I. Title page

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

Theme: (3) Air Quality and Meteorology

Subtheme: (3b) Impacts and control of gaseous pollutants

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; Leora Nanus, San Francisco State University, San Francisco, CA 94132.

Grant contact person: Andrzej Bytnerowicz, US Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive, Riverside CA, 92507, tel. 951-680-1562; e-mail: abytnerowicz@fs.fed.us

Total funding requested: $296,540
II. Proposal Narrative

a. Abstract: The proposed study will characterize ozone, precursors of ozone (O3) formation, and gaseous pollutants that are important contributors to atmospheric nitrogen (N) deposition in the Lake Tahoe Basin. We will use passive samplers for monitoring of O3, nitric oxide (NO), nitrogen dioxide (NO2), ammonia (NH3), nitric acid (HNO3) and volatile organic compounds (VOCs) on a network of 32 sites inside and outside of the Basin. Using statistical and geostatistical models we will create distribution maps of the measured compounds for the entire Basin. On a subset of 10 monitoring sites, we will also measure real-time O3 concentrations with active UV absorption monitors to evaluate diurnal changes of the pollutant, calibrate passive O3 samplers, and use that data for evaluation of the exceedances of O3 air pollution standards in the Basin. At the same sites we will also measure N deposition with ion exchange resin (IER) collectors placed in forest clearings (bulk precipitation) and under tree canopies (throughfall). In these bulk and throughfall samples from the IER collectors we will measure the stable isotope composition (15N and 18O) of NO3 and of NH3 (15N) from passive sampler extracts to evaluate the origin of N deposition in the Basin. Results of this study will help to evaluate the present and future potential of O3 formation as well as the biological/ecological effects of N air pollutants and the resulting N deposition in the Lake Tahoe Basin. These results will also help to develop science-based management strategies aimed at improving air quality and ecological sustainability of the Basin.

b. Justification statement: Understanding the distribution of ozone (O3) 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 O3 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 O3 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 O3 (Dolislager et al., 2009a); (c) modeling of nitric acid (HNO3) transport from central California (Gertler et al., 2006). These three studies show that the local generation of O3 and other pollutants in the Basin is more important than long-range transport when it comes to exceedances of the state and national O3 standards and elevated levels of other pollutants within the Basin. However, very little is known about the spatial and temporal distribution of O3 precursors (nitrogen oxides, NOx, and volatile organic compounds, VOCs) in the Basin; this is needed for evaluating the potential for photochemical generation of O3 in the Basin and developing recommendations for air pollution control strategies. Such information is completely lacking for VOCs. While the concentrations and distribution of NOx were characterized during the Lake Tahoe Atmospheric Deposition Study (Dolislager et al., 2009b), the spatial coverage of that study was quite limited. In addition to their role in O3 formation, nitrogen oxides also contribute to atmospheric nitrogen (N) deposition. However, gaseous NH3 and HNO3 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, NH3 and to a lesser extent HNO3 were found to be the key components of the direct N deposition to Lake Tahoe (Dolislager et al., 2009 b; 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.

The proposed study will fill these gaps of our current understanding of the chemical environment of the Lake Tahoe Basin. We will use passive samplers for monitoring of NO, NO2, NH3, O3 and VOCs on a network of 32 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). On the subset of 10 monitoring sites, we will also measure real-time O3 concentrations with active UV absorption monitors. Using statistical and geostatistical models we will create distribution maps of the measured compounds. In addition, at the same 10 sites, we will measure N deposition in bulk and throughfall samples using the ion exchange resin collectors and will evaluate the origin of atmospherically-deposited NOx using stable isotope analysis of 15N(NO3) and 18O(NO3). Results of this study will 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.
c. Concise background and problem statement

