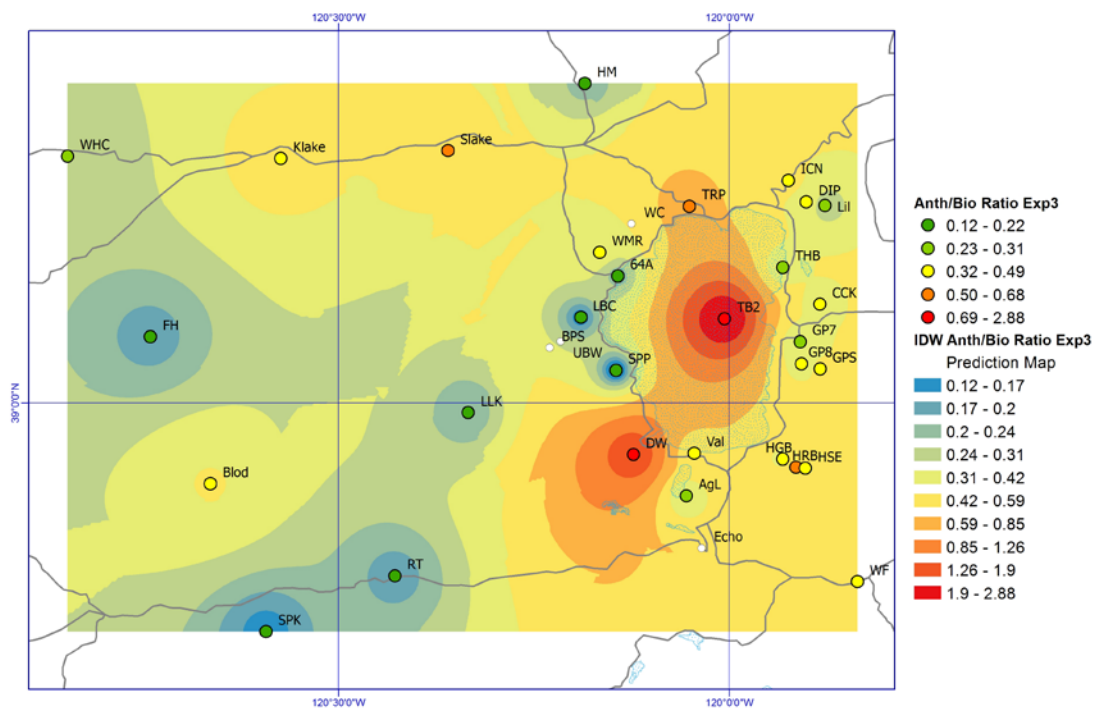


Figure 5.3-5. Anth/Bio Ratio prediction map for Exposure 3 (July 14-29). Sites with missing or invalid data are denoted as hollow circles.

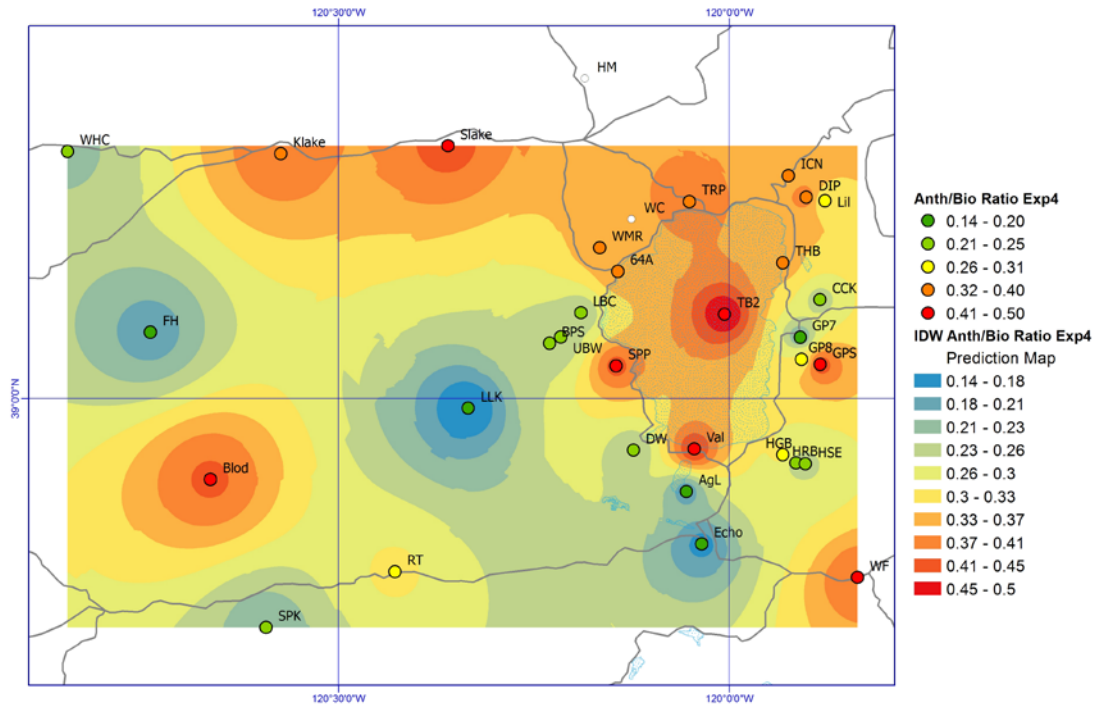


Figure 5.3-6. Anth/Bio Ratio prediction map for Exposure 4 (July 29-Aug. 12). Sites with missing or invalid data are denoted as hollow circles.

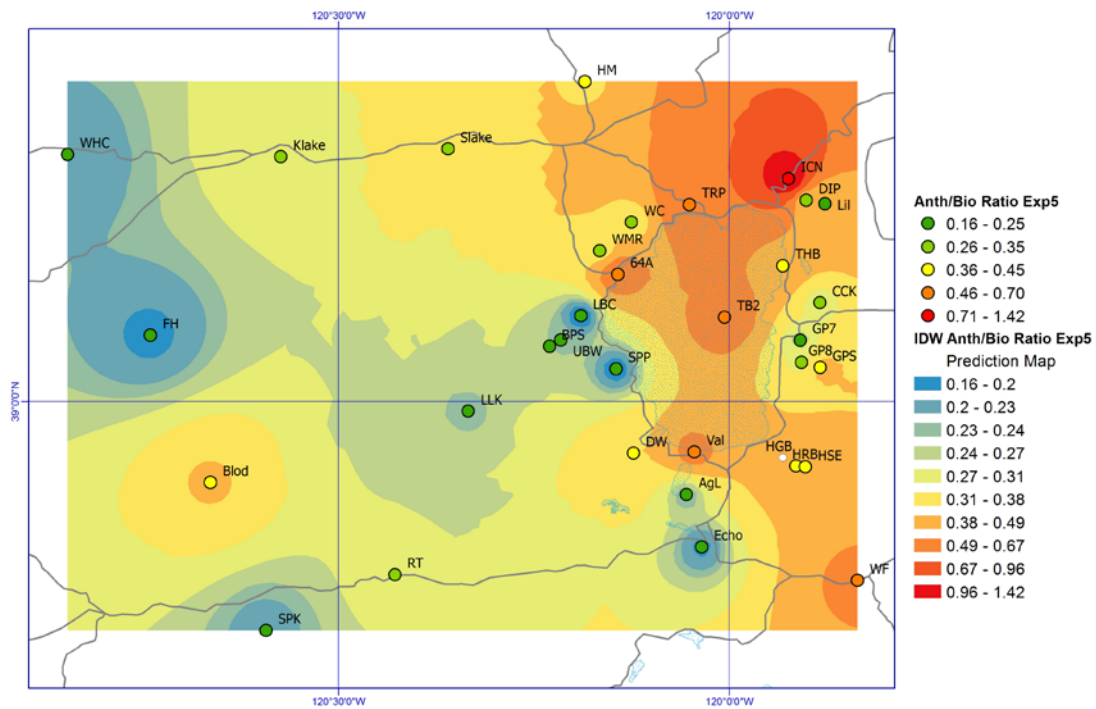


Figure 5.3-7. Anth/Bio Ratio prediction map for Exp5 (Aug. 12-25). Sites with missing or invalid data are denoted as hollow circles.

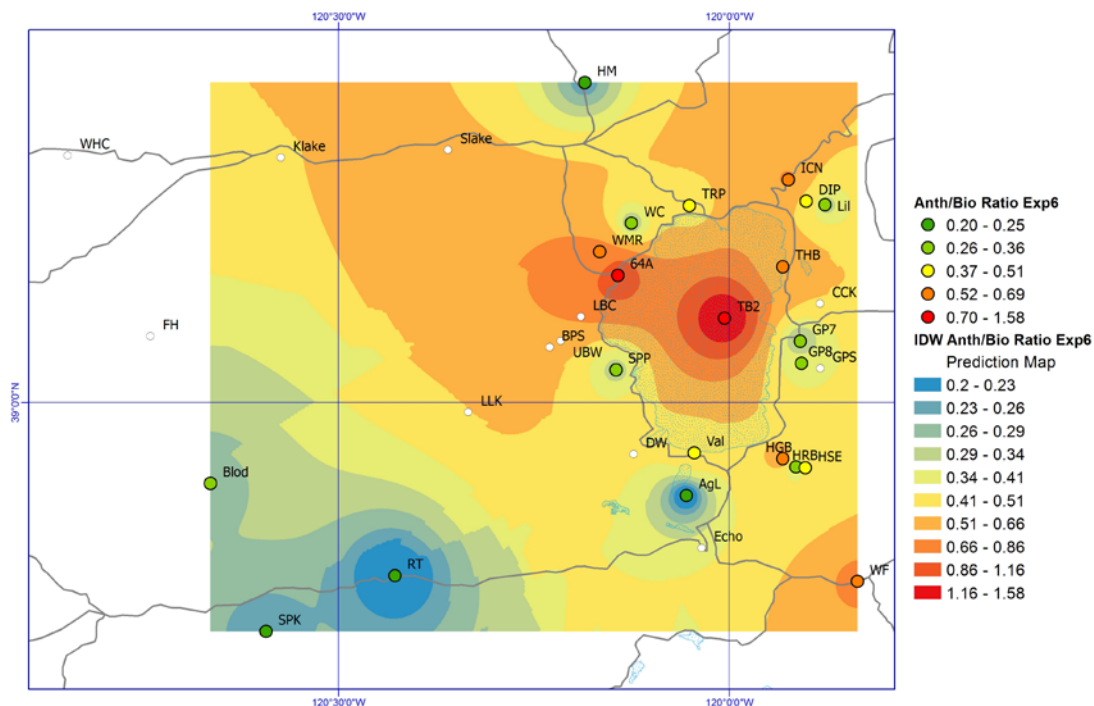


Figure 5.3-8. Anth/Bio Ratio prediction map for Exp 6 (Aug. 25- Sept. 8). Sites with missing or invalid data are denoted as hollow circles.

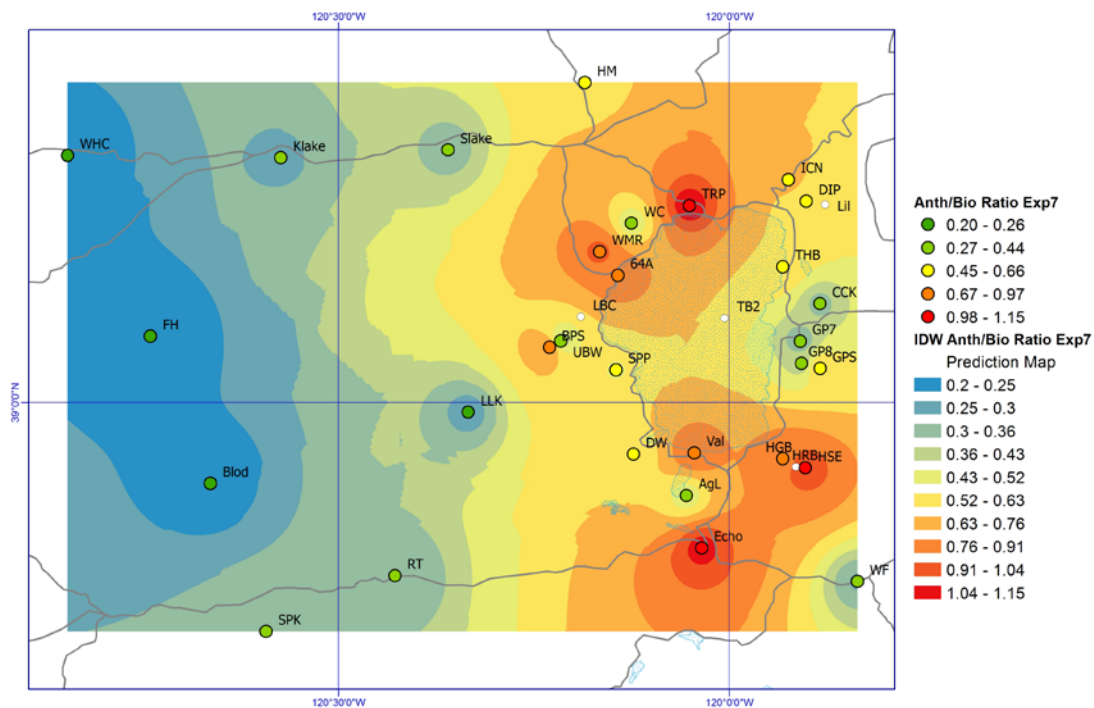


Figure 5.3-9. Anth/Bio Ratio prediction map for Exp7 (Sept. 8- 22). Sites with missing or invalid data are denoted as hollow circles.

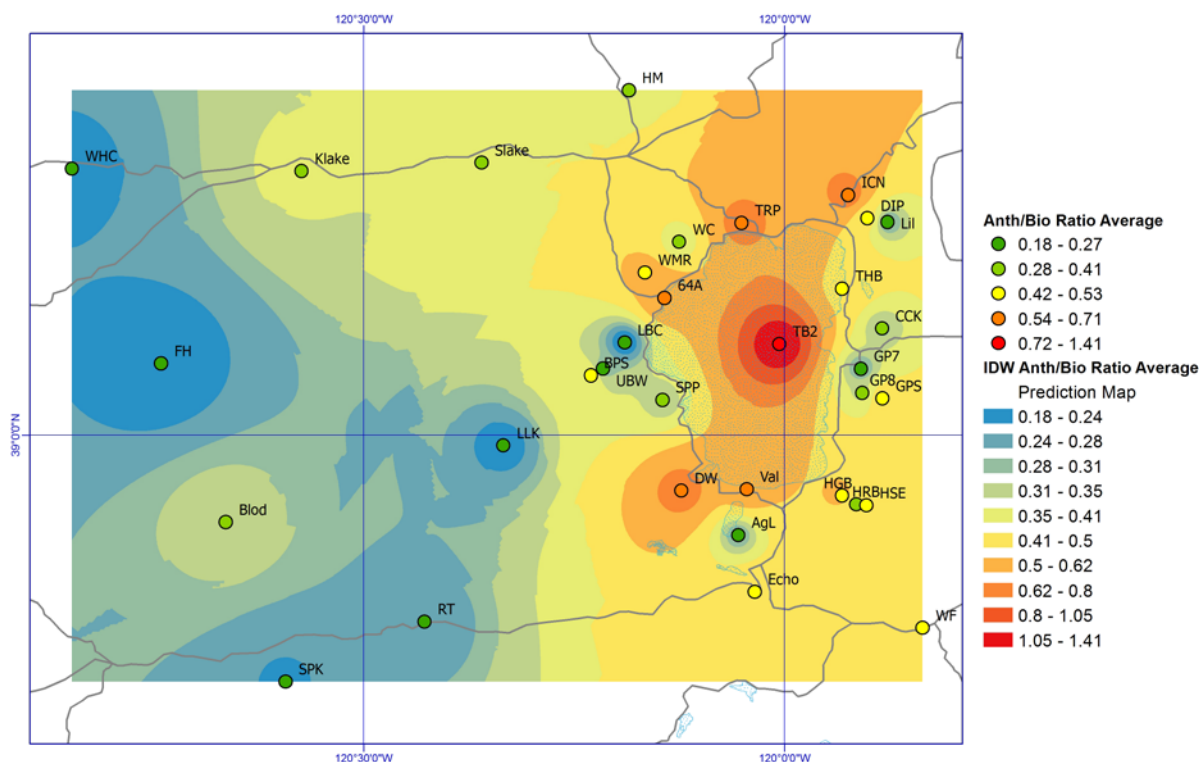


Figure 5.3-10. Anth/Bio Ratio prediction map for seasonal average Exp3-7 (July 14- Sept. 22). Sites with missing or invalid data are denoted as hollow circles.

Toluene/Benzene Ratios. **Figure 5.3-11** shows the concentrations of benzene, toluene, ethylbenzene and m/p-xylene (BTEX) as well as toluene/benzene (Toluene/benze) ratios for all sampling period and all sites arranged according to their elevations. BTEX is associated with motor vehicle emissions (e.g. Zielinska et al., 2012) whereas toluene/benzene ratios provide information regarding the photochemical age of the emissions (de Gouw et al., 2005). For aromatic VOC, the day time reaction with OH radicals is the dominant loss mechanism during transport through the atmosphere. The rate coefficients for the reaction of toluene and benzene with OH radicals are equal to $5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (Atkinson and Arey, 2003), thus toluene reacts approximately 5 times faster with OH radicals than benzene. The ratio of toluene/benzene in fresh emissions was estimated to be 3.7 ± 0.3 (De Gouw et al., 2005). The lower the ratio is, the more aged the air plume is. Although the VOC data were collected over 2-week periods, and local emissions versus regional transport may interchange during such a long time period, some general conclusions can be drawn from the toluene/benzene ratios. First, the highest Toluene/benze ratios (>1.5) are observed for lower elevation sites (3,500' to 6,000', **Figure 5.3-11a**) and the sites situated close to the Lake Tahoe (**Figure 5.3-11b**). For the sites situated on the western slope of the Sierra-Nevada Mountain (**Figure 5.3-11a**) the highest Toluene/benze ratios are observed for the Exp2 and Exp3 periods, including Sly Park (Exp3), Riverton (Exp3), and Blodgett (Exp2). Similarly, the Lake sites show the highest ratios for Exp2 and Exp3 periods, namely 64 Acres (Exp2 and Exp3), Valhalla (Exp3) and Tahoe Regional Park (Exp3). The higher elevation sites (**Figure 5.3-11c** and **d**) show Toluene/benze ratios below 1.2, although the highest ratios (>1) are also generally observed for Exp2 and Exp3 periods. This may indicate higher influence of local traffic at these sampling periods and sites.

