



An empirical inferential method of estimating nitrogen deposition to Mediterranean-type ecosystems: the San Bernardino Mountains case study

A. Bytnerowicz^{a,*}, R.F. Johnson^b, L. Zhang^c, G.D. Jenerette^b, M.E. Fenn^{a,*}, S.L. Schilling^a, I. Gonzalez-Fernandez^d

^a USDA Forest Service, PSW Research Station, 4955 Canyon Crest Drive, Riverside, CA 92507, USA

^b Center for Conservation Biology & Botany and Plant Sciences, University of California, Riverside, CA 92521, USA

^c Air Quality Research Division, Environment Canada, Toronto, Ontario M3H 5T4, Canada

^d Ecotoxicología de la Contaminación Atmosférica, CIEMAT, Madrid, Spain

ARTICLE INFO

Article history:

Received 18 January 2015

Received in revised form

16 March 2015

Accepted 19 March 2015

Available online 8 April 2015

Keywords:

Nitrogen deposition

Complex terrain

Forests

Inferential deposition model

Critical loads

ABSTRACT

The empirical inferential method (EIM) allows for spatially and temporally-dense estimates of atmospheric nitrogen (N) deposition to Mediterranean ecosystems. This method, set within a GIS platform, is based on ambient concentrations of NH_3 , NO , NO_2 and HNO_3 ; surface conductance of NH_4^+ and NO_3^- ; stomatal conductance of NH_3 , NO , NO_2 and HNO_3 ; and satellite-derived LAI. Estimated deposition is based on data collected during 2002–2006 in the San Bernardino Mountains (SBM) of southern California. Approximately 2/3 of dry N deposition was to plant surfaces and 1/3 as stomatal uptake. Summer-season N deposition ranged from $<3 \text{ kg ha}^{-1}$ in the eastern SBM to $\sim 60 \text{ kg ha}^{-1}$ in the western SBM near the Los Angeles Basin and compared well with the throughfall and big-leaf micrometeorological inferential methods. Extrapolating summertime N deposition estimates to annual values showed large areas of the SBM exceeding critical loads for nutrient N in chaparral and mixed conifer forests.

Published by Elsevier Ltd.

1. Introduction

Elevated deposition of reactive nitrogen (N) has serious ecological effects in forests and other ecosystems such as water contamination or biodiversity changes that include shifts in lichen communities or invasion of alien plant species (Galloway et al., 2003; Fenn et al., 2011; Greaver et al., 2012). In the Mediterranean ecosystems of California, deposition of N is dominated by dry deposition (Bytnerowicz and Fenn, 1996). Forests and other ecosystems downwind of large air pollution source areas, such as the Los Angeles Basin or Central Valley of California, experience high concentrations of N compounds including nitrogen oxides (NO_x), ammonia (NH_3), nitric acid (HNO_3), particulate nitrate (NO_3^-) and ammonium (NH_4^+) as well as various organic compounds (Bytnerowicz and Fenn, 1996). Elevated N deposition is also an integral part of a complex of multiple stressors affecting the health of

California forests (Grulke et al., 2009).

Many factors can potentially regulate dry deposition to vegetation (Lovett, 1994). The most important factors controlling dry N deposition to vegetation are ambient concentrations of N compounds, physicochemical conditions controlling their deposition velocities, canopy characteristics and prevailing micrometeorology (Hertel et al., 2011). Highly reactive and water soluble NH_3 and HNO_3 are characterized by high deposition velocities and are readily deposited to leaf surfaces and plant canopies (Hanson and Lindberg, 1991). Gaseous N pollutants are also taken up through stomatal pores followed by their dissolution in the apoplast. This process is controlled by the degree of stomatal aperture and by gas concentrations in the sub-stomatal cavity (Massad et al., 2010). Additionally, HNO_3 , due to its reactivity with cuticular waxes, may be transported into the leaf interior via transcuticular transport (Bytnerowicz et al., 1999; Padgett et al., 2009). Nitrogen dioxide (NO_2), and especially nitric oxide (NO), are less water soluble than NH_3 and HNO_3 and their deposition fluxes to vegetation are thought to be controlled chiefly by stomatal uptake (Saxe, 1986; Raivonen et al., 2009). For NH_3 , the difference between

* Corresponding authors.

E-mail addresses: abytnerowicz@fs.fed.us (A. Bytnerowicz), mfenn@fs.fed.us (M.E. Fenn).

concentrations in ambient air and the stomatal cavity determines the NH_3 compensation point and direction of the NH_3 flux. When ambient concentrations of NH_3 are higher than in the stomatal cavity, plants act as a sink, and when this gradient is reversed, plants function as a source (Massad et al., 2010; Raivonen et al., 2009).