**Ozone:** O₃ 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 O₃ levels in the Lake Tahoe Basin, it is necessary to understand the underlying chemistry of O₃ formation. The two factors to consider are nitrogen oxides (NOx = NO + NO₂) and volatile organic compounds (VOCs). NO reacts with O₃ to produce more NO₂ in a process that is only limited by the availability of O₃. During the daylight hours NO₂ decomposes photochemically to reproduce NO. The ratio between NO and NO₂ is governed by the photolytic rate J(NO₂). The photolysis of NO₂ leads to the formation of O₃. Since O₃ is removed by the reaction with NO and is produced via the photochemical reaction, it seems that the net production of O₃ would be limited. However, through a series of reactions involving NO, VOCs, and the hydroxyl radical (OH), additional NO₂ is formed, which can subsequently photolyze to generate O₃ via a chain reaction mechanism. This chain reaction is eventually terminated by a process that yields nitric acid (HNO₃). Thus the chemical processes involving NOx and VOCs leading to O₃ formation in the Lake Tahoe Basin also result in the formation of HNO₃, an important contributor to the overall deposition of N.

Ambient O₃ 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 O₃ concentrations from the Sacramento Valley and Sierra Nevada foothills from entering the Basin (Figure 2). This result confirms the conclusions for the Lake Tahoe Deposition study (Dolislager et al. 2009b), 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 O₃ concentrations at a sufficiently fine resolution to evaluate Basin-wide exceedances of O₃ air pollution standards and its phytotoxic potential.

**Volatile Organic Compounds (VOCs):** As outlined above, hydrocarbons play a crucial role for the accumulation of ozone to occur in the atmosphere. The rates of O₃ formation and accumulation are nonlinear functions of the mixture of VOC and NOx in the atmosphere. Depending upon the relative mixing ratios of VOC and NOx and the specific mix of VOC present, the rate of O₃ formation can be more sensitive to changes in VOC alone or to changes in NOx alone or to simultaneous changes in both VOC and NOx (Fujita et al., 2003). One could expect the Tahoe Basin to be NOx limited due to the abundance of natural VOCs 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, biogenic hydrocarbons are only represented by one compound (isoprene) on this list. Since we expect biogenic hydrocarbons to be abundant in the Lake Tahoe Basin, especially those emitted by pines (i.e. α– and β– pinenes), we propose to monitor not only anthropogenic, but also biogenic hydrocarbons (as listed below in Table 1).

**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., 2009b), observed the following:

- Three-fourths of the deposited N is due, primarily, to NH₃ with a smaller contribution from HNO₃.
- The long-range transport of O₃ from out-of-basin sources contributes to elevated O₃ levels on rare occasions; although it does add to the regional atmospheric burden. (It should be noted that the data indicated late afternoon elevated O₃ levels at one site, Cave Rock, consistent with the impact of long range transport.)

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 NOx data collected by CARB at Echo Summit. They found HNO₃ was responsible for most of the N deposition, except in areas influenced by local NH₃ and NO₂ concentrations. Using these results, coupled with geo-spatial modeling (Tarnay 2001b), they concluded most of the HNO₃ and NH₃ were from 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. (2001) 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.
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 (Figure 3), 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., 2009b).

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 the lake 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 at which 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.

d. Goals, Objectives and hypotheses to be tested

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).
7. Characterize the origin of N pollutants and N deposition based on analysis of δ¹⁵N(NO₃), δ¹⁸O(NO₃), and ¹⁵NH₃.
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 NOx 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.

e. Approach, methodology and location of research

The study is planned for two years. The first year (2010/2011) will be devoted to field measurements and the second year (2011/2012) to chemical analyses, data processing, and writing reports and scientific papers.

**Monitoring network:** Monitoring of all the pollutants of interest will be based on passive sampling. 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 samplers will be deployed on a network of 32 sites located inside and outside of the Lake Tahoe Basin, the same as was used in summer 2002 for characterizing O₃ and HNO₃ distribution (Bytnerowicz et al., 2004) – please see Figure 1. Since extensive air quality determinations have been performed at the Big Hill site characterizing the upslope movement of polluted air masses from the California Central Valley into the Sierra Nevada (Dolislager et al., 2009), we intend to add that location to the original monitoring network. A subset of 10 sites with an optimal spatial distribution will be used for real-time O₃ measurements, N deposition collections, and stable isotope analysis. Passive samplers will be changed every 2 weeks starting June 15, 2010 and ending September 15, 2010.