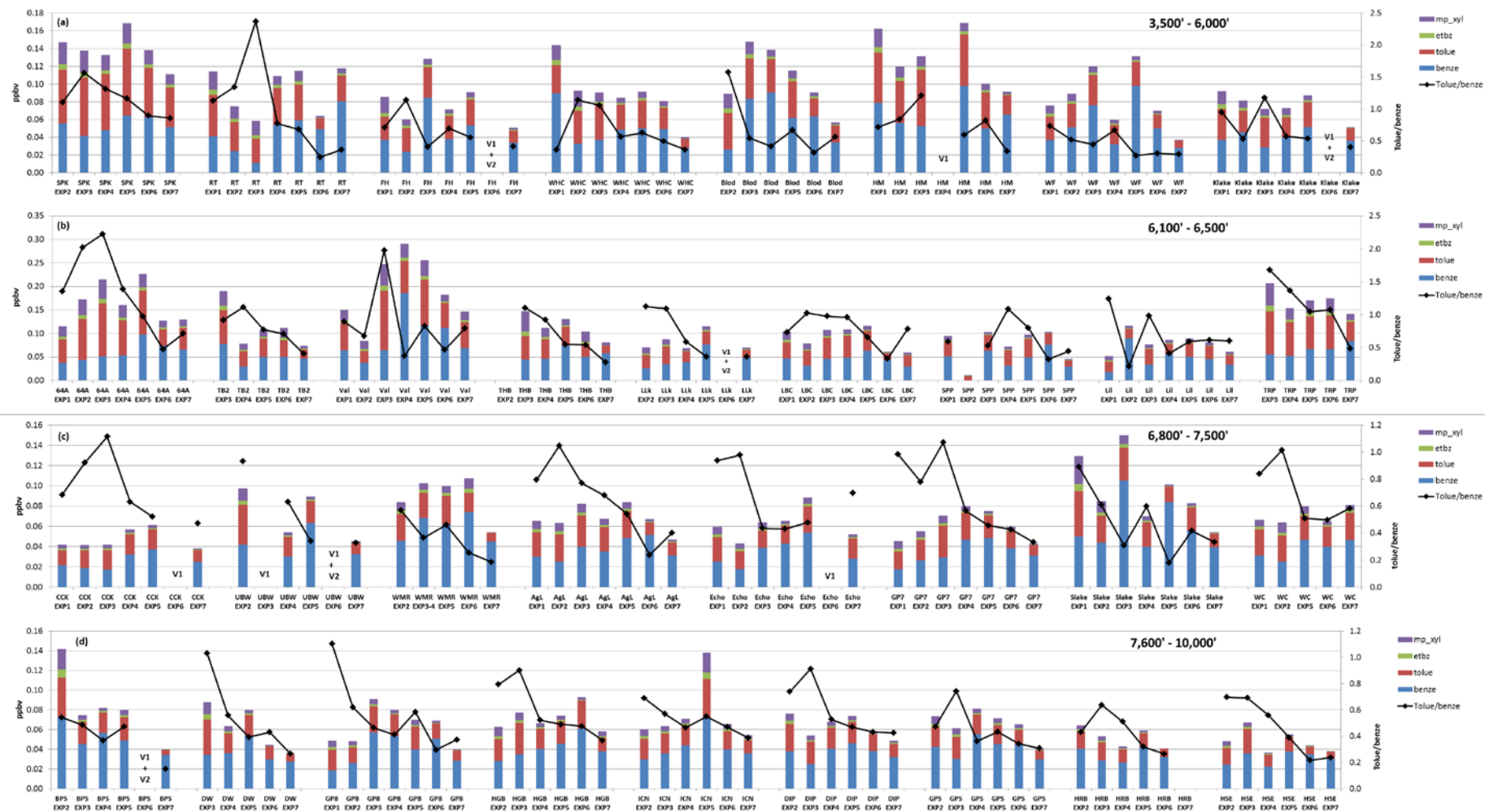


Figure 5.3-11. BTEX concentrations and Toluene/Benzene ratios for all monitoring periods (Exp1 through Exp7) and sites, arranged according to their elevations. See Table 2 for sites abbreviations. V1 = data for n-hexane up to n-undecane void and V2= data for 1,3-butadiene and isoprene void due to GC/MS instrument malfunction.

5.4 *Atmospheric Nitrogen Deposition, N Stable Isotopes and Effects on Sensitive Indicators*

Dissolved inorganic N (DIN) deposition at the ten megasites ranged from 1.0–1.8 kg ha⁻¹ yr⁻¹ in bulk deposition (forest clearings) and 1.3 – 5.6 kg ha⁻¹ yr⁻¹ in throughfall (**Table 5.4-1**). Nitrogen deposition during the 3-month summer period was low at the ten megasites (0.3 – 1.4 kg ha⁻¹ yr⁻¹), largely because precipitation was also low in summer (10-35 mm). Annual throughfall deposition was greater than 5 kg ha⁻¹ yr⁻¹ at the Angora Lookout, Genoa Summit 9000 and Valhalla sites and less than 2 kg ha⁻¹ yr⁻¹ at Lower Blackwood Creek and Upper Incline. Mid-range annual throughfall N deposition inputs (2-3 kg ha⁻¹) were measured at the remaining sites: Genoa Peak 7000, Genoa Peak 8000, Thunderbird Lodge, and Watson Creek (**Figures 5.4-1** through **5.4-6**).

Table 5.4-1. Annual deposition (kg ha⁻¹ yr⁻¹) of NH₄-N, NO₃-N and total dissolved inorganic N (DIN) in open-site bulk deposition ion exchange resin collectors and throughfall collectors.

Site	NH ₄ -N	NO ₃ -N	DIN
Open			
Angora Lookout	n.d.	n.d.	n.d.
Genoa Peak 7000	0.97	0.65	1.61
Genoa Peak 8000	0.56	0.41	0.97
Genoa Summit 9000	0.80	0.78	1.58
Lower Blackwood Creek	n.d.	n.d.	n.d.
Sugar Pine Point State Park	1.06	0.72	1.79
Thunderbird Lodge	0.84	0.61	1.45
Upper Incline	0.62	0.43	1.05
Valhalla	n.d.	n.d.	n.d.
Watson Creek	0.84	0.45	1.29
Throughfall			
Angora	2.88	2.75	5.63
Genoa Peak 7000	1.98	1.25	3.23
Genoa Peak 8000	1.58	1.73	3.30
Genoa Summit 9000	2.42	2.90	5.32
Lower Blackwood Creek	0.99	0.32	1.31
Sugar Pine Point State Park	n.d.	n.d.	n.d.
Thunderbird Lodge	1.80	1.32	3.12
Upper Incline	1.04	0.61	1.65
Valhalla	3.61	1.86	5.48
Watson Creek	1.60	0.78	2.39

In the summertime, deposition of $\text{NH}_4\text{-N}$ in throughfall and bulk deposition was more than double that of $\text{NO}_3\text{-N}$, while in the winter/spring exposure period deposition of $\text{NH}_4\text{-N}$ was 1.3-1.4 times that of $\text{NO}_3\text{-N}$. The site with the highest annual throughfall deposition of $\text{NH}_4\text{-N}$ was Valhalla ($3.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$). The only instance in which deposition of $\text{NH}_4\text{-N}$ was less than that of $\text{NO}_3\text{-N}$ was at Genoa Peak 8000 and Genoa Summit 9000 in winter/spring and in the annual deposition data for these same two sites. During these periods the $\text{NH}_4\text{-N}:\text{NO}_3\text{-N}$ ratios at these two upper Genoa Peak sites ranged from 0.7 – 0.9. In summertime $\text{NH}_4\text{-N}:\text{NO}_3\text{-N}$ ratios were 1.3 at the upper Genoa Peak 8000 and Genoa Summit 9000 sites and 1.7 at the Genoa Peak 7000 site, again demonstrating the higher prevalence of N deposition in reduced forms during summer.

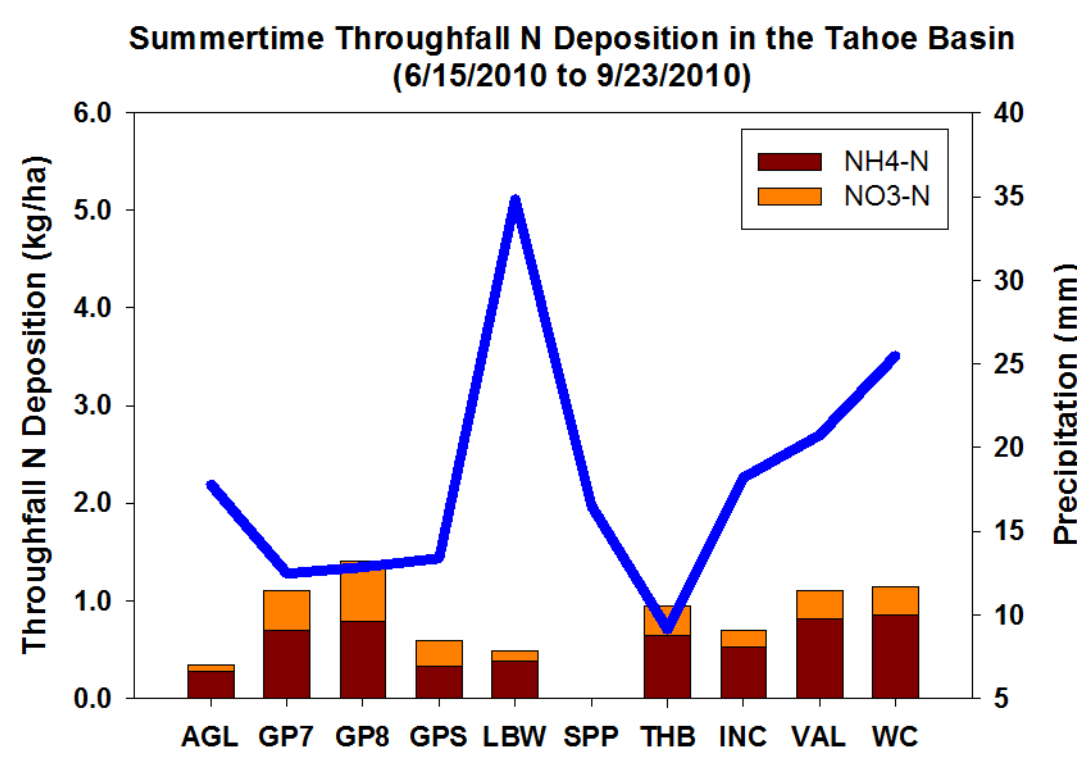


Figure 5.4-1. Summertime throughfall deposition of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ at the ten mega sites in the Tahoe Basin.

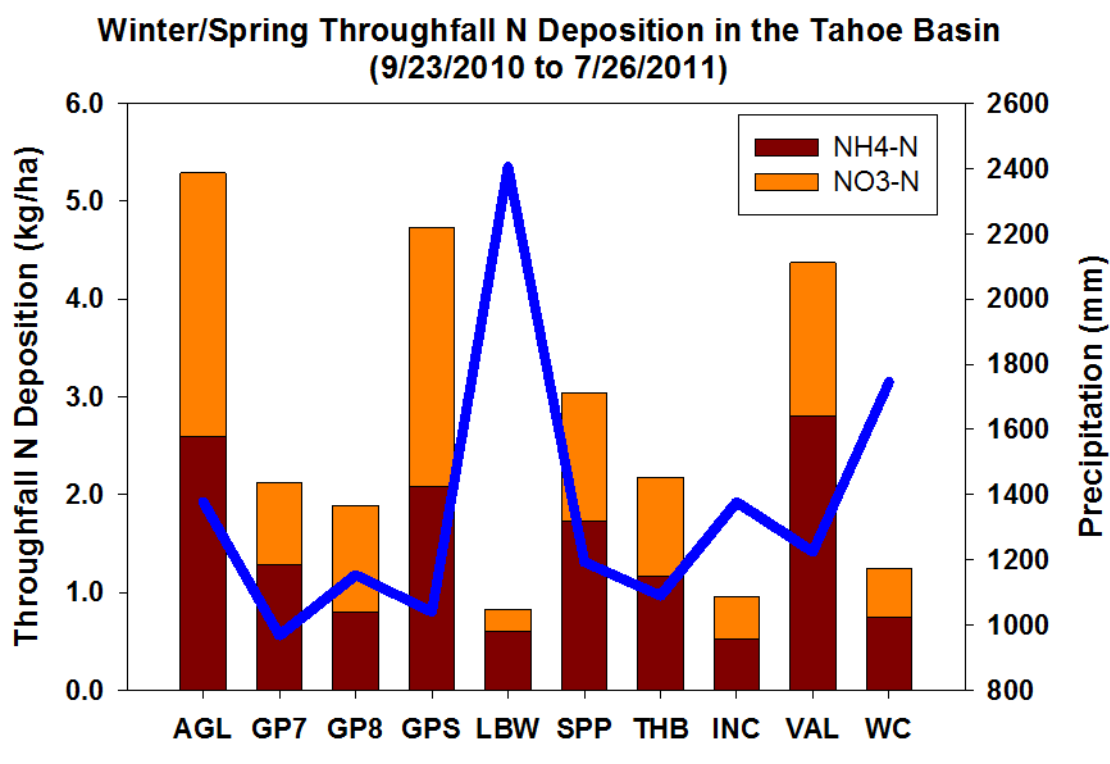


Figure 5.4-2. Winter and springtime throughfall deposition of NH₄-N and NO₃-N at the ten mega sites in the Tahoe Basin.

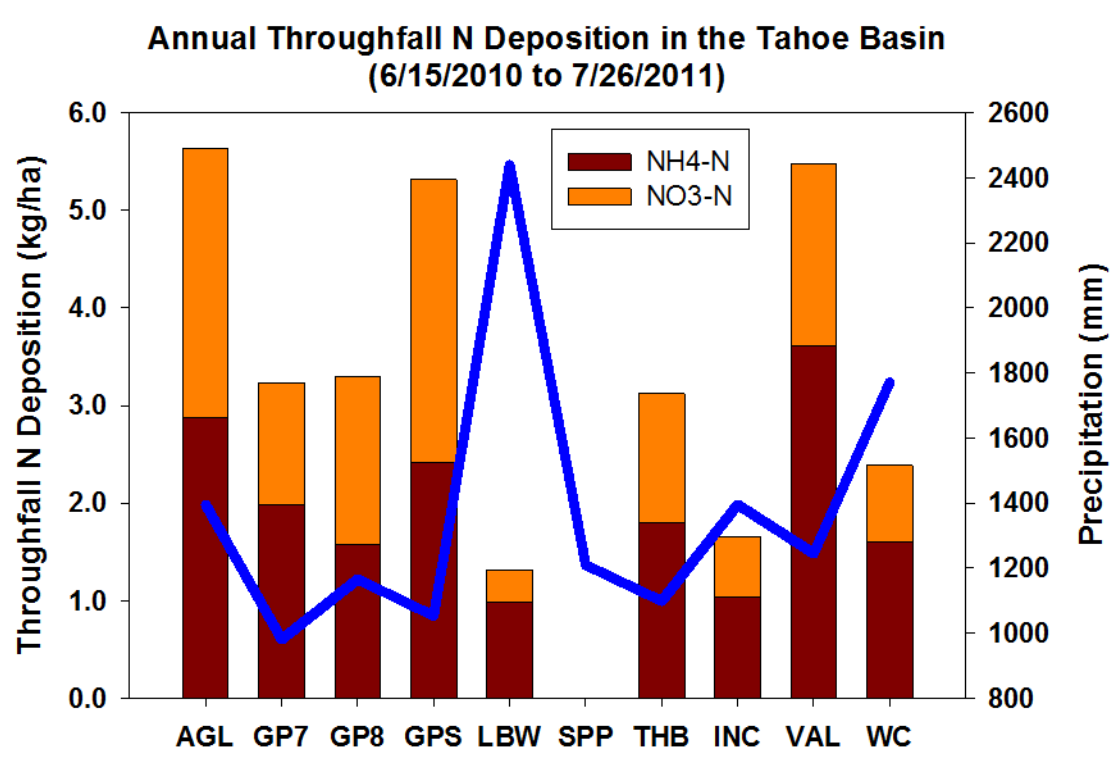


Figure 5.4-3. Annual throughfall deposition of NH₄-N and NO₃-N at the ten mega sites in the Tahoe Basin.