While other gaseous N compounds, such as peroxyacetyl nitrate (PAN), may also contribute to atmospheric N inputs (Zhang et al., 2009), most of N dry deposition is caused by NH_3 , HNO_3 , NO, and NO_2 as well as surface deposition of particulate nitrate (NO_3^-) and ammonium (NH_4^+) (Hanson and Lindberg, 1991).

Reliable, fine-scaled, and time-specific information on N deposition is essential for understanding its potential effects on ecosystems. However, current approaches used to accomplish this goal in arid and semi-arid zones are inadequate, mainly due to high uncertainty in estimates of dry deposition fluxes. The CMAQ (Community Multi-scale Air Quality) modeling system is the most commonly used in the United States to estimate N deposition. CMAQ has been used at larger (regional) scales with a typical resolution of 36×36 km, and more recently at 12×12 km for the U.S. (<http://www.epa.gov/AMD/Research/RIA/cmaq.html>). CMAQ has also been run at a finer resolution of 4×4 km in California (Fenn et al., 2010; Tonnesen et al., 2007). However, even the finer resolution simulated deposition results are often not adequate for the landscape-level spatial and temporal detail of N deposition information required for understanding potential ecological impacts. Simulated deposition models provide useful outputs for broad-scale studies or analyses, but are inadequate for site-specific or more focused ecosystem response studies. These limitations also apply to the new hybrid TDEP model (Schwede and Lear, 2014) which improves the accuracy of CMAQ in regard to N deposition estimates, especially for chemically-reduced forms, by merging ambient monitoring data with modeled data. Both CMAQ and TDEP are based on the 12×12 km grid scale and thus have limited capacity to simulate orographic effects on deposition in montane regions (Dentener et al., 2014; Hertel et al., 2011).

Throughfall analysis is a widely-used technique, providing a lower-bound estimate of total N deposition to plant canopies (Lovett and Lindberg, 1993). This method has been widely used in mesic conditions giving reasonable estimates of N deposition in forests and other ecosystems. However, in the Mediterranean climate this method has some major limitations related to the unpredictable and often insufficient precipitation required for removal of canopy-intercepted N. Consequently, during prolonged dry periods no throughfall samples are collected until the next precipitation event. It isn't known to what extent throughfall underestimates total N deposition under these conditions (Fenn et al., 2005; Lovett and Lindberg, 1993). In addition, throughfall measurements do not account for N gases taken up by vegetation via stomatal uptake (Draaijers et al., 1997) or by other canopy retention mechanisms (Lovett and Lindberg, 1993).

In estimates of dry N deposition to uniform vegetation canopies, such as lowland forests and forest plantations, micrometeorological methodologies, such as eddy correlation, aerodynamic gradient method, eddy accumulation or mass balance techniques, have been widely used (Fowler et al., 2009). However, use of such methods for extended periods or over large areas is impractical because of their complexity and instrumental requirements (Baldocchi et al., 1988). In addition, these methodologies cannot be applied in complex topography with non-uniform vegetation coverage. For such conditions inferential methods have been used to evaluate dry deposition fluxes of various elements important to ecosystems (Hanson and Lindberg, 1991; Lovett, 1994). In this approach fluxes are determined as the product of concentration and the deposition velocity of a given gaseous compound (Baldocchi et al., 1988).

Passive samplers based on diffusion of gases to the collecting media provide valuable pollutant concentration information needed for inferential estimates of N dry deposition at the landscape level (Bytnerowicz et al., 2000; Krupa and Legge, 2000). Determinations of NO, NO_x and NH_3 concentrations across the landscape have been successfully conducted using passive samplers in California and other parts of the country (Bytnerowicz et al., 1999; Roadman et al., 2003). Passive samplers for HNO_3 (Bytnerowicz et al., 2005), have been used in recent monitoring campaigns in remote areas of California, Alaska, and northern Alberta (Bytnerowicz et al., 2010).