**Ozone measurements:** Passive Ogawa samplers will be used for monitoring O₃ (Koutrakis et al., 1993). Each sampler contains two cellulose filters coated with nitrite (NO₂⁻) which is oxidized by O₃ to NO₃⁻ and analyzed with ion chromatography. The rate of NO₃⁻ formation (amount of NO₃⁻ formed on a filter over time of exposure) serves as a measure of O₃ concentration. At 10 sites the two-week averaged O₃ concentrations determined with passive samplers will be compared with real-time O₃ concentrations obtained with portable UV absorption 2B Technologies monitors (Bognar and Birks, 1996). The empirically derived coefficients will be used for calculating O₃ concentrations for passive samplers. In addition, comparison between passive samplers and the collocated UV absorption monitors will help to generate maps of the summer-season hourly O₃ concentrations for the entire Lake Tahoe Basin.

**VOC measurements:** Deployment of VOC passive samplers at 32 sites in the Tahoe Basin area will greatly improve our understanding of the relative importance of anthropogenic versus biogenic emission sources in this area. We selected three of the most abundant and important biogenically-emitted hydrocarbons from the O₃ production standpoint: isoprene and α- and β- pinenes. Since the Tahoe Basin is mostly populated with conifers, we expect pinenes to be the most abundant biogenic species. Isoprene is only emitted by deciduous trees, which are not very common in this area. Nevertheless, since isoprene is a very reactive species, we propose to monitor it as well, using a separate Radiello sampler that was especially designed for light hydrocarbons, including isoprene and 1,3-butanediene. Anthropogenic species selected for monitoring consist of 14 hydrocarbons that are characteristic for motor vehicle emissions (Table 1), including such reactive and toxic compound like 1,3-butanediene. Heavier hydrocarbons, such as n-undecane and n-dodecane are mostly characteristic for diesel vehicle emissions. Thus, we will be able to assess the contribution of diesel traffic to the VOC burden in the Tahoe Basin area. Since benzene and heavier hydrocarbons (C₁₀-C₁₂) are also less reactive and have longer lifetimes, by investigating their ratios to various more reactive species (such as toluene, xylene, etc.) we will be able to comment on the importance of a long range transport versus local emission sources.

For monitoring selected VOC species we will use passive VOC Radiello samplers. After sampling, the collected pollutants will be desorbed from the sampling media by thermal or chemical means and analyzed quantitatively. The average ambient concentration of pollutants for 2-week long periods will be calculated by dividing the mass of pollutant measured analytically by the product of sampling rate and sampling time. Table 1 below lists the species we propose to monitor for this project, for which sampling rates are published (http://www.radiello.com or http://www.sigmaaldrich.com/analytical-chromatography/sample-preparation/radiello/learning-center/applications.html ).
Table 1. List of proposed species to be quantified for this project

<table>
<thead>
<tr>
<th>No.</th>
<th>Biogenic Compounds</th>
<th>No.</th>
<th>Anthropogenic Compounds</th>
<th>No.</th>
<th>Anthropogenic Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Isoprene</td>
<td>4</td>
<td>1,3-Butadiene</td>
<td>11</td>
<td>Styrene</td>
</tr>
<tr>
<td>2</td>
<td>α-Pinene</td>
<td>5</td>
<td>Benzene</td>
<td>12</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>3</td>
<td>β-Pinene</td>
<td>6</td>
<td>Toluene</td>
<td>13</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>7</td>
<td>Ethylbenzene</td>
<td>14</td>
<td>n-Octane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>m/p-Xylene</td>
<td>15</td>
<td>n-Nonane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Cyclohexane</td>
<td>16</td>
<td>n-Decane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1,2,4-Trimethylbenzene</td>
<td>17</td>
<td>n-Dodecane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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) and Carbopack X (for isoprene and 1,3-butadiene). The cartridges will be deployed in the diffusive sampling bodies according to the manufacturer's instruction (http://www.radiello.com). After sample collection cartridges will be analyzed on a Varian 3800 gas chromatograph (GXC) with Saturn 2000 mass spectrometry (MS) detection equipped with a Gerstel TDSA-3 thermal desorption unit. Initial desorption is set for five minutes at 300 °C before transfer onto a Tenax trap cooled to -150 °C. After preconcentration on the trap, the sample will be injected at 240 °C onto a 60 m, widebore, Phenomenex ZB-1 column for separation before the MS detection. Calibration of the system will be conducted with a VOC mixture (purchased from AiR Environmental) that contains the most commonly found hydrocarbons, including those listed in Table 1.