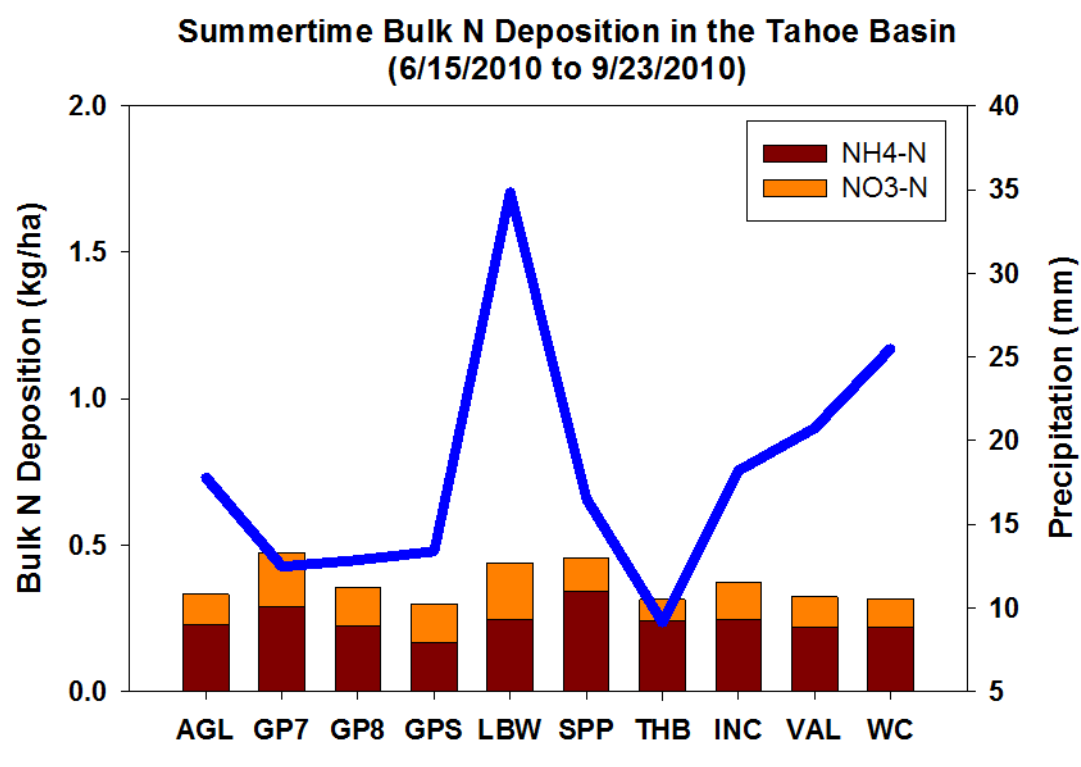


Figure 5.4-4. Summertime bulk deposition of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in forest clearings at the ten mega sites in the Tahoe Basin.

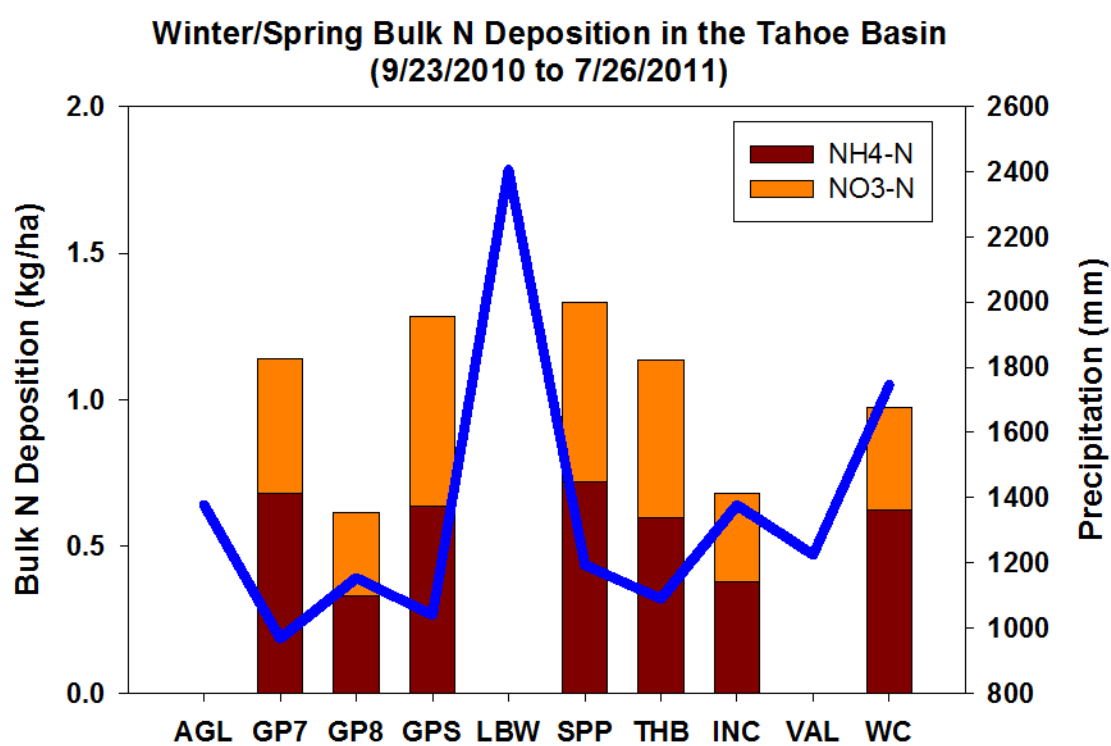


Figure 5.4-5. Winter and springtime bulk deposition of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in forest clearings at the ten megasites in the Tahoe Basin.

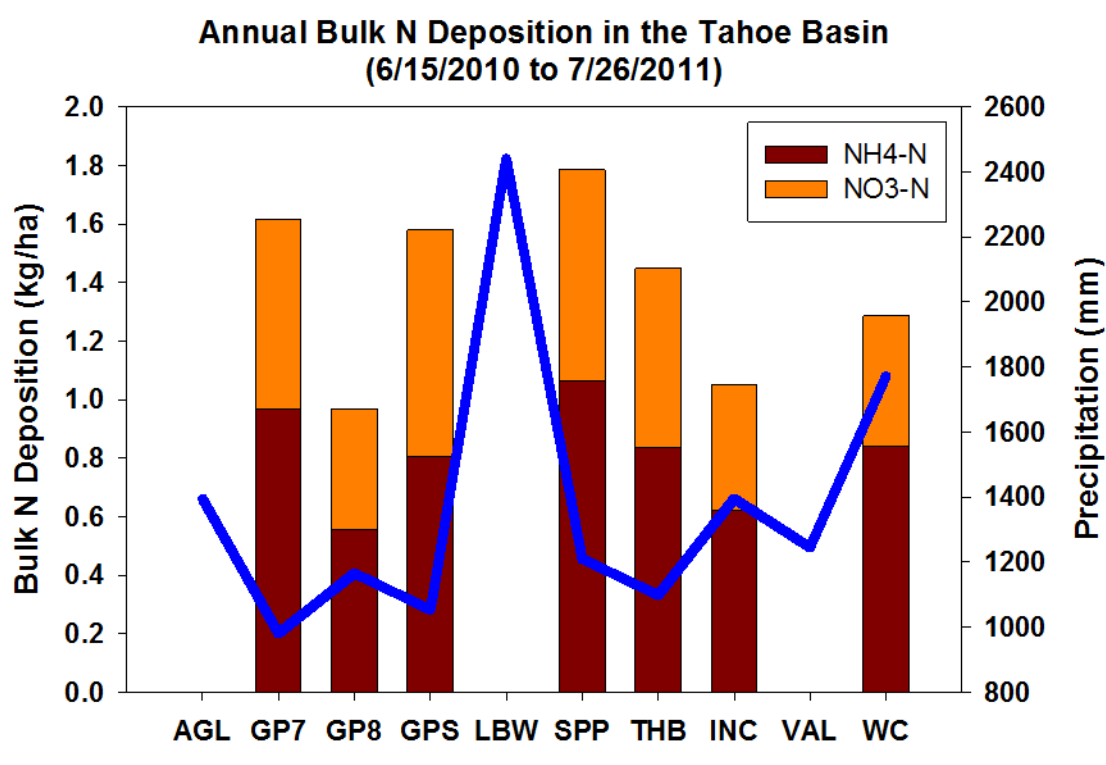


Figure 5.4-6. Annual bulk deposition of NH₄-N and NO₃-N in forest clearings at the ten megasites in the Tahoe Basin.

Throughfall deposition of NH₄-N was highest at Valhalla, a highly utilized recreational site near the Lake and a few hundred meters from Highway 89 and 4 km from the urbanized zone surrounding South Lake Tahoe. Angora Lookout and Genoa Summit 9000 had the highest throughfall deposition of NO₃-N. This suggests that much of the NH₄-N in throughfall at Valhalla was from local anthropogenic sources of NH₃ such as motor vehicles, and possibly sewage and recreational activities. Higher deposition of NO₃-N at sites further away or at higher elevation than the urban zone, such as Angora Lookout and Genoa Summit 9000 is likely a result of atmospheric transport and photochemical reactions leading to production of HNO₃. Downwind production of HNO₃ would contribute to elevated throughfall NO₃-N deposition at sites such as Angora Lookout and Genoa Summit 9000.

Dual Isotope analysis of NO₃. $\delta^{15}\text{N}$ values in bulk deposition and throughfall samples were more enriched along the south and southeastern portions of the basin (**Figures 5.4-7 through 5.4-10**)---the same region where the highest levels of atmospheric deposition were reported. This is likely the result of chronic NO_x emissions from motor vehicles in the urbanized regions surrounding greater South Lake Tahoe. Isotopic analyses of NH₄-N deposition are currently underway. This should provide information on the major emissions sources of reduced forms of N deposited within the Basin.

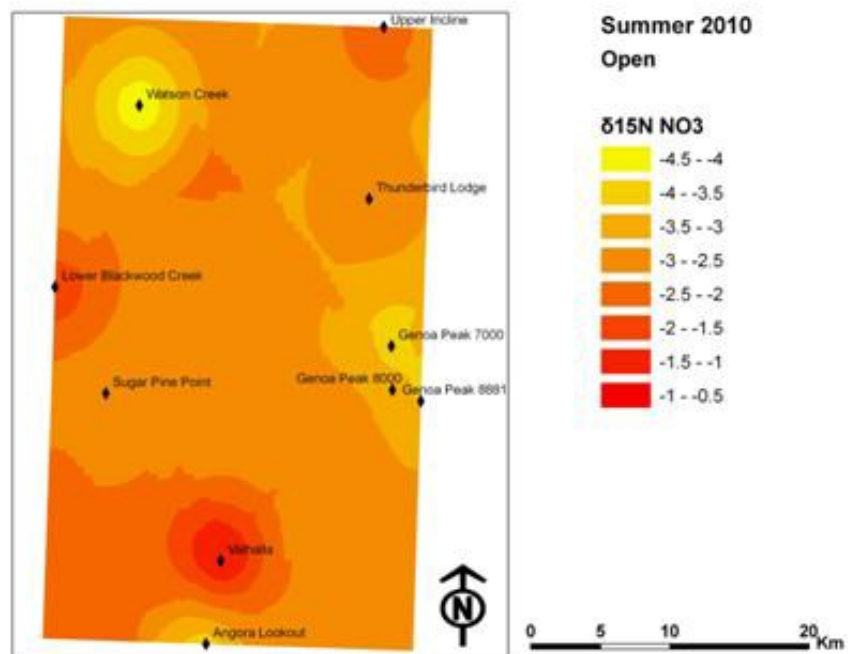


Figure 5.4-7. Spatial patterns of $\delta^{15}\text{NO}_3$ in bulk precipitation at the ten mega during summer.

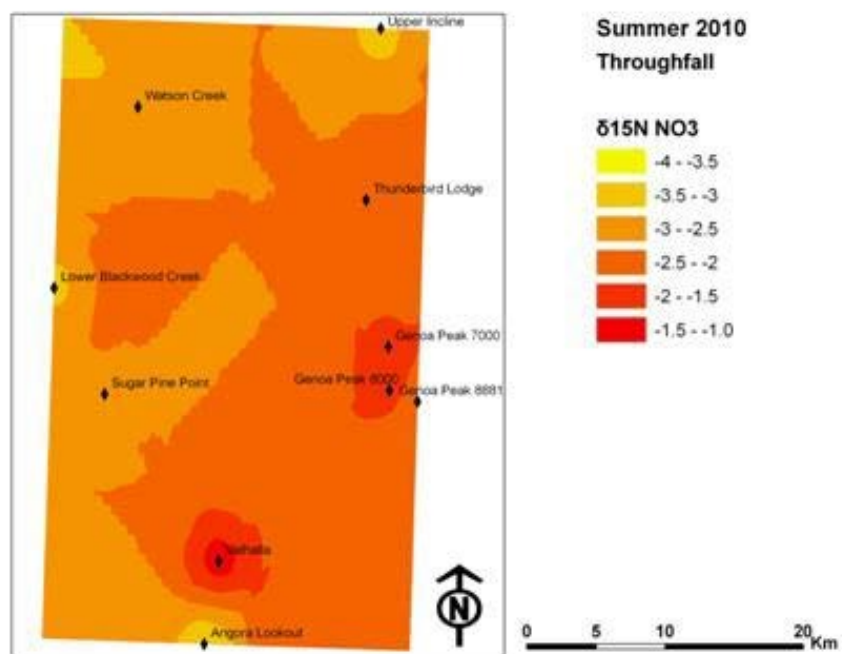


Figure 5.4-8. Spatial patterns of $\delta^{15}\text{NO}_3$ in throughfall at the ten mega sites during summer.

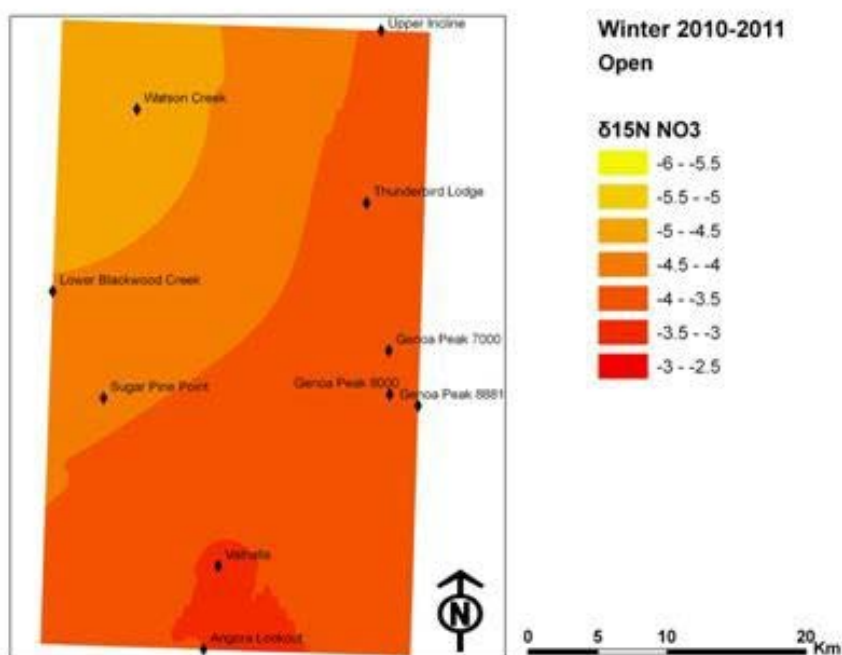


Figure 5.4-9. Spatial patterns of $\delta^{15}\text{NO}_3$ in bulk precipitation at the ten mega sites during winter and spring.

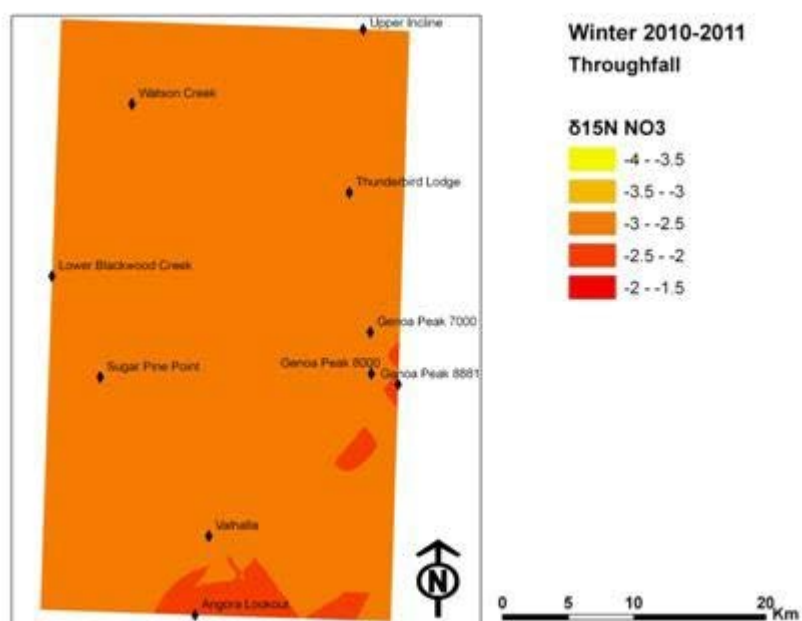


Figure 5.4-10. Spatial patterns of $\delta^{15}\text{NO}_3$ in throughfall at the ten mega sites during winter and spring.

Changes in Lichens. The epiphytic lichen *Letharia vulpina* was sampled and analyzed for percent N at the ten megasites. The clean-site threshold for percent N is 1.0% (Fenn et al., 2008). Above this level of N the proportion of oligotrophic lichen species declines and eutrophic species increase in abundance. In the mixed conifer forests of California, epiphytic communities of lichens shift to eutrophic dominance at a throughfall deposition level of around $5.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$. The clean site percent N threshold is exceeded at half of the megasites: Valhalla, Angora Lookout and the three Genoa Peak elevational gradient sites (**Figure 5.4-11**). These five sites are on the southern or southeastern side of the Lake and are exposed to elevated N emissions from urban or agricultural areas. The percent N in lichens at Genoa Peak 7k (1.09%) is only slightly higher than the N enrichment threshold, but the other four sites range from 1.3 – 1.6% N, showing considerable N enrichment and a high likelihood of major changes in lichen community composition. In fact at Angora Lookout, Valhalla and Genoa Peak 9k annual throughfall deposition was above the threshold or critical load ($5.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$) at which epiphytic lichen communities in California mixed conifer forests shift to a preponderance of eutrophic species (Fenn et al., 2008). Percent N in lichen tissue at the megasites was significantly correlated ($r^2 = 0.75$) with annual throughfall N deposition (**Figure 5.4-11**). Similarly, N concentration in lichen tissue was correlated ($r^2 = 0.70$) with annual N deposition determined with the inferential approach for calculating dry deposition in the summer (because of low rainfall and throughfall sample collection) plus throughfall deposition for the winter/spring period (**Figure 5.4-12**). A recent synthesis from a network of sites throughout western North America demonstrated that throughfall N deposition in western forests can be predicted from surveys of lichen N concentrations (Root et al., in review).