In the inferential approach for estimating N fluxes, it is important to use reliable values for conductance (leaf, branch level) or deposition velocity (canopy level) for the major dry-deposited compounds. These values for specific N gases are available in the literature and are mainly based on various micrometeorological studies (Hanson and Lindberg, 1991; Zhang et al., 2003, 2009). Branch rinsing techniques have been used for removal of the surface deposited ions and their vegetation fluxes (Lovett and Lindberg, 1984; Bytnerowicz et al., 1987; Hanson and Lindberg, 1991; Watanabe et al., 2008). These methods cannot distinguish sources of the surface-deposited NO_3^- (HNO_3 or particulate NO_3^-), nor NH_4^+ (NH_3 or particulate NH_4^+) (Dasch, 1989) and may underestimate deposition to foliar surfaces due to the trans-cuticular uptake or translocation processes of the deposited chemical species (Garten and Hanson, 1990). However, despite these deficiencies the branch-rinsing method may be very useful for development of in-canopy deposition models (Hanson and Lindberg, 1991). These include an inferential method developed for mixed conifer forest stands in southern California to determine surface fluxes and also internal uptake of major N gases (Bytnerowicz et al., 1999). Consequently, research presented here is a further refinement and improvement of this approach, applicable to the landscape level. With this approach, gaseous concentrations of reactive N are measured with passive samplers across a landscape-scale monitoring network. Atmospheric N deposition is calculated within a GIS platform using: time-averaged concentrations of NH_3 , NO, NO_2 , and HNO_3 ; empirically-obtained surface deposition conductance and literature-based stomatal conductance values for the key plant species representative of various vegetation types in the study area; and layers of vegetation cover and leaf area index. Others have previously applied passive sampler concentration data for N pollutants in the inferential approach combined with various estimates of particulate and wet N deposition (Allen et al., 2011; Schmitt et al., 2005).

The objectives of the study were: (1) Describe a new approach based on empirical data and a GIS-based inferential platform to estimate atmospheric N deposition to forests and other ecosystems in Mediterranean areas characterized by complex topography; (2) Provide fine-resolution (landscape level) estimates of deposition applicable for understanding their potential biological effects in terrestrial ecosystems; (3) Compare results of the described methodology with other approaches such as the big-leaf inferential model, throughfall and the hybrid TDEP model, and; (4) Evaluate exceedances of critical loads for sensitive indicators of nutrient N deposition.

2. Methods

2.1. Study area

The monitoring network located within the San Bernardino Mountains of southern California consisted of 13 sites in 2002 and 2006 and 17 in 2003–2005. Distribution of the monitoring sites from the 2006 season for which deposition maps were developed is

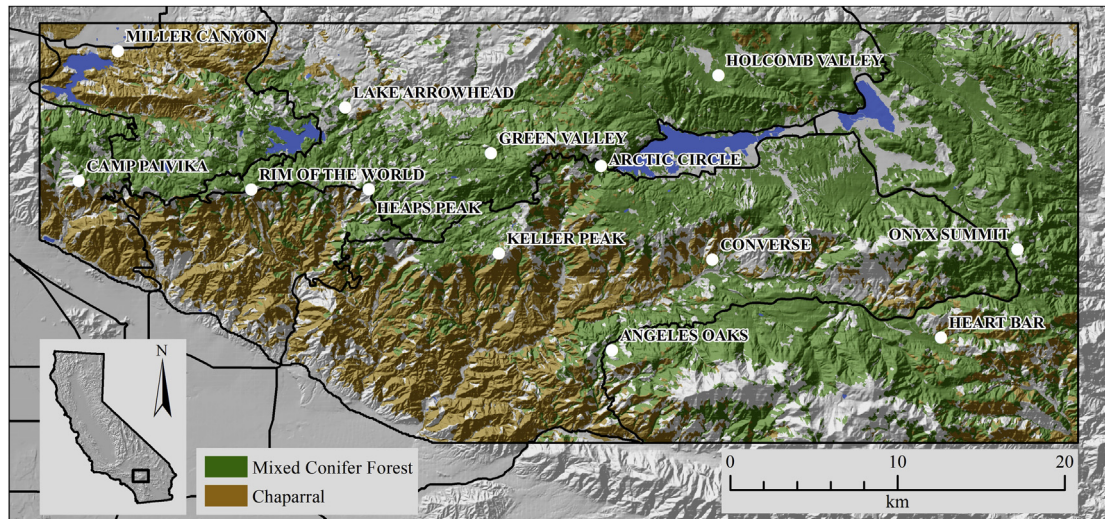


Fig. 1. Air pollution monitoring network in 2006. This map shows the distribution of sites with two major types of ecosystems, chaparral and mixed conifer forest, water bodies, roads, and terrain features.

shown in Fig. 1. The 1406 km² study area is situated in mountainous terrain roughly 80–150 km east of Los Angeles and is oriented east-west along the length of the San Bernardino Mountains.

2.2. Air chemistry

Concentrations of major N gases, HNO₃, NH₃, NO and NO₂ were determined with passive samplers during the 2002–2006 summer seasons. Concentrations of air pollutants were determined as 14 day averages during the June–September summer periods of 2002 through 2006. Ogawa passive samplers were used for NH₃, NO₂ and NO_x monitoring (Roadman et al., 2003; Ogawa USA, Inc., 2006), while the USDA FS passive sampler (Bytnerowicz et al., 2005) was used for HNO₃ monitoring. Passive samplers were placed ~2 m above ground level. Coefficient of variation (CV) as a measure of uncertainty was calculated for each two replicate measurements of NO (8%), NO₂ (8%), NH₃ (9%), and for 3 replicate measurements of HNO₃ (11%) for each monitoring site and period during the 2006 monitoring season.