Measurement of inorganic N gases: Ogawa passive samplers will be used for monitoring NOx and NO2. Each NO2 sampler contains two filters coated with triethylene amine (TEA) and each NOx sampler consists of two filters coated with TEA and an unspecified oxidizer. Both NOx and NO2 are collected as NO2⁻ which is extracted in water and determined with ion chromatography, and their ambient concentrations will be calculated using calibration curves (Bytnerowicz et al., 2007). From the difference between NOx and NO2 concentrations, NO concentrations will be calculated. Passive samplers developed by the US Forest Service (Bytnerowicz et al., 2005) will be 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 will be analyzed by ion chromatography, and concentrations of HNO3 will be calculated using calibration curves. Three replicate HNO3 samplers will be exposed at each site. Ogawa passive samplers (Roadman et al., 2003), with two replicate filters coated with citric acid, will be used for NH3 monitoring. Ammonia reacts with citric acid on the filters producing ammonium citrate. After water extraction, NH4⁺ concentrations in filter extracts will be determined colorimetrically on a TRAACS 2000 Autoanalyzer, and ambient NH3 concentrations will be calculated based on a comparison of passive samplers against the co-located annular denuder systems (Koutrakis et al., 1993).

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 will be installed in order to measure annual throughfall and bulk deposition of NO3⁻ and NH4⁺. Deposition will be 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 will provide data on spatial patterns of N deposition inputs for the summer and winter seasons. The added benefit of the IER samplers is that dual isotope analysis of the NO3 samples (δ15N, δ18O; Nanus et al., 2008) can also be done to characterize source emissions for NOx deposition both within and outside of the Basin. At the same 10 sites where the IER collectors are deployed, NH3 extracted from passive samplers for NH3 will also be analyzed for 15NH3 to characterize source emissions of reduced N.

The stable isotope data from the IER collectors and passive samplers will be used to distinguish precursor sources of atmospheric N in samples collected across the Tahoe Basin monitoring network. The dual isotopic analyses for NO3 will be done using the denitrifier method (Cascioiti et al., 2002; Sigman et al., 2001). These data will provide an additional approach for evaluating the relative importance of within-basin versus upwind emissions sources of the NOx deposited to the Tahoe Basin. Both seasonal and spatial patterns will be 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).
Spatial statistical analyses: We will use spatial statistical models to develop distribution maps of O₃ and its precursors, similar to those in Figure 2. Additionally, we will use modeled weather data on a grid (cooperation with Matthias Falk submitting a proposal for sub-theme 3c or from another source) in a spatial regression model to quantify and understand the sources of variation in the spatial and temporal biweekly O₃ data (Lee 2003, Preisler et al 2002, Preisler et al. 2003). The regression models will also help us quantify the contributions of each of the precursors to the spatial variability of ozone. For the 10 sites co-located with active monitors we will estimate a regression model for predicting diurnal O₃ values. In a recent paper (Preisler et al. 2009) we used the following model to predict hourly O₃ values at four sites in the central Sierra Nevada:

\[ o_3 = \alpha + site \cdot s(day) + s(hr) + \sum_k s(X_k) + error \]