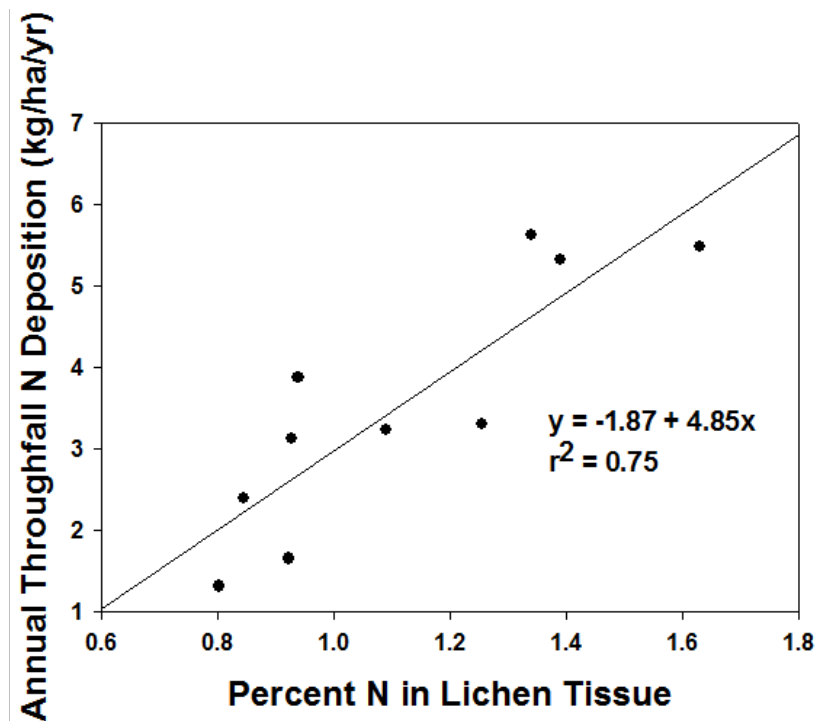


Figure 5.4-11. Relationship between percent N in tissue of the epiphytic lichen *Letharia vulpina* and annual throughfall deposition of N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) at the ten megasites.

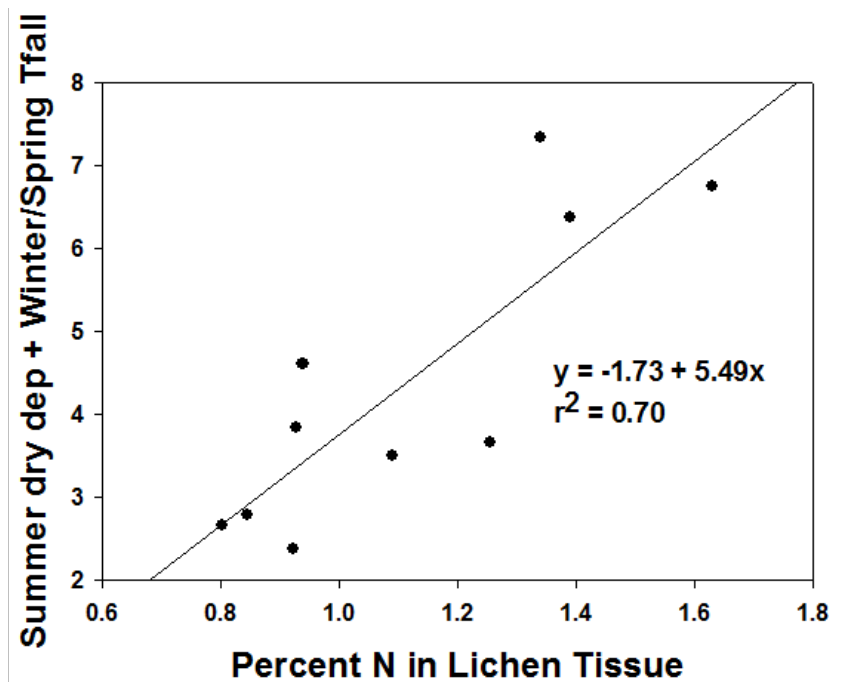


Figure 5.4-12. Relationship between percent N in tissue of the epiphytic lichen *Letharia vulpina* and annual N deposition at the ten megasites. Summertime dry deposition of N was calculated using the inferential method. Deposition in spring and winter was measured as throughfall. These two measures were combined to estimate annual N deposition as shown on the y-axis.

5.5 Meteorological interpretation of ozone distribution data from 10 mega sites - relationships between diurnal patterns and large scale weather patterns

Wind/Pollution Roses. To investigate the ozone environment in the Lake Tahoe Basin, an ozone monitoring network was set up in the summer of 2010. Hourly ozone concentrations were measured at 10 sites around the Lake. The National Weather Service's National Centers for Environmental Prediction (NCEP) runs a series of computer analyses and forecasts operationally. NOAA's Air Resources Laboratory (ARL) routinely uses the NCEP model data air quality transport and dispersion modeling calculations. In 1989 ARL began to archive some of these datasets for future research studies (Air Resources Laboratory, online). Archived wind data for the summer of 2010 were retrieved at three hour increments from the North American Mesoscale (NAM) 12 km meteorological model from the ARL. An extraction procedure was implemented to concatenate the initial field (+0 h forecast) and the +3 h forecast for each cycle, four times daily, into daily files that can be accessed via the website. Various spatial and temporal analyses of these ambient ozone measurements and wind data yielded insights into the nature of the ozone air quality within the Tahoe Basin.

The wind roses for the 10 sites around the lake, show that the predominant wind direction for the months of July, August and September is from the west (**Figure 5.5-1**) and therefore is the predominant ozone direction as well (**Figure 5.5-2**). There is some evidence of a lake breeze occurring at the Blackwood and Sugar Pine Point sites due to the easterly signature that shows up. However, the lake breeze may be strongly washed out due to the predominant summertime synoptic westerly flow and the Washoe Zephyr.

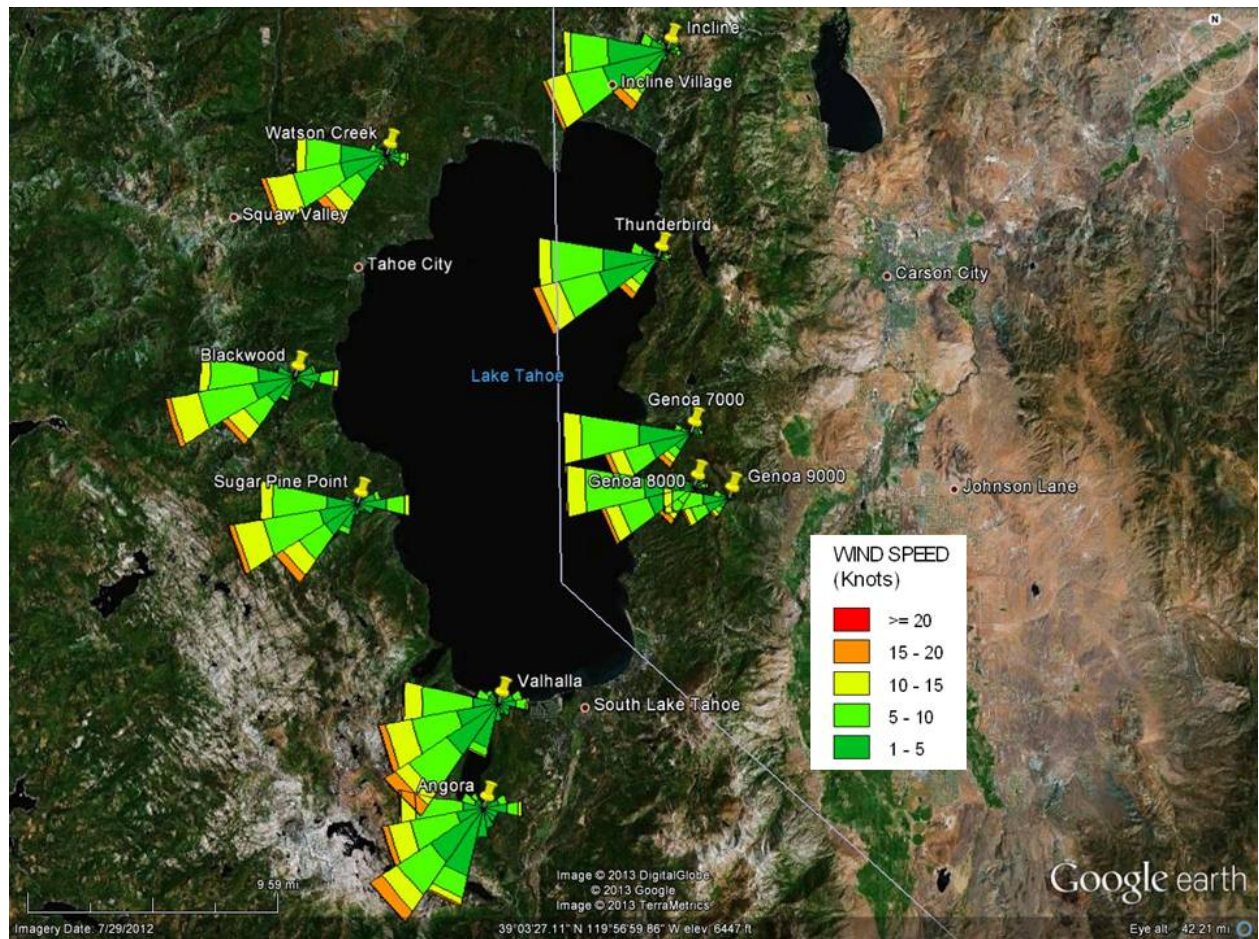


Figure 5.5-1. Wind roses for all 10 mega sites throughout the sampling period (July-September 2010). The yellow pins identify the locations of the sites. The length of the triangles represent the relative proportion of winds from that direction toward the monitoring site with the color shading representing the proportion of various wind speeds.

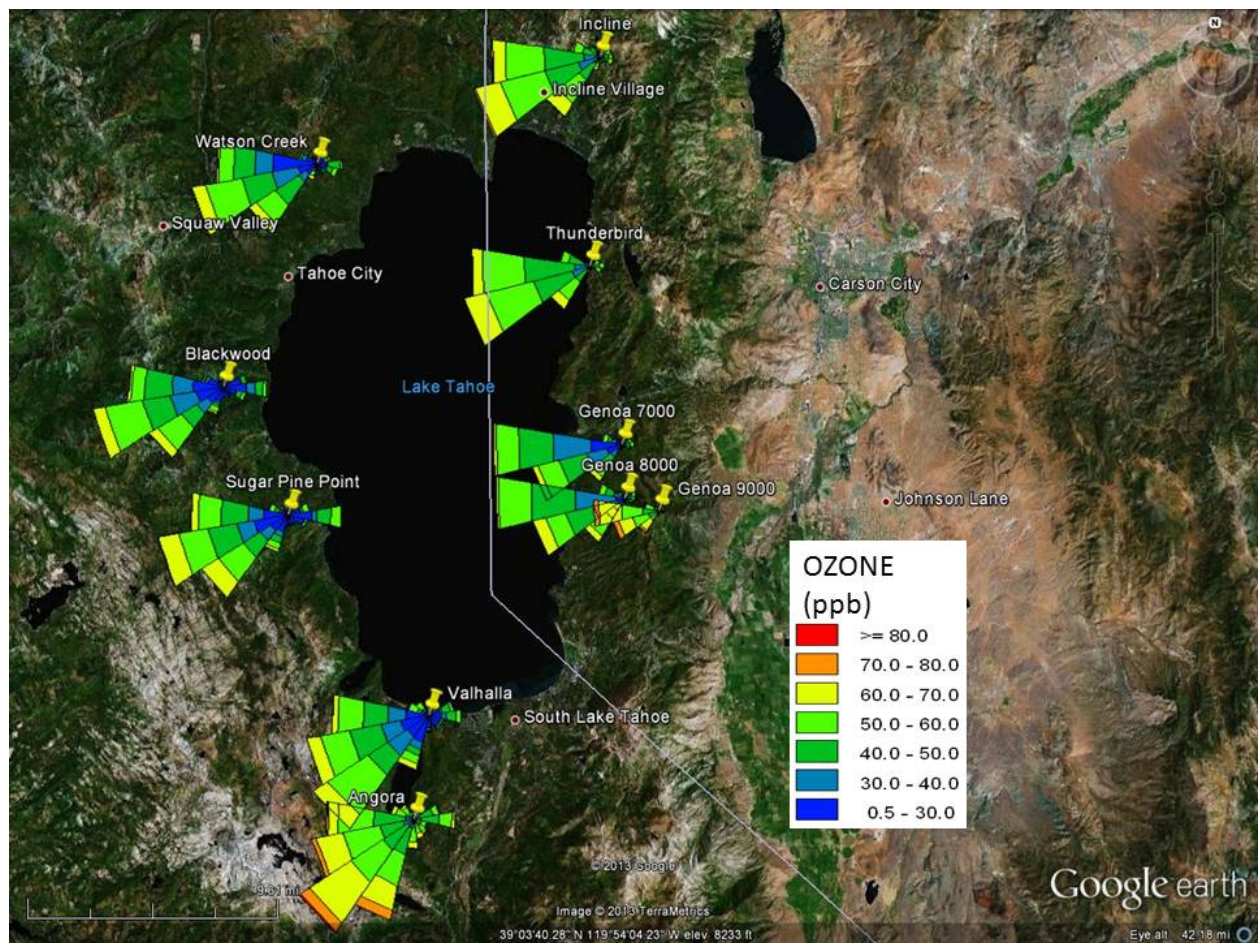


Figure 5.5-2. Ozone pollution roses for all 10 mega sites throughout the sampling period (July-Sept 2010). The yellow pins indicate the location of the monitoring sites and the color of the triangles indicate the frequency distribution of ozone concentrations (ppb) when the winds are from that direction.

Synoptic Graphs. The 10-day, 15-day and 20-day running mean of the daily maximum 8-hr average ozone concentration for all ten mega sites in the basin were calculated to show the larger scale ozone pattern and to reduce the local effects (e.g., titration, lake breeze, slope flows, etc.) on the ozone concentration spatial pattern. This is done to eliminate the “noise” of the local effects and show the trends in the larger scale patterns to better determine transport of ozone into the basin. The 10-day running mean will show more influence of local effects which is why there is a stronger dip around day 195. However, the 20 day running mean is more smooth which shows the larger scale pattern of ozone around the basin. The 10-day, 15-day and 20-day running mean average of ozone for all sites throughout the summer show a clear dip in ozone during the middle of July and a sharp increase in ozone towards the end of July to the beginning of August (**Figure 5.5-3**). The ozone starts to steadily decrease towards the end of August and throughout September.

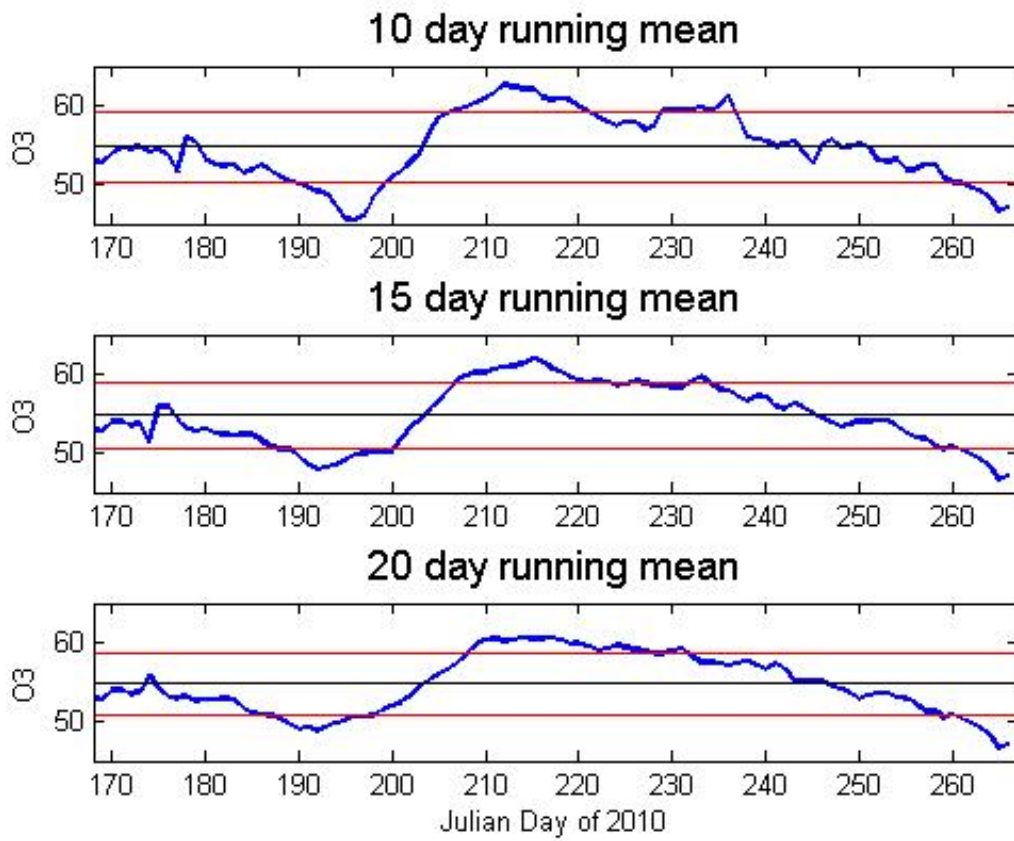


Figure 5.5-3. The 10-day, 15-day and 20-day running mean of daily maximum 8-hour average ozone concentrations (ppb) for all ten mega sites (heavy blue line) throughout the sample period (July-Sept 2010). The black line indicates the average for the summer. The red lines indicate one standard deviation above and below the summer mean concentration.

The National Weather Service launches balloons twice daily around the nation, at designated sounding sites. The 00Z (4 pm PST the previous day) 700mb (~10,000 ft. altitude) winds were taken from these balloon soundings at the Reno and Oakland sites, since they are closest to Lake Tahoe. The 700mb winds were analyzed to represent the synoptic flow pattern sufficiently high to be above the ridge tops and less influenced by boundary layer conditions. In **Figure 5.5-4**, which summarizes July 2010 conditions, the black line shows the wind speed in meters per second with the legend on the right side. The red dots show the wind direction with the legend on the left side.