2.3. Leaf area

Leaf area index (LAI) values were obtained from satellite imagery (NASA, 2010) for periods corresponding with the passive sampler exposures. Leaf area was calculated using LAI values from MODIS imagery and U.S. Forest Service vegetation maps (USFS, 2008). MODIS LAI data were from the Terra satellite with a spatial resolution of 1 km and a temporal resolution of 8 days. They were distributed by the USGS as the MOD15A2 (Collection 5) data product and were available for the entire study period. MODIS values were temporally resampled to weighted values that matched passive sampler exposure periods. Forest Service “Existing Vegetation” data were at a scale of 1:24,000, and were used as fixed values throughout the study period. We calculated leaf area as double the MODIS index value multiplied by the planimetric surface area where the cover was vegetation. An example of LAI for one of the individual periods used in our calculations is presented in Appendix A (Fig. A–1).

All land cover categories used in this study (Appendix B, Table B-1) came from the U.S. Forest Service’s “Existing Vegetation” spatial datasets and were contemporaneous with the beginning of the study period (2002–2003). These categories do not reflect change

in land cover from the large wildfires of late 2003. They include comprehensive spatial and tabular databases for existing vegetation based on imagery and onsite field visits. A total of 38 cover type classes represented forest and non-forest types. Eighteen forest types were based on classification of the Society of American Foresters (SAF, 1980) and cover an area of 81,661 ha. The twenty non-forest types were based on classification of the Society for Range Management (SRM, 1994) and cover 58,996 ha.

2.4. Estimates of atmospheric N dry deposition by the empirical inferential method (EIM)

The EIM approach described here is based on general principles of inferential methods (Hanson and Lindberg, 1991). It is a refinement of a method developed for mixed conifer stands in the San Bernardino Mountains (Bytnerowicz et al., 1999) to accommodate the semi-arid conditions (scarce summer precipitation) of southern California forests. A major feature of this new method is utilizing ambient concentrations of inorganic gaseous drivers of N deposition (obtained from a network of passive samplers), their empirically derived (branch level) conductance for surface deposition and literature-based stomatal conductance. Calculations were done for individual 14-day air pollution monitoring periods during the June–September periods of each year. Dry deposition of inorganic N was calculated as a sum of surface deposition of NH₄⁺ and NO₃⁻ and stomatal uptake of NH₃, NO, NO₂ and HNO₃.

For surface deposition estimates, empirical deposition conductance (K) for NH₄⁺ (resulting from deposition of NH₃ + particulate NH₄⁺) and for NO₃⁻ (resulting from deposition of HNO₃ + particulate NO₃⁻) were calculated according to the formula:

$$K_{\text{NH}_4^+} = F_{\text{NH}_3 + \text{NH}_4^+} / C_{\text{NH}_3} \quad (1)$$

$$K_{\text{NO}_3^-} = F_{\text{HNO}_3 + \text{NO}_3^-} / C_{\text{HNO}_3} \quad (2)$$

where:

$F_{\text{NH}_3 + \text{NH}_4^+}$: NH₃ + NH₄⁺ surface flux to branches

C_{NH_3} : ambient concentration of NH₃

$F_{\text{HNO}_3 + \text{NO}_3^-}$: HNO₃ + NO₃⁻ surface flux to branches

C_{HNO_3} : ambient concentration of HNO₃

Foliar surface conductance values for NH_4^+ and NO_3^- were calculated based only on ambient NH_3 and HNO_3 because no data on concentration of ambient particulate NH_4^+ or NO_3^- were available for the network. This approach was justified because NH_3 and HNO_3 dominate NH_4^+ and NO_3^- surface deposition in California forests (Bytnerowicz and Fenn, 1996). Our estimates of surface conductance values were based on branch rinsing experiments for major tree species conducted in the San Bernardino Mountains (SBM) using a methodology developed for this Mediterranean ecosystem (Bytnerowicz et al., 1987). For ponderosa pine (*Pinus ponderosa* Dougl. Ex Laws.), white fir (*Abies concolor* [Gord. & Glend.] Lindl. ex Hildebr.) and California black oak (*Quercus kelloggii* Newb.), average deposition conductances for 4 vertical layers of mixed conifer canopy measured in summer 1993 at Barton Flats, a moderately polluted site in the SBM, were used (Bytnerowicz et al., 1999). For hoaryleaf ceanothus (*Ceanothus crassifolius*), determinations were made at the highly polluted site in the San Gabriel Mountains of southern California in summer 1985 (Bytnerowicz et al., 1987). For pinyon pine (*P. monophylla* Torr. & Frem.), K values were obtained at Joshua Tree National Park during the 2002–2005 summer seasons (Bytnerowicz, unpublished data, 2005). These K values were also applied to species with similar leaf morphology in other vegetation classes for which empirical data were not available. It was assumed that surface deposition was occurring during the entire time (day and night). The K values for various vegetation categories are shown in Appendix B, Table B-2. For missing cover types predicted deposition velocity values for dry conditions were applied (Zhang et al., 2003).