where \( X_k \) is the \( k^{th} \) weather variable (e.g., temperature, wind direction); \( s(X) \) is a nonparametric smooth spline function estimated from the data 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. With such a model we were able to ‘explain’ approximately 63% of the variability in the hourly O₃ values. Note that the above model has a site specific term describing the characteristic pattern of variation at a given site over the season. In our present study, since we have hourly data at only a subset of the sites, we will replace the term \( site:s(day) \) in our model by the biweekly values observed with the passive sampler. It is anticipated that, since the site specific seasonal effect is a slowly changing pattern, the biweekly O₃ levels will be to capture this source of variation. Once a model is developed for the 10 sites with co-located active and passive samplers, we will use this model to predict hourly O₃ values for the rest of sites that have only passive samplers, hence allowing us to produce spatially dense maps of O₃ distributions based on 1-h values and calculation of exceedances of O₃ air pollution standards. Maps of spatial distribution of O₃ and other measured compounds will be developed with Geostatistical Analyst, an extension of ArcGIS 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 concentration will be constructed using kriging or inversed distance weighted (IDW) methods (Johnstone et al., 2001).

f. Relationship of the research to previous and current relevant research, monitoring, and/or environmental improvement efforts

The proposed research is a logical continuation of previous efforts focusing on understanding air quality and its effects on the human health-based national and state air pollution 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. 2009a, b; Gertler et al, 2006; Koracin et al., 2004; Tarney et al, 2001a,b; 2005:).

This research will be conducted by a team consisting of researchers and air quality specialists of the US Forest Service, Desert Research Institute, the San Francisco State University and St. Mary’s College. We will establish a large-scale field monitoring network with dense and well-distributed sites allowing for generation of reliable maps of the distribution of key pollutants and O₃ precursors (for O₃, NO, NO₂, NH₃, HNO₃ and selected VOCs). We will be also able to produce maps of exceedances of the air pollution standards for O₃ and of atmospheric N deposition. We are planning a close collaboration with Dr. Matthias Falk, UC Davis, who will develop a comprehensive meteorological data base for the Basin (proposal for Subtheme 3c of this RFP). Results of the proposed study supported by the best-available meteorological data sets will improve our understanding of the role of biogenic and anthropogenic VOCs and NOx in O₃ formation within the Basin. Such improved knowledge will lead to science-based recommendations regarding management strategies that could be recommended for effective control of O₃ levels in the Basin. The established monitoring network will allow for cost-effective measurements of N deposition and stable isotopic analyses of atmospheric N needed for a better understanding of N deposition sources and empirically-based estimates of N deposition in the Basin. All these efforts will help in creating a knowledge base for future investigations of potential ecological impacts of ambient O₃ and N deposition in the Tahoe Basin under various scenarios of the changing climate for California and Nevada (Cayan et al., 2006).

g. Strategy for engaging with managers and obtaining permits

The Forest Service R5 Air Resource Management Program (ARM) staff will facilitate securing necessary permits or permission to locate and secure monitoring equipment at the proposed locations. In addition, the ARM
staff will use the coordination opportunity to engage Forest and Regional resource staff and line officers in
discussions of the research objectives and potential management implications. Upon completion of the project,
ARM staff will facilitate a broader discussion with Lake Tahoe Basin staff, Tahoe Regional Planning Agency
(TRPA), surrounding Air Pollution Control Districts, and the California Air Resources Board. One venue for that
discussion could be the bi-annual Air and Land Managers (ALM) meeting in California. ALM is an executive level
meeting between Federal land agencies, CARB, and Air Districts. Existing data interpretation from 2002 and this
project will also be very important to the Forest Plan revisions in the Sierra Nevada that are planned in the coming
years.

h. Description of deliverables/products and the plan for how data and products will be reviewed and made available
to end users

The proposed study will produce:

- tables and graphs of O₃, NO, NO₂, NH₃, HNO₃ and VOCs concentrations for the 2010 summer season for 32
  monitoring sites in the Lake Tahoe Basin area. These data will include six 2-week long averages for the June 15
  - September 15, 2010 period as well as the averages for the entire season.
- geostatistical maps of the spatial distribution of O₃, NO, NO₂, NH₃, HNO₃ and VOCs for the Lake Tahoe Basin
  area (similar to those shown in Figures 2 and 3)
- tables and graphs of N deposition values for summer 2010 and winter 2010/2011
- tables and graphs of stable N and O isotopes for summer 2010 and winter 2011
- geostatistical maps of the spatial distribution of N deposition for the extended area of the Lake Tahoe Basin
- quarterly progress reports and a final report for the study
- several research papers to be published in high quality peer-reviewed journal
- Web-based data sets and maps that will be available to other scientists, managers and agencies