The Washoe Zephyr index was calculated via the pressure difference across the mountain using the mean sea level pressure at Reno (to represent the Great Basin side) and at Sacramento (to represent the Central Valley side). On days when a Washoe Zephyr is present, there is a lower pressure at Reno and a higher pressure at Sacramento which means the Washoe Zephyr index is a positive value. On days when a Washoe Zephyr is not present there is higher pressure at Reno and lower pressure at Sacramento which corresponds to a negative value of the Washoe Zephyr index plot. This technique was adapted from Zhong et al. (2008).

Preliminary analysis shows the sustained positive Washoe Zephyr index in the beginning of August may have implications in the rise of ozone at that time. This is a possible indication that the Washoe Zephyr aids in the transport of background ozone to the basin from the Central Valley. However there are no significant correlations between a positive Washoe Zephyr index and jumps in ozone throughout the three month period (**Figures 5.5-4, 5.5-5, and 5.5-6**). The interesting thing to note is that even with this sustained period of positive Washoe Zephyr index and higher ozone at that time, there is not significantly strong wind flow occurring at the 700mb levels. This introduces the question of whether or not the wind is coming through the gaps and corridors of the mountains. During the period of low ozone, wind flow tended to be stronger, possibly acting as a ventilation system for the basin whereas, during the higher ozone period the wind flow was weaker. Other times of positive values of the Washoe Zephyr index and higher wind flow from the west/southwest do not seem to correlate with jumps in ozone indicating that the Washoe Zephyr and strong synoptic westerly wind flow does not tend to be the only driving force in higher ozone levels around the lake.

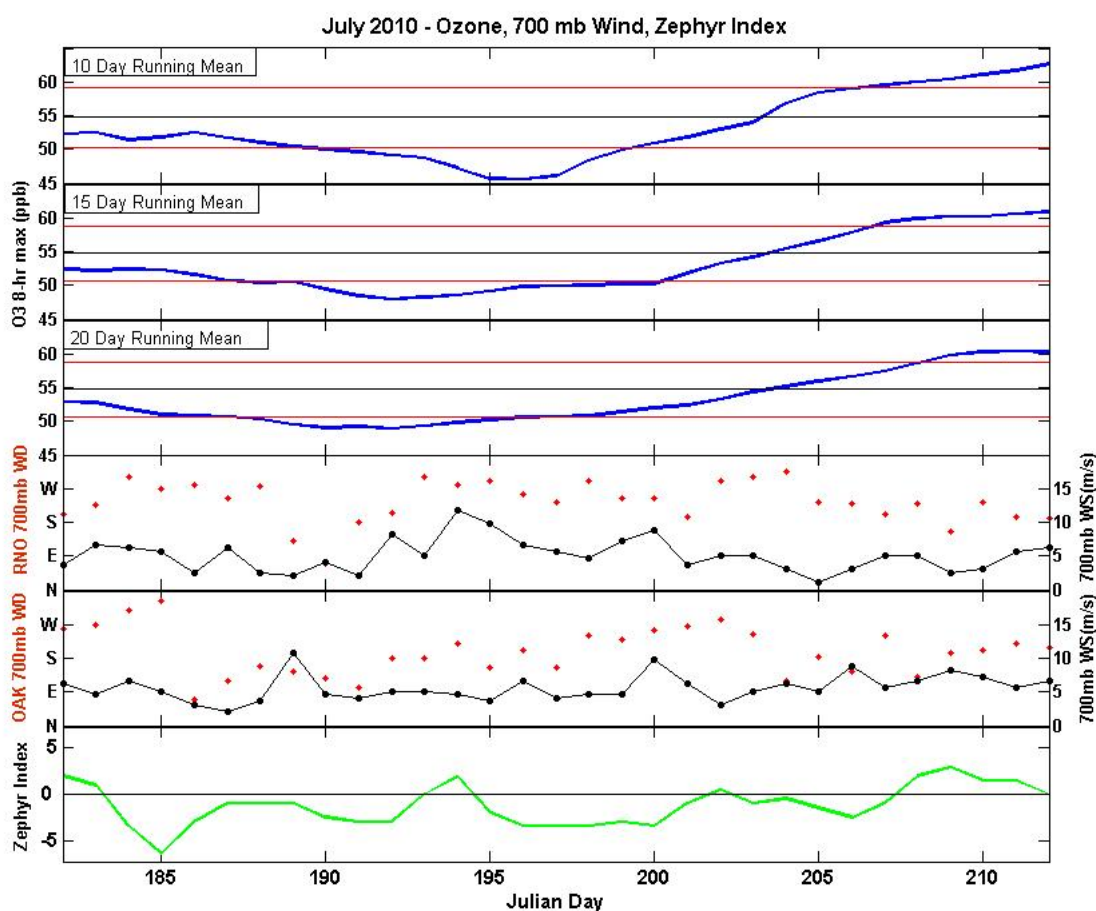


Figure 5.5-4. The 10, 15 and 20-day running mean of the daily maximum 8-hour average ozone concentrations at each of ten mega sites during the month of July. The 700mb wind speed (black line, legend on right) and direction (red dots, legend on left) at Reno. The 700mb wind speed (black line, legend on right) and direction (red dots, legend on left) at Oakland. The Zephyr Index pressure difference between Sacramento and Reno; a positive value indicates a day with a potential Washoe Zephyr.

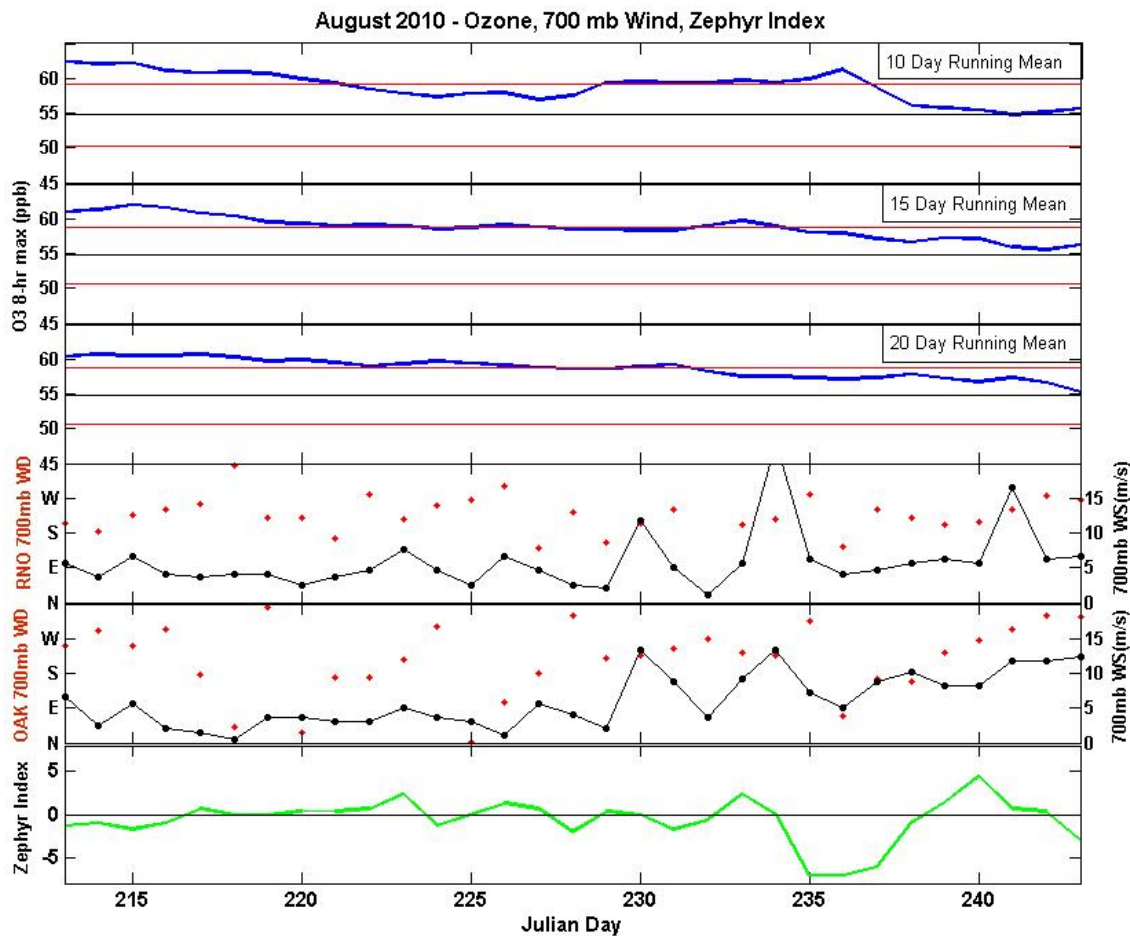


Figure 5.5-5. The 10, 15 and 20-day running mean of the daily maximum 8-hour average ozone concentrations at each of the ten sites for the month of August. The 700mb wind speed (black line, legend on right) and direction (red dots, legend on left) at Reno. The 700mb wind speed (black line, legend on right) and direction (red dots, legend on left) at Oakland. The Zephyr Index pressure difference between Sacramento and Reno; a positive value indicates a day with a potential Washoe Zephyr.

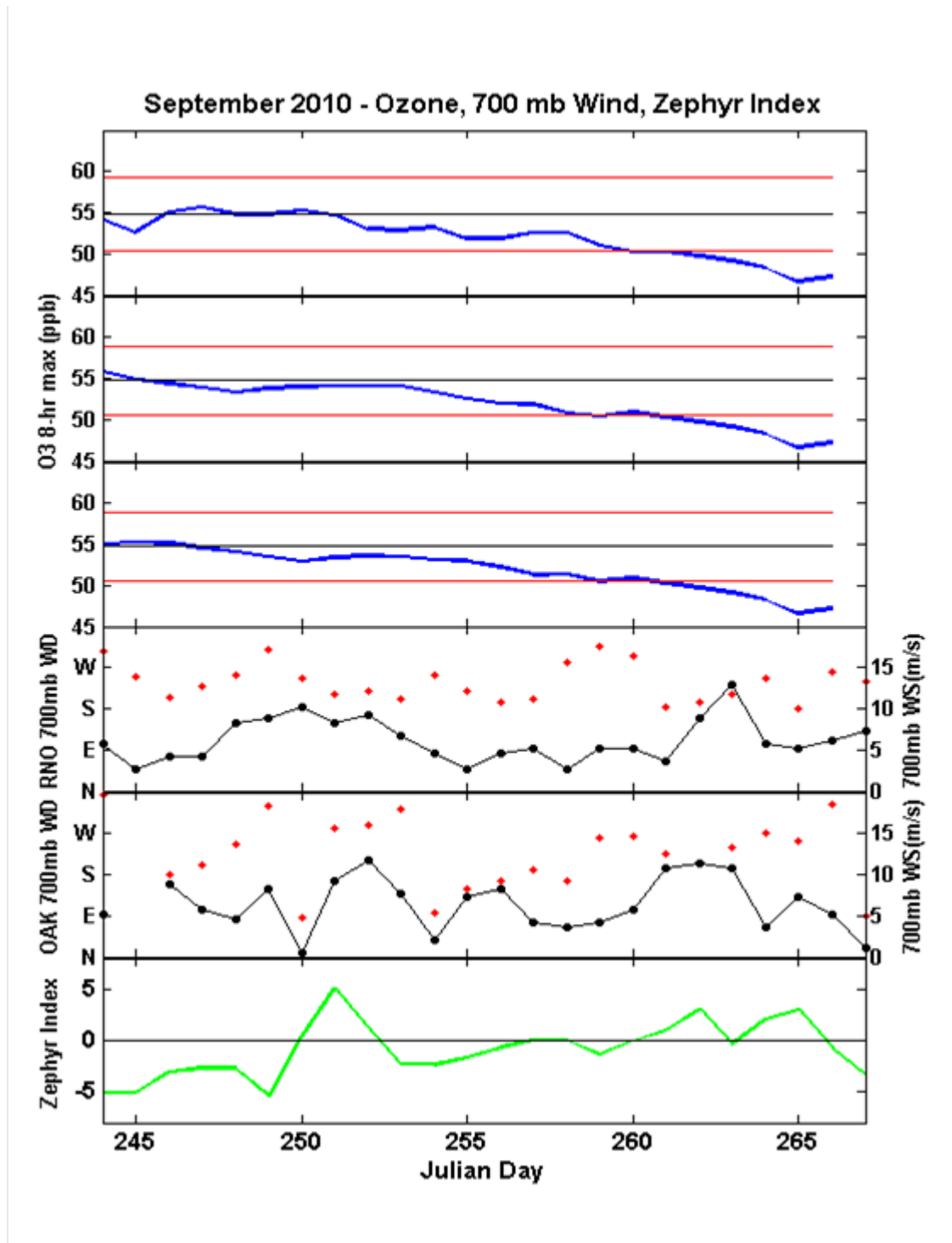


Figure 5.5-6. The 10, 15 and 20-day running mean of the daily maximum 8-hour average ozone concentrations at all ten mega sites for the month of September. The 700mb wind speed (black line, legend on right) and direction (red dots, legend on left) at Reno. The 700mb wind speed (black line, legend on right) and direction (red dots, legend on left) at Oakland. The Zephyr Index pressure difference between Sacramento and Reno; a positive value indicates a day with a potential Washoe Zephyr.

Synoptic Maps. Using the running means graphs, two distinct ozone periods were examined in detail. A period of low ozone concentrations was identified from July 9th - July 14th. A period of high ozone concentrations was identified from July 29th - August 3rd. Using these two periods, the lower levels of the atmosphere were analyzed synoptically with a composite of mean sea level pressure for each period and higher levels of the atmosphere were analyzed synoptically with a composite of 500mb and 700mb geopotential heights for each period. This analysis will show the general flow of the atmosphere at these three levels and help determine if transport is occurring, and if so, from where it is coming (**Figures 5.5-7 through 5.5-12**).

The overall mean sea level pressure pattern (lower levels in the atmosphere) between high ozone periods and low ozone periods is typical of the climatological summers for the Basin. Geopotential height composite at 700mb for both High Ozone Period of July 29th – August 3rd and Low ozone Period of July 9th - July 14th resembles those of the 500mb flow patterns. There is a high pressure influence off the California coast and a low pressure monsoonal influence over Arizona. The mean sea level pressure pattern does not show large differences in the flow for the high ozone periods and the low ozone periods. The overall flow for both periods, following the colored contour lines, is coming from the south. However, at higher levels, such as 500mb, there are flow pattern differences between the two periods of high and low ozone. Following the colored contour lines for the low period of ozone, the flow coming into the basin is from the west, however following the colored contour lines for the high period of ozone, the flow is coming from the southwest. This could well be air flow directly from San Francisco, Sacramento and the Central Valley delivering O₃ and O₃ precursors into the Basin. Linking this southwest flow with the period of high ozone is an indication that possible transport from these areas is enhancing background ozone levels in the Basin. Questions would still remain on how significant of an impact the upper level pattern differences have on surface ozone concentrations around the Basin and how the upper level ozone is mixing down into the Basin, which would need to be resolved through the use of chemical and meteorological modeling.

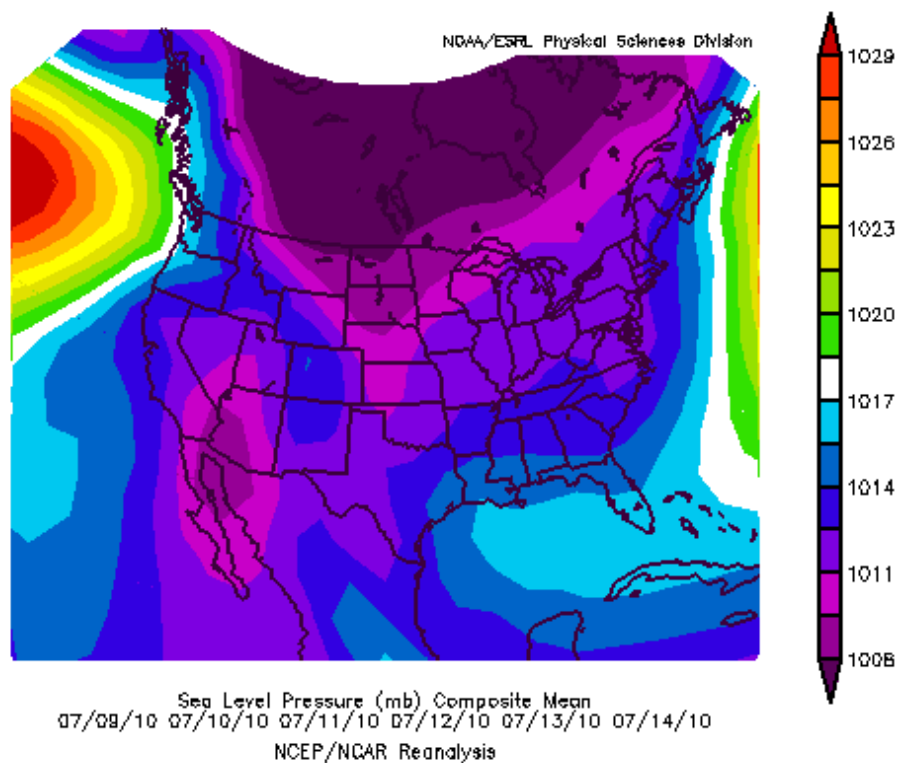


Figure 5.5-7. Mean Sea Level Pressure composite for the Low Ozone Period of July 9th – 14th