Surface deposition (F_{surface}) was calculated for each ~14 day period according to the formula:

$$F_{\text{surface}} = c \times \text{LAI} \times K \quad (3)$$

In which:

- c concentration of HNO_3 or NH_3 ($\mu\text{g m}^{-3}$)
- LAI leaf area index
- K deposition conductance for NO_3^- or NH_4^+ (cm s^{-1})

Stomatal uptake values of reactive N gases for various vegetation categories were calculated based on summer-season average conductance (c_s) for H_2O vapor of key tree and shrub species in forest ecosystems of the San Bernardino and Sierra Nevada Mountains available from the literature. These values were converted to stomatal conductance for NH_3 , NO, NO_2 and HNO_3 according to Graham's law of molecular diffusion (Massman, 1998) by multiplying c_s for H_2O by 1.029, 0.775, 0.626 and 0.534, respectively. In our calculations it was assumed that stomatal uptake was occurring only during daylight hours. The calculated summer-season average values for daytime c_s for the reactive N gases for various vegetation categories are presented in Appendix B, Table B-3.

Stomatal uptake (F_{stomatal}) was calculated for daylight hours of each ~14 day period according to the formula:

$$F_{\text{stomatal}} = c \times \text{LAI} \times c_s \quad (4)$$

In which:

- C concentration of NH_3 , NO, NO_2 or HNO_3 ($\mu\text{g m}^{-3}$)
- LAI leaf area index
- c_s stomatal conductance for NH_3 , NO, NO_2 or HNO_3 (cm s^{-1})

Summer-time atmospheric dry N deposition was calculated as the sum of all components (surface deposition of NO_3^- and NH_4^+ and

stomatal uptake of NH_3 , NO, NO_2 and HNO_3) for all exposure periods.

The NH_3 compensation points for all the SBM monitoring sites during summer 2006 were calculated following various methodologies available in the literature. A method based on summertime daylight air temperature (K) and N deposition ($\text{kg N ha}^{-1} \text{ yr}^{-1}$) was selected as most appropriate for the SBM (Massad et al., 2010). A detailed description of the different approaches used and calculation results are presented in Appendix C.

Annual deposition estimates of total N deposition were obtained from CMAQ model output (Tonnesen et al., 2007). The CMAQ model output used here is the total wet and dry deposition of reduced (NH_3 , NH_4^+) and oxidized (NO, NO_2 , NO_3^- , N_2O_5 , HNO_3 , HONO, and PAN) forms of nitrogen. The spatial resolution for simulated deposition was on a 4×4 km grid with a temporal resolution of one month. These data were produced with CMAQ version 4.4 using the Western Regional Air Partnership (WRAP) 2002 emissions datasets, and meteorological data from the National Center for Atmospheric Research (NCAR)/Penn State mesoscale Model (MM5) (Tonnesen et al., 2007). CMAQ summer dry deposition was compared with CMAQ annual total wet and dry deposition at 1550 point locations (centers of the 1×1 km MODIS LAI cells) across the full rectangular extent of the study area to provide a summer/annual ratio of 0.436. This value was used throughout this study for extrapolation of the EIM summer dry deposition values to annual values of total N deposition used for evaluation of critical loads (CL) exceedances.

2.5. GIS platform

Nitrogen deposition was estimated as the sum of canopy surface accumulation and its internal accumulation through stomatal uptake. These calculations were performed within the GIS platform containing various layers of data (details are provided in Appendix D).