Results of this work will help in understanding O₃ formation and for recommending O₃ control strategies for the
Lake Tahoe Basin. Results of this study will also create a knowledge base for future evaluations of the biological
and ecological effects of air pollution and N deposition (exceedances of critical levels for NH₃ or reactive N; and
critical loads for N deposition; effects of ozone on ecosystems).
### III. Schedule and major milestones/deliverables (table with estimated start and end dates)

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Start Date</th>
<th>End date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive sampler monitoring of O₃, NO, NO₂, NH₃, HNO₃, and VOCs</td>
<td>6/15/2010</td>
<td>9/15/2010</td>
</tr>
<tr>
<td>Monitoring of O₃ with active monitors</td>
<td>6/15/2010</td>
<td>9/15/2010</td>
</tr>
<tr>
<td>Passive sampler monitoring for ^1⁵^NH₃ analyses</td>
<td>6/15/2010</td>
<td>9/15/2010</td>
</tr>
<tr>
<td>Summertime monitoring of N deposition with ion exchange resin collectors</td>
<td>6/15/2010</td>
<td>9/15/2010</td>
</tr>
<tr>
<td>Winter-time monitoring of N deposition with ion exchange resin collectors</td>
<td>9/15/2010</td>
<td>5/1/2011</td>
</tr>
<tr>
<td>Chemical analyses of O₃, NO, NO₂, NH₃, HNO₃ and VOCs passive samplers</td>
<td>7/1/2010</td>
<td>3/1/2011</td>
</tr>
<tr>
<td>Chemical analyses of ion exchange resin collectors</td>
<td>5/1/2011</td>
<td>10/1/2011</td>
</tr>
<tr>
<td>N &amp; O stable isotope analyses of ion exchange resin extracts</td>
<td>5/1/2011</td>
<td>10/1/2011</td>
</tr>
<tr>
<td>Passive sampler data processing</td>
<td>3/1/2011</td>
<td>10/1/2011</td>
</tr>
<tr>
<td>Ozone active monitors data processing</td>
<td>9/15/2010</td>
<td>1/1/2011</td>
</tr>
<tr>
<td>Development of statistical models of O₃ distribution</td>
<td>3/1/2011</td>
<td>1/1/2012</td>
</tr>
<tr>
<td>N deposition data processing</td>
<td>10/1/2011</td>
<td>1/1/2012</td>
</tr>
<tr>
<td>N &amp; O stable isotope data processing</td>
<td>10/1/2011</td>
<td>1/1/2012</td>
</tr>
<tr>
<td>Generation of geostatistical maps of O₃, NO, NO₂, NH₃, HNO₃ and VOCs distribution</td>
<td>3/1/2011</td>
<td>1/1/2012</td>
</tr>
<tr>
<td>Analysis of spatial and temporal changes in O₃ precursors and O₃ formation leading to formulation of management recommendations</td>
<td>3/1/2011</td>
<td>1/1/2012</td>
</tr>
<tr>
<td>Preparation of a final report</td>
<td>1/1/2012</td>
<td>6/1/2012</td>
</tr>
<tr>
<td>Submission of a final report</td>
<td>6/15/2012</td>
<td></td>
</tr>
<tr>
<td>Preparation and submission of peer reviewed publications</td>
<td>1/1/2012</td>
<td>1/1/2013</td>
</tr>
</tbody>
</table>
IV. Literature cited


Preisler, H.K., Zhong, S., Esperanza, A. Brown, T.J. and Bytnerowicz, A. 2009. Estimating contribution of wildland fires to ambient ozone levels in National Parks in the Sierra Nevada, California". Environmental Pollution (In press).


V. Figures

Figure 1. Location of the monitoring sites in the 2002 California Air Resources Board study (Bytnerowicz et al., 2002).

Figure 2. Distribution of summer-time average O₃ concentrations in 2002.
Figure 3. Distribution of summer-time average HNO$_3$ concentrations in 2002.