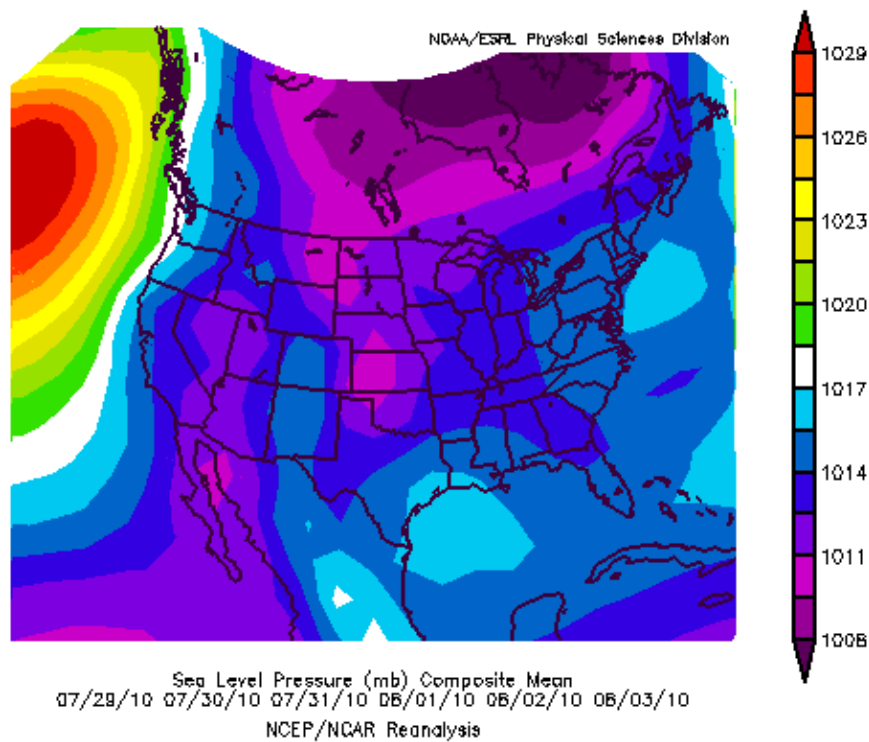


Figure 5.5-8. Mean Sea Level Pressure Composite for the High Ozone Period of July 29th – August 3rd

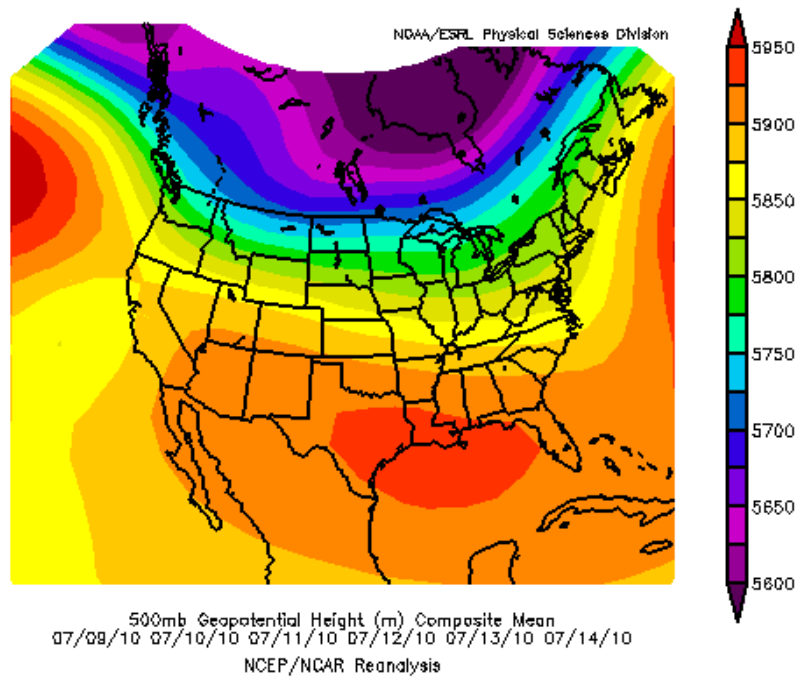


Figure 5.5-9. Upper Level Flow, Geopotential height composite at 500mb for Low Ozone Period of July 9th - July 14th

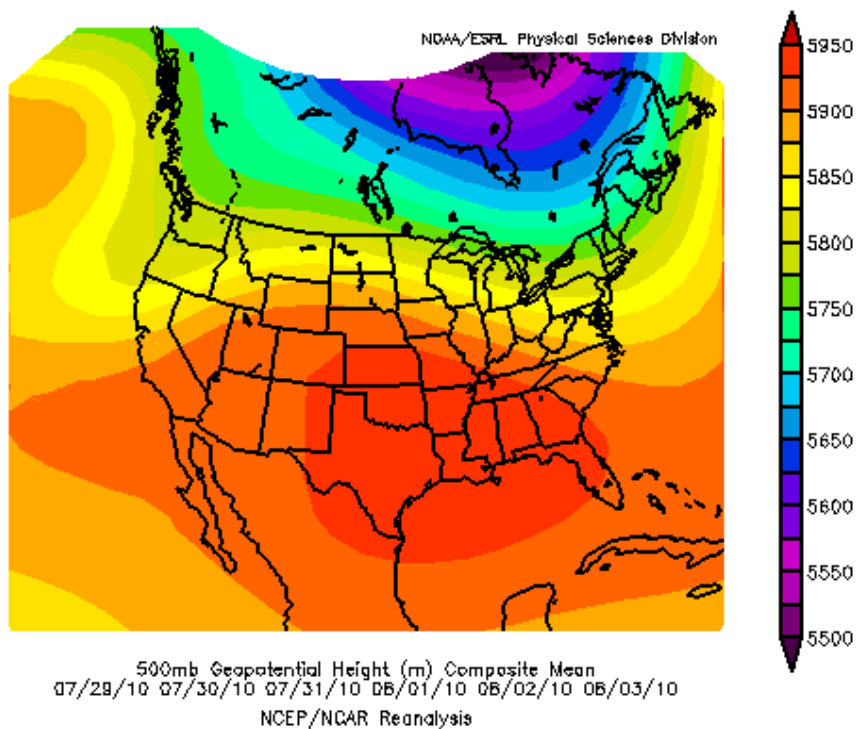


Figure 5.5-10. Upper Level Flow, Geopotential height composite at 500mb for High Ozone Period of July 29th - August 3rd

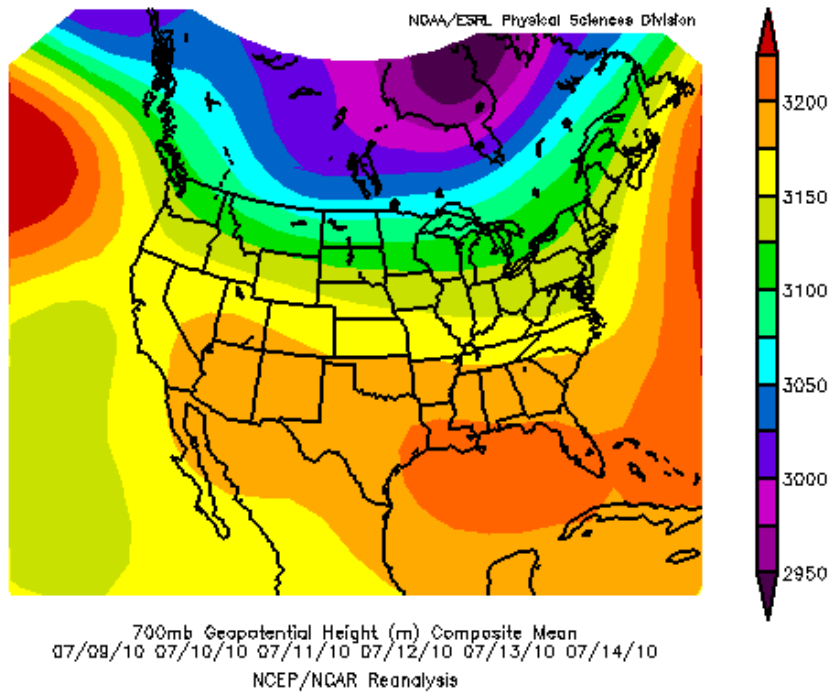


Figure 5.5-11. Upper Level Flow, Geopotential height composite at 700mb for Low Ozone Period of July 9th - July 14th

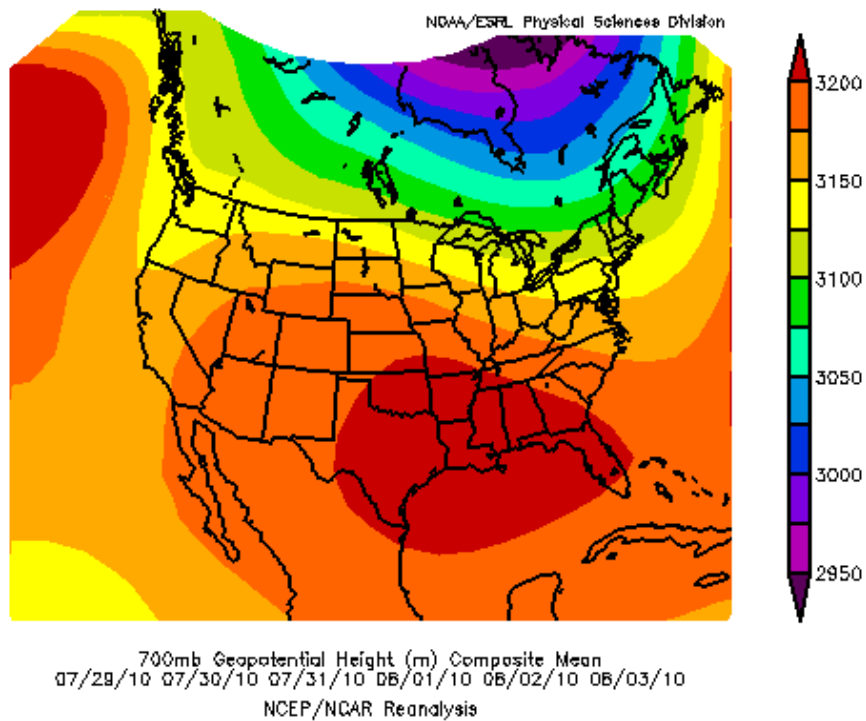


Figure 5.5-12. Upper Level Flow, Geopotential height composite at 700mb for High Ozone Period July 29th - August 3rd

5.6 Meteorological interpretation of ozone distribution data from 10 mega sites - results from regression model

Side-by-side boxplots were produced for the hourly ambient ozone concentrations as a first step to understand the intra- and inter-site variabilities in concentrations (**Figure 5.6-1**).

Notable features of the patterns in **Figure 5.6-1** were:

- 1) The mid-day hourly ozone values were on average very stable (mean = 52 ppb) and consistent among the locations (Figure 5.6-1, bottom right panel). The between site variation was negligible (± 1.62 ppb) and the within site variation was small (± 7.6 ppb) compared to the overall variability during the day (± 13.4 ppb).
- 2) Both between and within site variability during night-time hours were large, however, with the between site variability (SD) = 13.3 ppb and the within site variability (SD) = 11.3 ppb.
- 3) Except for the Thunderbird site (THB) and Angora site (Agl), there seem to be an increasing trend in the overall night time O₃ values with increasing elevation and increasing distance from 'busy' road.
- 4) The drop in O₃ values in the evening (hence also the increase in the morning) are sharpest at the sites west of the Lake.
- 5) The Angora (AgL) and the GPS sites show a small increase in average O₃ values during night-time hours.

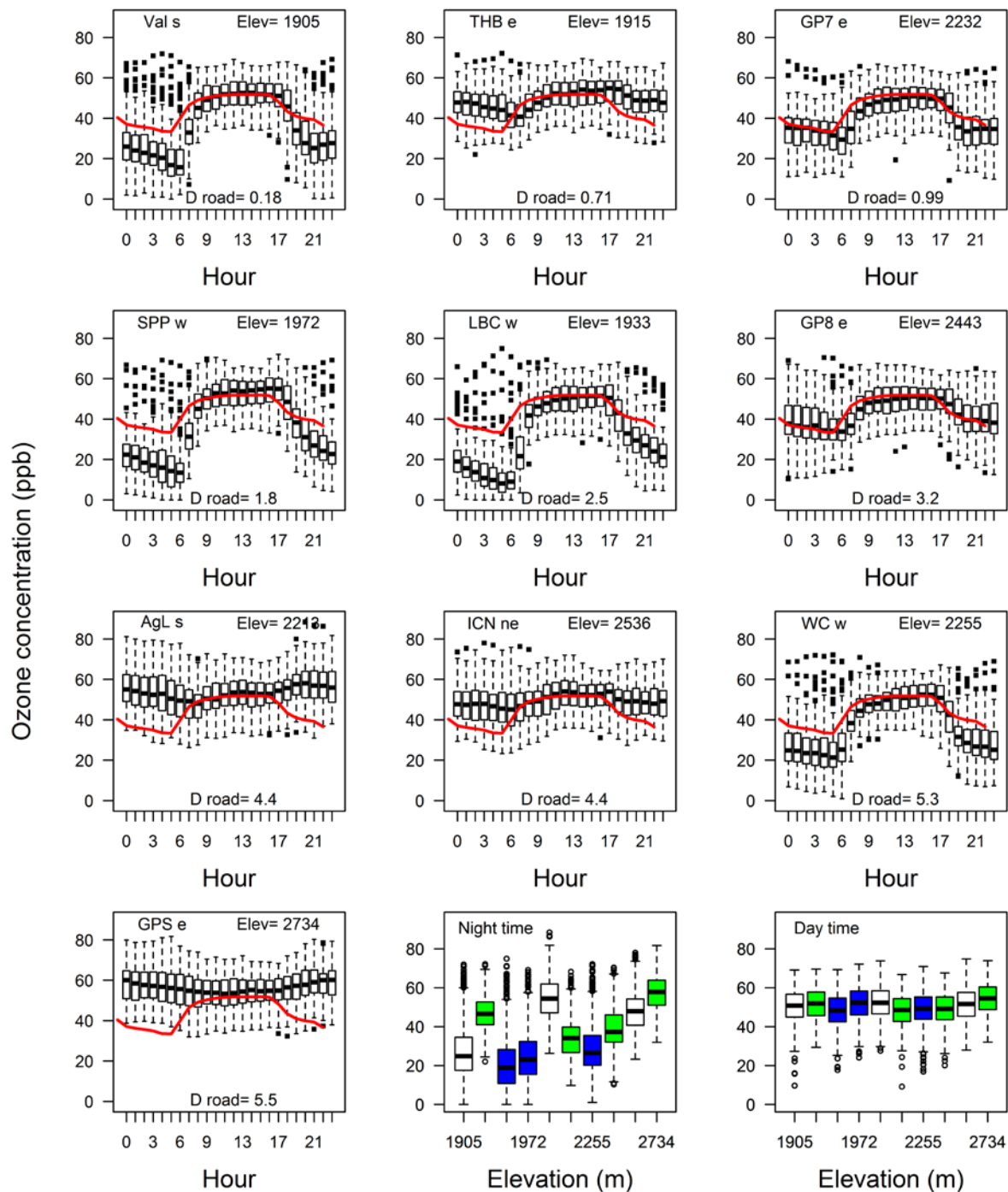


Figure 5.6-1. Boxplots of diurnal O₃ concentrations (ppb) at the 10 mega-sites. The red curve through the points is the average for all sites. The plots also give the elevation (m), distance from 'busy' road (km), and whether it is east (e), west (w), north (n), or north-east (ne) of the Lake. Green boxplot in the lower right and middle panels indicate sites east of the Lake and blue indicate sites west of the Lake

Results from the regression analysis indicate that the effects of temperature and wind speed on O₃ concentrations were minimal. The effect of RH was significant and negative, i.e., higher O₃ concentrations were observed when RH values were low (as expected).

Wind direction had the largest effect on the hourly ozone concentrations but the pattern of the effect depended on the site and whether it was day-time or night-time and whether it was a weekday (Monday –Thursday) or a weekend (Friday, Saturday, Sunday). Following are some results regarding wind direction as seen in **Figures 5.6-2 through 5.6-5**.

- 1) The largest wind effects were seen on weekends during night-time hours (**Figure 5.6-2**). At almost all the sites, ozone concentrations were highest when the wind direction was between 150-250 degrees (winds generally from south or southwest). The site most affected by this was WC-14 (northwest of the lake). The pattern for THB-6 was different in that it experienced higher concentrations with winds having a westerly component (i.e., between 180-360 degrees).
- 2) Patterns of wind direction effects at night-time during weekdays are similar to those on weekends but are much smaller (**Figure 5.6-3**).
- 3) Daytime patterns of wind direction effects on weekends are similar to night-time patterns but are significantly smaller (**Figure 5.6-4**).
- 4) Daytime patterns on weekdays are mostly not significant (**Figure 5.6-5**).
- 5) The standardized residuals (s) from the full model (full model included wind direction, RH and the bi-weekly passive O₃ values) seemed to ‘explain’ most of the ***between site variability*** seen in the residuals of the null model (null model included no explanatory) (**Figure 5.6-6**).
- 6) The standardized residuals from the full model (full model included wind direction, RH and the bi-weekly passive O₃ values) seemed to ‘explain’ most of the ***diurnal variability*** seen in the residuals of the null model (null model included no explanatory) (**Figure 5.6-7**).
- 7) The estimated smooth surface for bi-weekly passive O₃ concentrations at all passive sites and for the season (July – September) (**Figure 5.6-8**) confirms the spatial distribution of ozone concentrations performed with the Geostatistical Analyst software (see **Figure 5.1-3**). The graph shows that the Lake Tahoe Basin is separated from the polluted Central Valley air by a field of low O₃ concentrations on the western side of the Lake. The graph also points to the Lake possibly being a center of photochemical reactions producing O₃ for the entire Basin.