2.6. Comparison with dry deposition calculated using the big-leaf inferential model

Dry deposition fluxes of three gaseous N species (HNO_3 , NH_3 and NO_2) were also estimated using the big-leaf inferential model. Nitric oxide was not included in the deposition budget considering its very low deposition velocities and potential emissions from soils (Zhang et al., 2002). Fluxes of the three N species were calculated as a product of their respective air concentrations and dry deposition velocities (V_d) at a 14-day time resolution, equivalent to the exposure periods for the passive samplers. The bi-weekly V_d values were obtained by averaging daily ones, which were calculated using the big-leaf model of Zhang et al. (2003). Two major modifications were made to the original model for this application. One modification was the LAI data in the model. The monitoring sites considered in the present study were mostly forested with 8 day resolution LAI available. To take advantage of this LAI data set, the model was modified to handle new landcover types, i.e., the original Society of American Foresters categories and associated LAI values were directly used in the model with other model parameters remaining the same. Another modification was to set the in-canopy aerodynamic resistance to a zero value considering that the tree densities surrounding the study sites were much lower than those in eastern North America where the original model had been developed and evaluated. Sensitivity tests suggested that the default in-canopy aerodynamic resistances in the original model were too large for low density forests. The V_d calculations were performed for all landcover categories within a 2 km radius surrounding each monitoring site, and the area-weighted V_d values were used for flux calculations. Meteorological data at the

monitoring sites were not collected; as an alternative, forecasted surface-layer meteorology data from the Canadian weather forecast model, which was archived for dry deposition studies since the late 1990s (Brook et al., 1999), was used for calculating V_d .

2.7. Comparison with throughfall deposition measurements

Throughfall samples were collected with “passive” throughfall collectors based on a mixed bed (cation and anion resin) ion exchange resin (IER) column (Fenn and Poth, 2004; Fenn et al., 2009). The IER columns were filled with pre-rinsed Amberlite™ IRN 150 Mixed Bed analytical grade ion exchange resin beads. Precipitation or throughfall samples were collected by a polyethylene funnel or snow tube and channeled through the resin column, where ions were retained by the ion exchange resin. The IER columns for the summer exposures were installed in May and changed out in October resulting in winter exposures from October to May. After the field exposure periods the IER columns were extracted with 2N KCl, and NO_3^- and NH_4^+ concentrations in the extracts were determined colorimetrically (Technicon TRAACS autoanalyzer). Atmospheric deposition fluxes were determined by extrapolating from the area of the collector funnel opening and the amounts of N that was extracted from the IER columns. Values from the winter and summer exposure periods were summed to determine annual throughfall N deposition. Throughfall samples were collected from 2002 to 2005.

2.8. Uncertainty analysis

To assess the uncertainty of deposition estimates we used a Monte Carlo based approach for one representative time period of high deposition, August 24 – September 6, 2006, with HNO_3 chosen as the main source of N deposition. Monte Carlo approaches allowed us to quantify overall uncertainty and partition uncertainty across the dominant components of deposition. To calculate uncertainty we generated 1000 realizations of N deposition for the entire SBM domain (kg N) using a randomly generated normal variable with the data specific mean and standard deviation. We implemented this randomization for the dominant sources of uncertainty: atmospheric concentration (c), leaf area index (LAI), and deposition conductance (K) individually and for all sources combined. For atmospheric concentration, the coefficient of variance (CV) for replicate measurements of HNO_3 were used (7.7%). For LAI, the standard deviation for each estimate was included in the MODIS LAI data product on a pixel-by-pixel basis and was used directly. For deposition conductance, the CV values of each estimate were directly calculated from experimentally measured variation. Each Monte Carlo realization was implemented at the smallest spatial unit of analysis (patch or patch portion as described in Section 3.4).

Two different applications of Monte Carlo were made. The first considers the study area as a whole; results are provided in tabular form and present ranges of total deposition in the study area arising from each source of uncertainty. The second calculates each source of uncertainty at the individual spatial unit of analysis level (patch or patch fragment) and produces a value appropriate for presenting the distribution of uncertainty as a map.

For the study area as a whole, it was necessary to calculate random values twice, once using only random values greater than baseline (non-random input) values and once for values less than baseline. This was done for each source of uncertainty. In each realization, deposited N was calculated once for every patch and then all these values were summed. This was repeated 1000 times providing a set of values for total deposited N. The first time, only random values from the normal distribution that were lower than

the baseline input were used. The second time, random values greater than input were used. These two sets of results provided ranges of lower and upper total deposition for each source of uncertainty which were compared with baseline results.

For analysis at the spatial unit scale, results of 1000 realizations for each unit provided a range of total deposited N values. Each spatial unit's range was analyzed in turn to provide a 95th percentile value as a measure of its uncertainty. These unit results were then aggregated on an area-weighted basis into the landcover patch comprising them. The resulting patch-level uncertainty values were converted to kg N ha^{-1} for a display of their distribution across the study area. The uncertainty presented in the map series was the range from the 47.5th percentile below to 47.5th percentile above the baseline value for the patch.