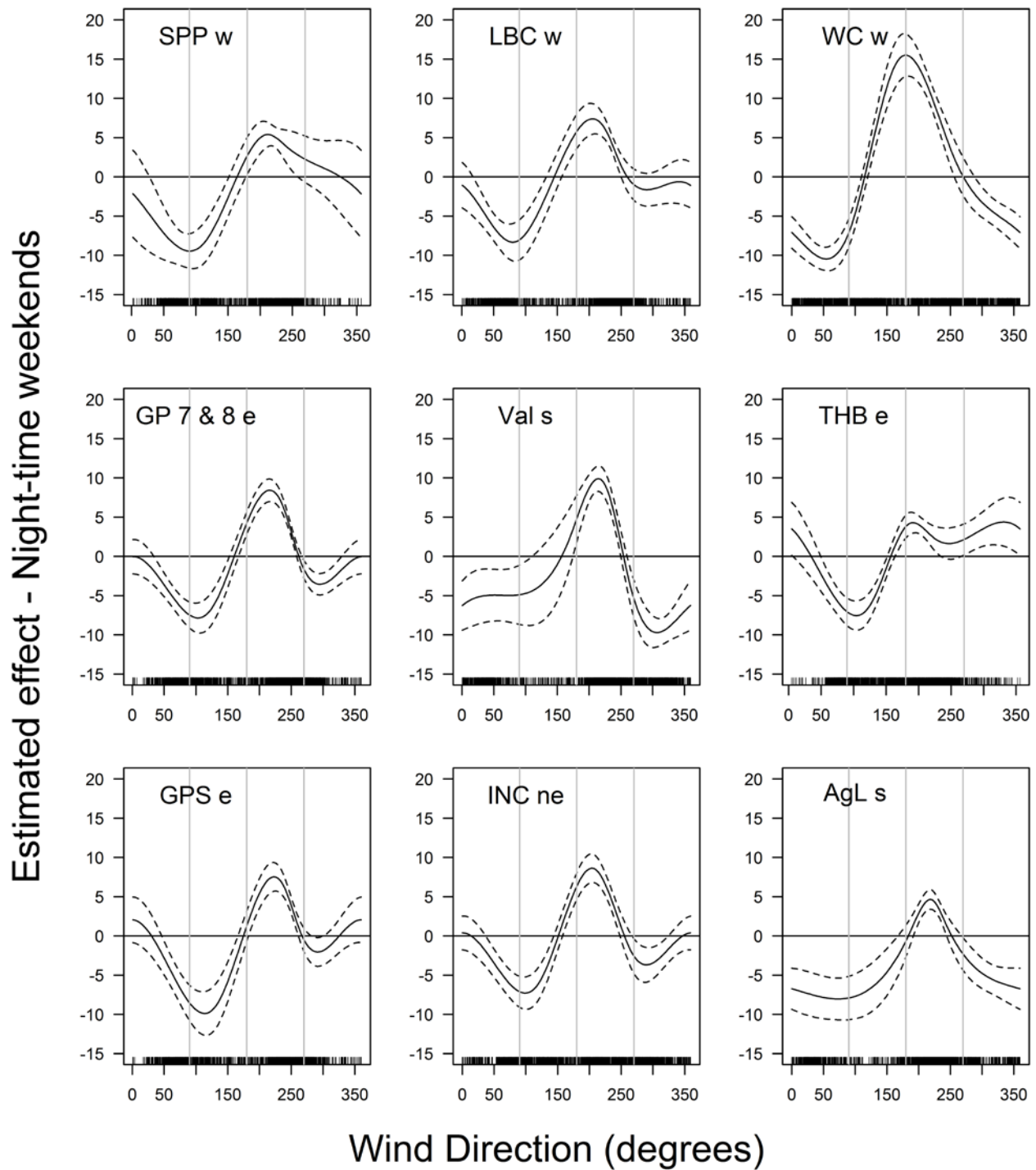


Figure 5.6-2. Estimated effects of wind direction on night-time O₃ concentrations on weekends. The dashed curves are approximate point-wise 95% CL. The effect is not significantly different from zero (i.e., the effect is average) when the horizontal zero line is within the 95% CLs.

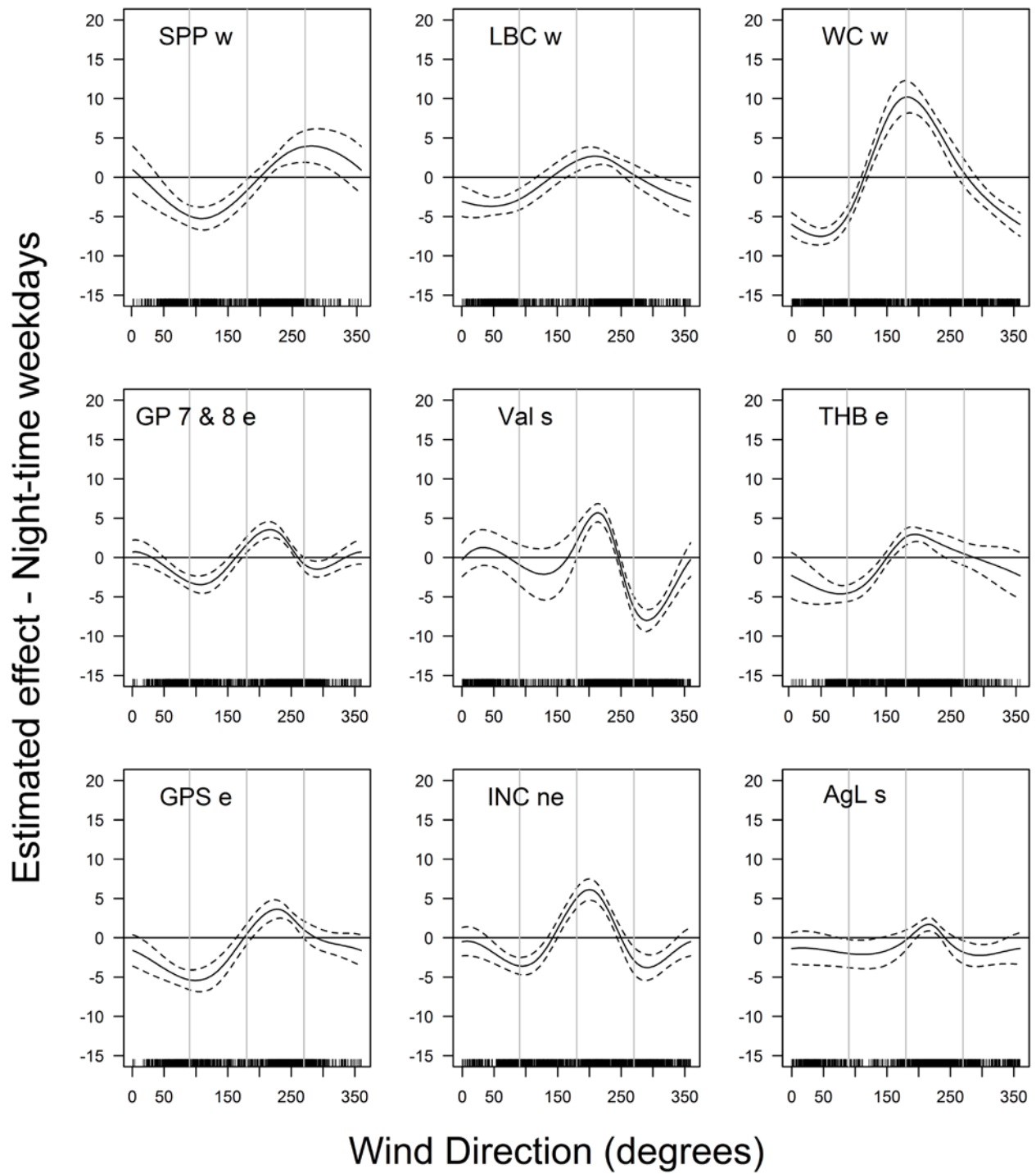


Figure 5.6-3. Estimated effects of wind direction on night-time O₃ concentrations on weekdays. The dashed curves are approximate point-wise 95% CL. The effect is not significantly different from zero (i.e., the effect is average) when the horizontal zero line is within the 95% CLs.

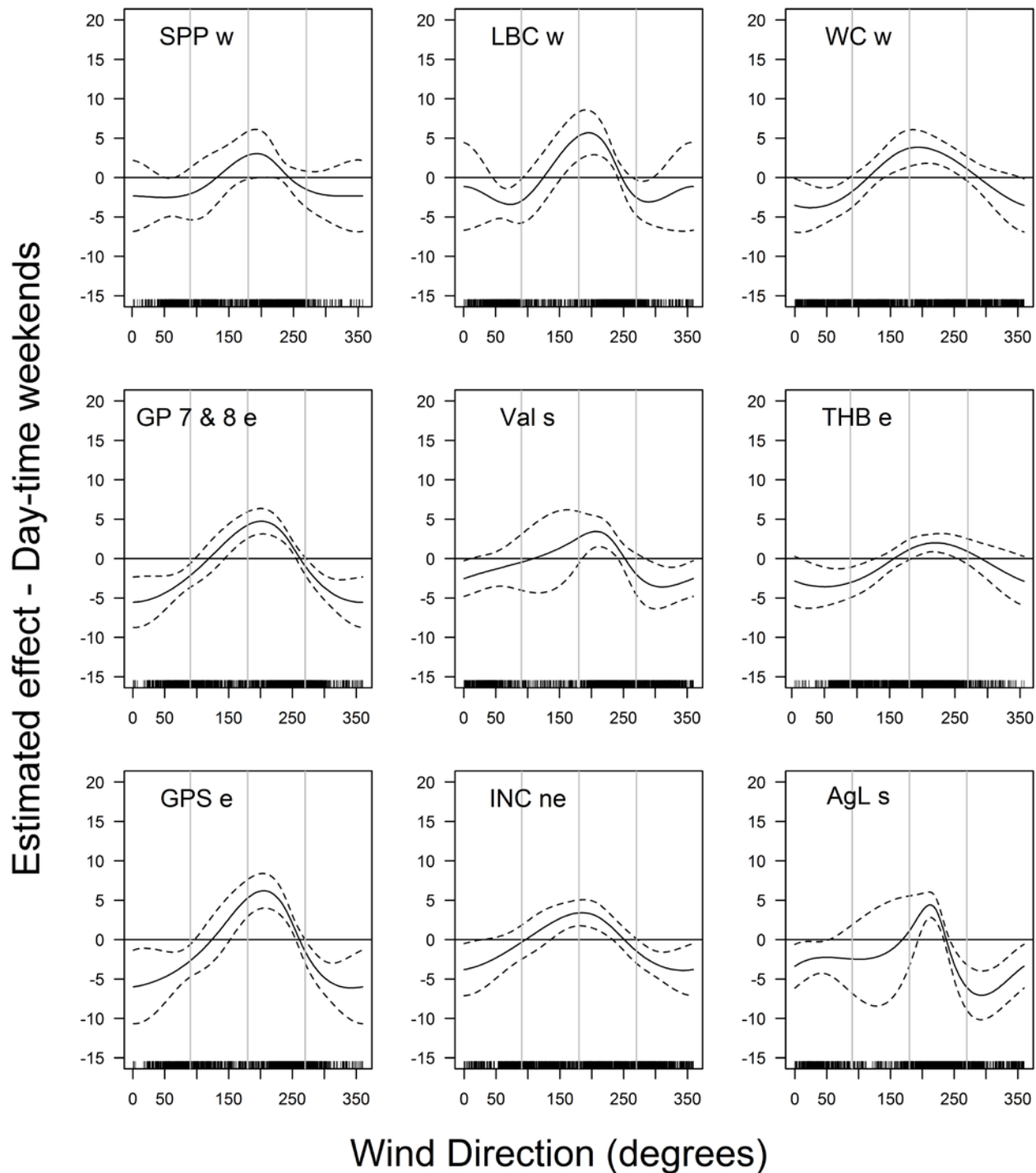


Figure 5.6-4. Estimated effects of wind direction on daytime O_3 concentrations on weekends. The dashed curves are approximate point-wise 95% CL. The effect is not significantly different from zero (i.e., the effect is average) when the horizontal zero line is within the 95% CLs.

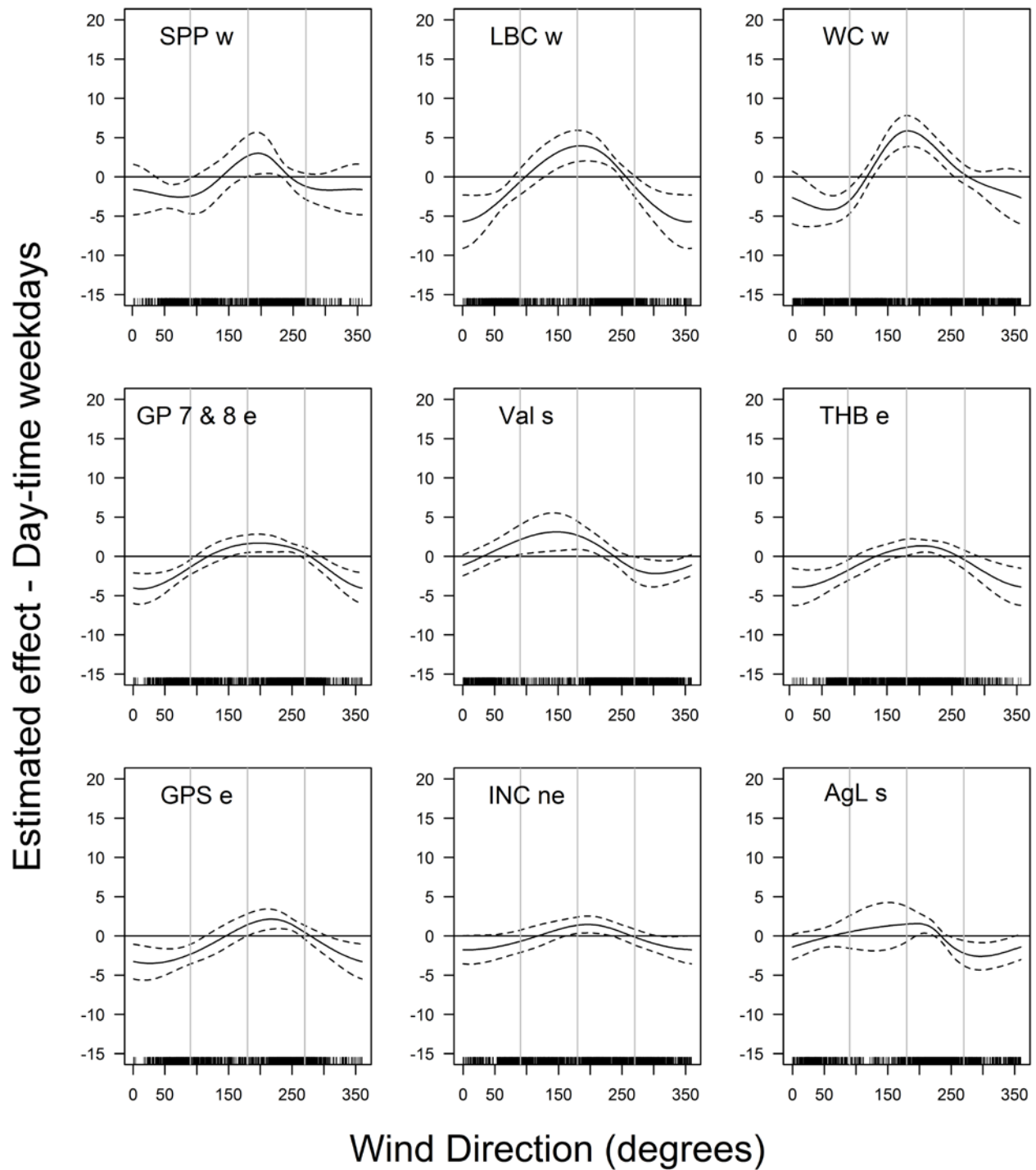


Figure 5.6-5. Estimated effects of wind direction at all sites at daytime on weekdays. The dashed curves are approximate point-wise 95% CL. The effect is not significantly different from zero (i.e. the effect is average) when the horizontal zero line is within the 95% CLs.

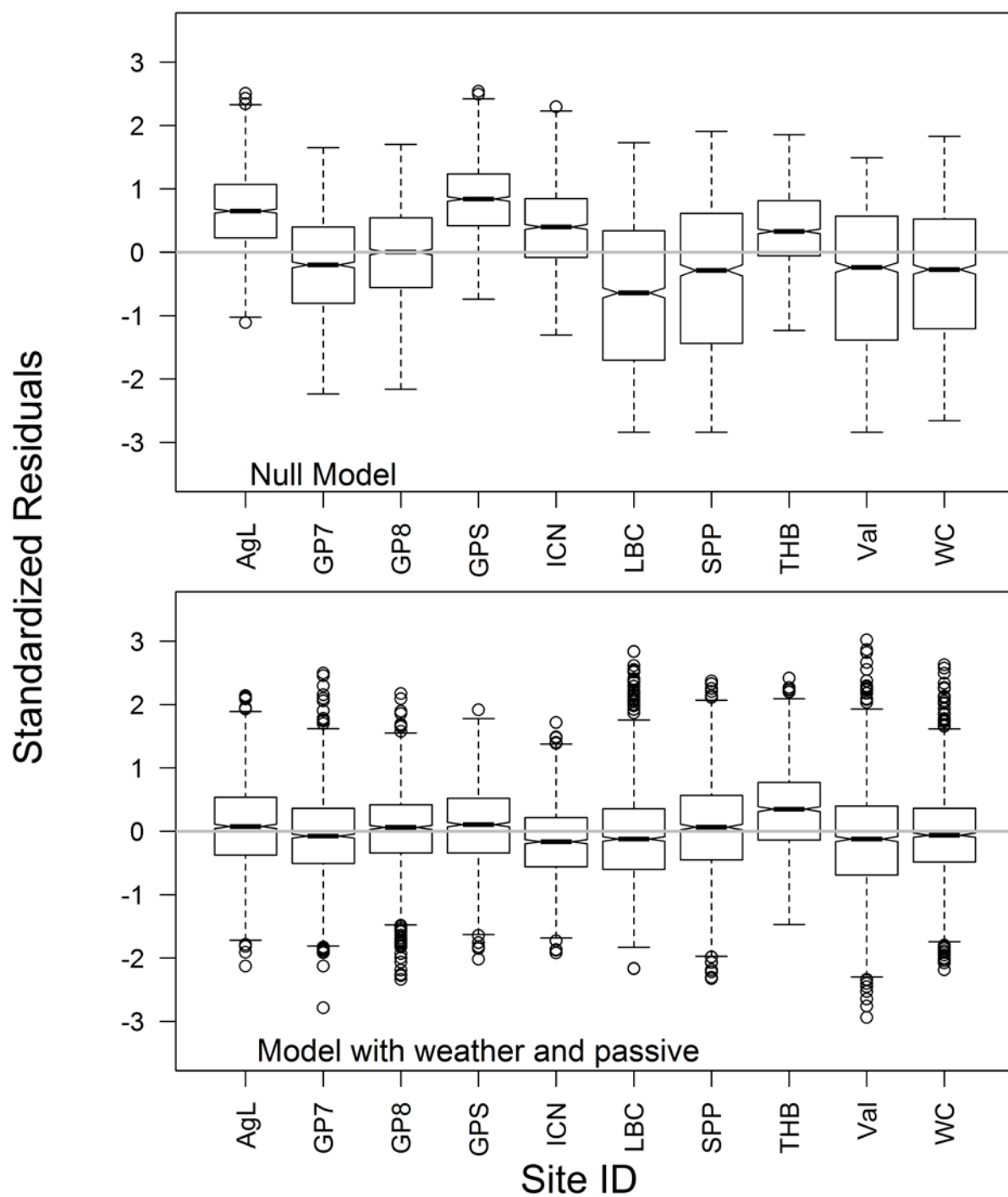


Figure 5.6-6. Standardized residuals, by site, from the null model where no explanatories are used (top panel) and the full model where explanatory variables are included (bottom panel). The notches around the median show approximate 95% CL for the median. Note that the residuals from the THB site are still higher than average (the zero line) implying that the variables in the full model are not fully ‘explaining’ the higher O₃ concentrations seen at this site.

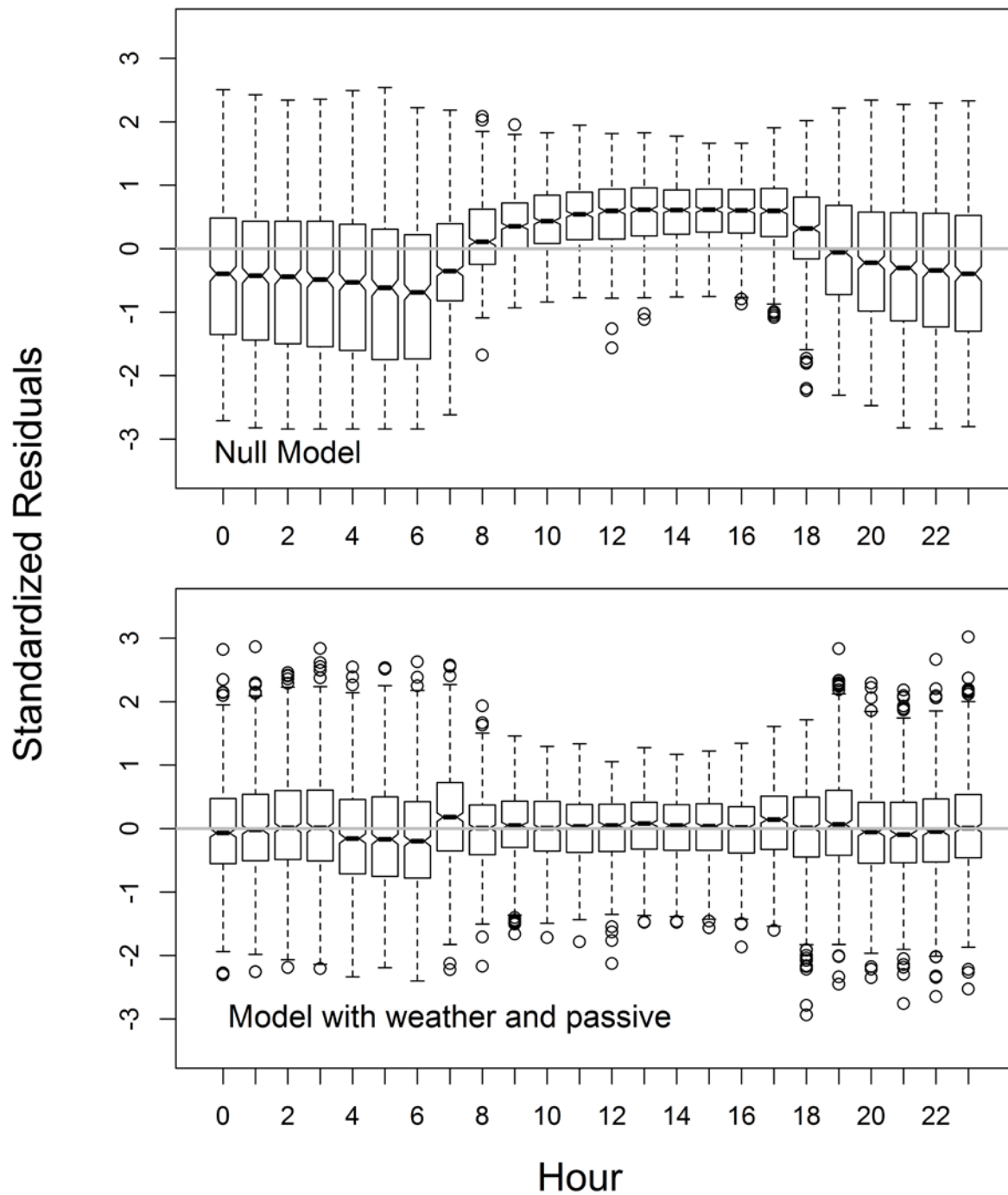


Figure 5.6-7. Standardized residuals, by hour of day, from the null model where no explanatory variables are used (top panel) and the full model where explanatory variables are included (bottom panel). The notches around the median show approximate 95% CL for the median. The diurnal pattern seen in the null residuals are not apparent in the residuals from the full model. The full model seems to be least adequate between 4 and 7am.

Relationships between passive O₃ values and maximum daily 8 hr average O₃

All the observed daily maximum 8-hr O₃ concentrations that exceeded the 70 ppb level occurred at ‘remote’ sites of Genoa Summit 9000; Incline Village, and Angora Lookout with flat diurnal patterns and distances to ‘main’ roads being greater than 4km (**Figure 5.6-9**). Also, these exceedences seem to happen almost exclusively when the passive sampler O₃ concentrations were greater than 50 ppb. When the passive sampler O₃ concentrations are greater than 50 ppb and the distance to road is greater than 4km, then the probability that the daily maximum 8-hr O₃ concentration is greater than 70 ppb is 0.13 (13%) with a 95% confidence level of 0.09 – 0.18 (9-18%).

In general, different diurnal patterns of O₃ values were observed during June – September 2010 at the ten mega sites. Most of these differences were adequately ‘explained’ by wind direction, day-of-week, and the value of passive O₃ at the site. Almost all sites seemed to have higher O₃ values at night during weekend days with wind coming from the south to south-west. Site 6 (Thunderbird) was the only site where the fit was not adequate.

The only sites that exceeded the maximum daily 8-hr average criterion of > 70 ppb were the remote sites with closest distance to ‘busy’ roads being greater than 4 km. Those exceedences were observed when the passive O₃ values were greater than 50 ppb. When the observed passive O₃ concentration was greater than 50 ppb, the expected probability of an exceedence on a given day was estimated at 13% (9 -18 %) for remote locations and 0.8% (0.1– 0.54%) for non-remote sites. When the observed passive O₃ concentration was less than 50ppb, the expected probability of exceedence was zero for all sites regardless of distance to a busy road. However, given that so few exceedences were observed, it will be hard to extrapolate these results to other years. Also, since that most of the variations seen between and within sites seem to be due to local conditions in the Basin (see discussion in section 4.1), it is not wise to extrapolate these results to sites outside the Basin. Clearly data from other years and in particular hourly ambient data from sites outside the Basin are needed if maps of exceedences are to be produced for a region larger than the Tahoe Basin.

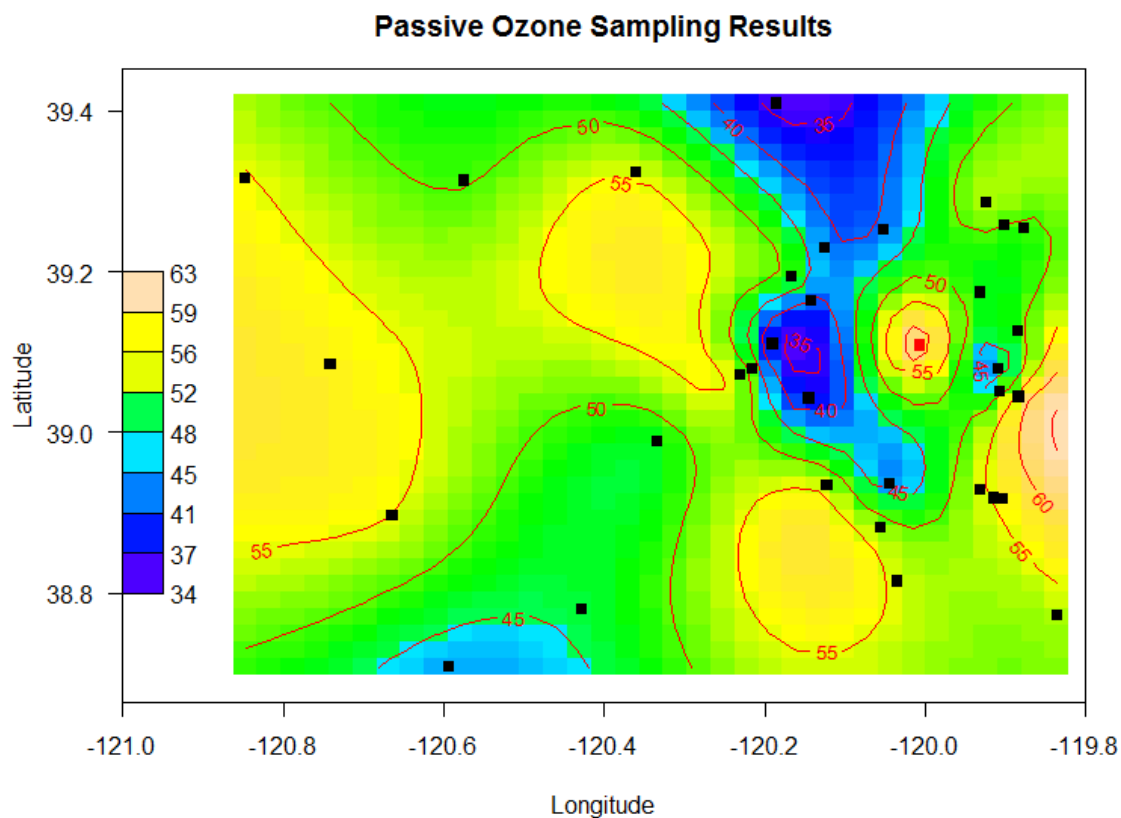


Figure 5.6-8. Estimated smooth surface for bi-weekly passive O_3 concentrations at all passive sites and for the whole season (June – Sept, 2010). The dots represent the locations of the passive sites. The red dot denotes the location of the passive site on Lake Tahoe (i.e., site TB2).

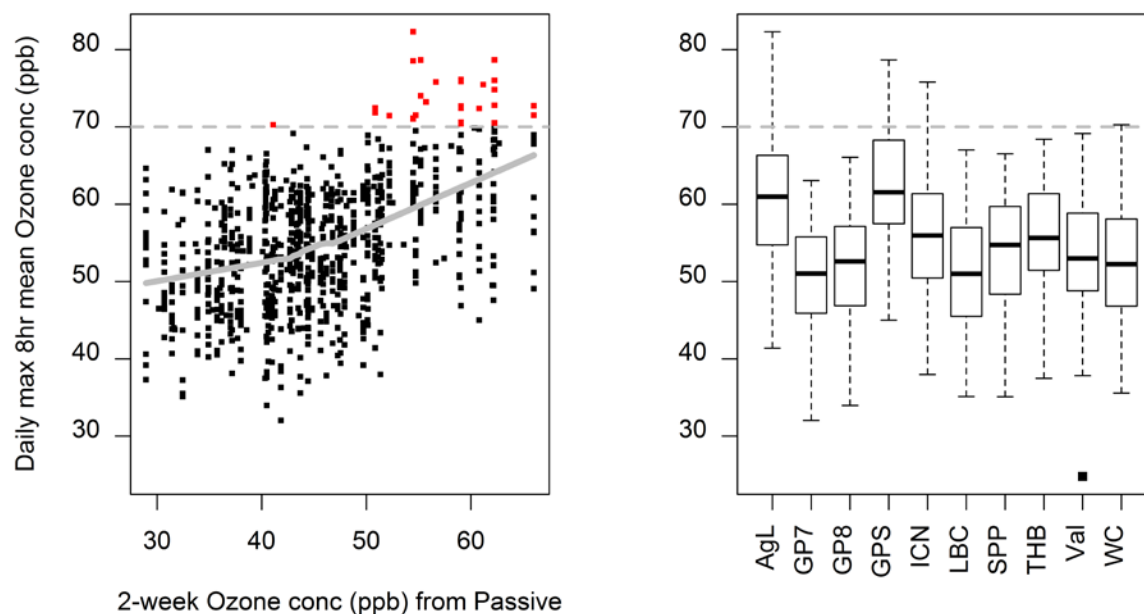


Figure 5.6-9. Daily maximum 8-hr average O_3 concentrations versus the mean 2-week O_3 concentrations measured at the same ten sites with passive samplers (left panel). Statistical summary of the daily maximum 8-hr average O_3 concentrations by site ID (right panel).

6. Conclusions and Recommendations

Based on four hypotheses tested in this study we have drawn the following conclusions and made some recommendations:

Hypothesis 1: While long-range transport from the Central Valley of California has little effect on the air pollution status in the Lake Tahoe Basin, locally emitted VOCs and NO_x significantly contribute to increasing O_3 concentrations and deterioration of air quality.

- High concentrations of O_3 were observed on the western slope of the Sierra Nevada mountain range and were likely caused by emissions from the Central Valley of California. For this region, the Toluene/Benzene (Tol/Bz) ratios were generally low, which indicates aged air masses and likely regional transport.
- High O_3 concentrations were found in the middle of Lake Tahoe, accompanied by high Tol/Bz and NO/NO_2 ratios, as well as high anthropogenic VOC concentrations (especially the higher molecular weight hydrocarbons n-decane and n-undecane). These results may indicate the influence of local spark ignition and diesel engine emissions (for example from large boats).
- High solar radiation (direct and reflected from the lake surface) over the Lake may promote photochemical reactions and increased production of secondary pollutants such

as O₃ and HNO₃ vapor.

- High O₃ concentrations were also measured on the eastern side of the Basin at high elevation sites, which exhibited low Tol/Bz ratios. This may indicate long range transport of pollutants aloft from the Central Valley. However, higher NO/NO₂ ratios may also indicate additional effects of local emissions from the South Lake Tahoe area.
- Meteorological analysis of O₃ distribution data for the ten megasites (Section 4.5, Synoptic Maps) indicate that O₃ transport from the southwest (i.e., from San Francisco, Sacramento and the Central Valley) into the Basin may occur at higher elevation (i.e., 500mb). Questions still remain on how significant of an impact the upper level pattern differences have on O₃ levels around the Basin and how the upper level O₃ is mixing down into the Tahoe Basin, which should be resolved through the use of chemical and meteorological modeling.
- Different diurnal patterns of O₃ concentrations were observed among the ten mega sites during June – September, 2010. Most of these differences were adequately ‘explained’ by wind direction and day-of-week. Almost all sites seemed to have higher O₃ values at night during weekend days with wind coming from the south to southwest.
- While all sites had similar O₃ concentrations in a range of 55-60 ppb during the daytime, at night, the low elevation sites showed much lower concentrations due to their proximity to major traffic routes and possible titration of O₃ by the NO emissions from local traffic and possibly also from fires in local campgrounds. As site elevations increased, the nighttime O₃ concentrations also increased. The Angora Lookout and Genoa Summit 9000 sites show a small increase in average O₃ values during night-time hours.
- The only sites where the daily maximum 8-hour concentrations exceeded 70 ppb were the remote sites with the shortest distance to ‘busy’ roads being greater than 4 km. Those exceedances were observed when the ozone passive 2-week averages values were greater than 50 ppb.
- Eight-hour O₃ concentrations >75 ppb (greater than the federal primary O₃ standard) only occurred on a few occasions at high elevation locations.
- Because the 2010 summer season was quite typical from a perspective of the weather, the results of this study can be extrapolated to other years.
- Also, given that most of the variation between and within sites seems to be due to local conditions in the Basin, it is not possible to extrapolate these results to sites outside the Basin. Data from other years and in particular real-time hourly data from sites outside the Basin are needed if maps of exceedences are to be produced for a region larger than the Lake Tahoe Basin.

Hypothesis 2. Both naturally-emitted and anthropogenic VOCs contribute to O₃ formation in the Basin, however, α -pinene emitted from coniferous trees have the highest O₃-forming potential in the Basin.

- As indicated by Anthropogenic/Biogenic species ratios (see Section 4.3), biogenic species (isoprene and α -pinene) are generally more abundant than measured anthropogenic compounds at all sites and during all sampling periods. There were few exceptions, most notably at the TB2 site at the middle of the Lake (Anth/Bio>1).

- However, contrary to our expectation, isoprene concentrations are usually comparable to or higher than α -pinene concentrations. Isoprene is emitted from deciduous species, including various shrubs and ground covers. Both, isoprene and α -pinene are very reactive, however isoprene has higher ozone forming potential.

Hypothesis 3: Ammonia is the most important contributor to dry-deposited N in the forest ecosystems of the Lake Tahoe Basin.

- The highest NH_3 concentrations were measured west of the Lake Tahoe Basin indicating the influence of mobile and stationary pollution sources in the Central Valley of California. However, local NH_3 emissions seem to contribute to enhanced concentrations of the pollutant on the south-western side of the Basin.
- The highest concentrations of reactive gaseous inorganic N were determined near the western shore of the Lake indicating the effects of local emissions of NH_3 from vehicle emissions.

Hypothesis 4: Deposition of N in some parts of the Tahoe Basin is in exceedance of critical loads for sensitive receptors.

- Nitrogen deposition in throughfall was low (1-2 kg/ha/yr) at megasites to the north or west of the lake, but was moderately elevated (> 5 kg/ha/yr) at three sites south or east of the lake.
- Nitrogen concentrations in lichen tissue were above the 'clean-site threshold' at five of the ten megasites and throughfall N deposition at three sites was above the critical load at which epiphytic lichen communities become dominated by eutrophic species.
- Throughfall deposition of $\text{NH}_4\text{-N}$ was 60% greater than deposition of $\text{NO}_3\text{-N}$ indicating the importance of reduced forms of N in the Tahoe Basin.

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