2.9. Evaluation of critical loads

The detailed maps of summertime dry N deposition were extrapolated to annual deposition fluxes based on comparisons with CMAQ estimates for the study area. Annual deposition maps allow for mapped estimates of CL exceedances for sensitive ecological indicators for nutrient N deposition. Exceedances of empirical critical loads (CL) for nutrient N deposition were determined for the predominant ecosystems in this study: (a) chaparral (consisting of ceanothus mixed chaparral, coastal sage scrub and chamise chaparral cover types); and (b) mixed conifer forests (consisting of white fir, Sierra Nevada mixed conifer, interior ponderosa pine, Jeffrey pine, Pacific Douglas fir, Pacific ponderosa pine, and knobcone pine cover types). These are based on observed changes in epiphytic lichen communities (lowest, most conservative CL) and stream nitrate leaching (highest, least conservative CL) among all those developed for these ecosystems (Fenn et al., 2010, 2011; Pardo et al., 2011). In our study, maps of exceedances were developed for the CL values given in Table 1.

2.10. Scope of the study

Calculations of ambient concentrations and deposition were performed for each 14-day air pollution monitoring period from the summers of 2002 through 2006. We present a summary of these results for the entire 2002–2006 duration of the study and detailed results for the 2006 summer season (June 1 through September 30) for individual air pollutant concentrations and components of dry N deposition. We also present uncertainty analysis for the highly-polluted period of August 24 – September 6, 2006 and CL exceedance maps for 2006.

3. Results

3.1. Air chemistry

Gaseous N air pollutants showed a strong spatial concentration gradient during the 2002–2006 summers, with the highest values

Table 1
Annual and summer (June 1 through September 30) critical loads (CL)^a.

Annual CL	Indicator	Summer CL
3.1 $\text{kg N ha}^{-1} \text{ yr}^{-1}$	Lichens, mixed conifers	1.6 $\text{kg N ha}^{-1} \text{ summer}^{-1}$
5.5 $\text{kg N ha}^{-1} \text{ yr}^{-1}$	Lichens, chaparral	2.4 $\text{kg N ha}^{-1} \text{ summer}^{-1}$
14.0 $\text{kg N ha}^{-1} \text{ yr}^{-1}$	Nitrate leaching, chaparral	6.1 $\text{kg N ha}^{-1} \text{ summer}^{-1}$
17.0 $\text{kg N ha}^{-1} \text{ yr}^{-1}$	Nitrate leaching, mixed conifers	7.4 $\text{kg N ha}^{-1} \text{ summer}^{-1}$

^a Annual CL values are from Fenn et al. (2010). Summer CL values are based on the equivalent deposition threshold when only summer-time dry deposition is considered as determined by the EIM approach.

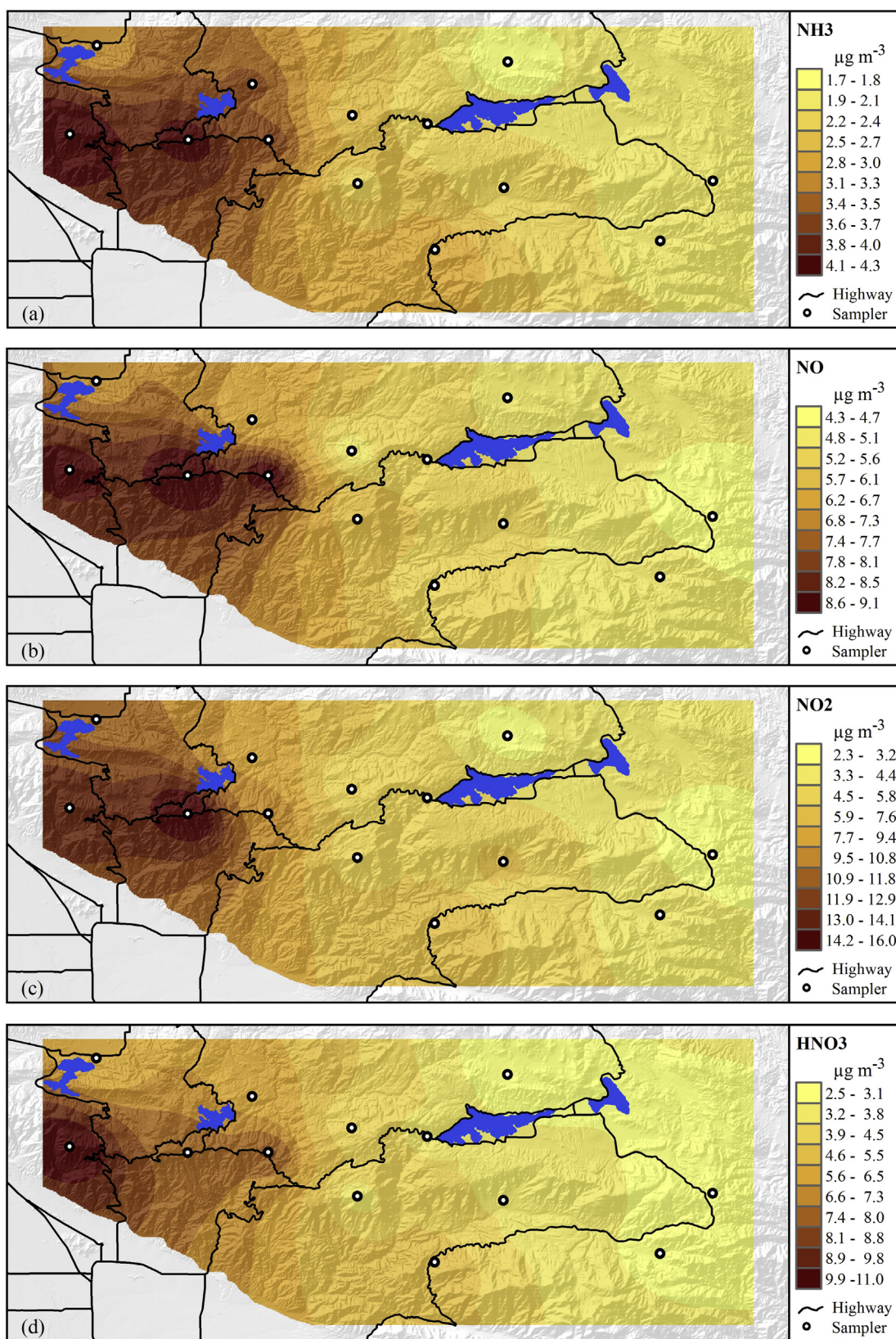


Fig. 2. Spatial distribution of average N gas concentrations in the SBM in summer 2006: (a) NH₃; (b) NO; (c) NO₂; and (d) HNO₃.

Table 2Ranges and averages of air pollutant concentrations in the San Bernardino Mountains during the 2002–2006 summer seasons measured with passive samplers ($\mu\text{g m}^{-3}$).

Year	NH ₃		NO		NO ₂		HNO ₃	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
2002	0.02 – 6.5	2.9	0.7 – 128.6	10.6	0 – 53.8	8.9	0.7 – 10.4	4.4
2003	1.2 – 27.8	5.2	0.2 – 45.7	8.8	1.2 – 33.4	8.4	0.2 – 12.2	2.7
2004	1.4 – 9.0	4.4	0.1 – 10.7	3.2	1.0 – 24.2	6.7	0.8 – 17.5	4.1
2005	0.5 – 9.1	3.2	0.0 – 11.7	4.9	0.3 – 23.3	8.7	0.5 – 15.5	4.4
2006	0.3 – 6.1	2.9	0.3 – 15.6	6.4	1.4 – 18.7	8.0	1.2 – 15.4	5.3

in the western portion of the San Bernardino Mountains and sharply decreasing concentrations eastwards. In summer 2006 the highest levels of pollutants occurred at Camp Paivika (NH₃, NO, HNO₃), Rim of the World (NH₃, NO and NO₂), and Heaps Peak (NO) (Fig. 2). Ranges of pollutant concentrations during the individual 14-day periods for the entire SBM area in 2006 were: NH₃ (0.3–6.1 $\mu\text{g m}^{-3}$); NO (0.3–15.6 $\mu\text{g m}^{-3}$); NO₂ (1.4–18.7 $\mu\text{g m}^{-3}$), and HNO₃ (1.2–15.4 $\mu\text{g m}^{-3}$). Average concentrations for the entire area in 2006 were: NH₃ (2.9 $\mu\text{g m}^{-3}$); NO (6.4 $\mu\text{g m}^{-3}$); NO₂ (8.0 $\mu\text{g m}^{-3}$); and HNO₃ (5.3 $\mu\text{g m}^{-3}$) (Table 2). Ranges and average values of the measured pollutants during all years of the study were generally similar. However, maximal values for NH₃ in 2003 were

higher than in other years; the range and mean values for NO in 2002 and 2003 were higher than those in 2004–2006; and maximal levels of NO₂ were highest in 2003 (Table 2).

3.2. Atmospheric deposition

Spatial distribution of surface deposition of NH₃ + NH₄⁺ and HNO₃ + NO₃⁻ in summer 2006 is presented in Fig. A-2. Both types of deposition showed a strong west-to-east gradient with highest values on mountain ridges in the western portion of the SBM. Deposition of NH₃ and NH₄⁺ sometimes reached values greater than 10 kg N ha⁻¹, but was much lower than that of HNO₃ + NO₃⁻ which

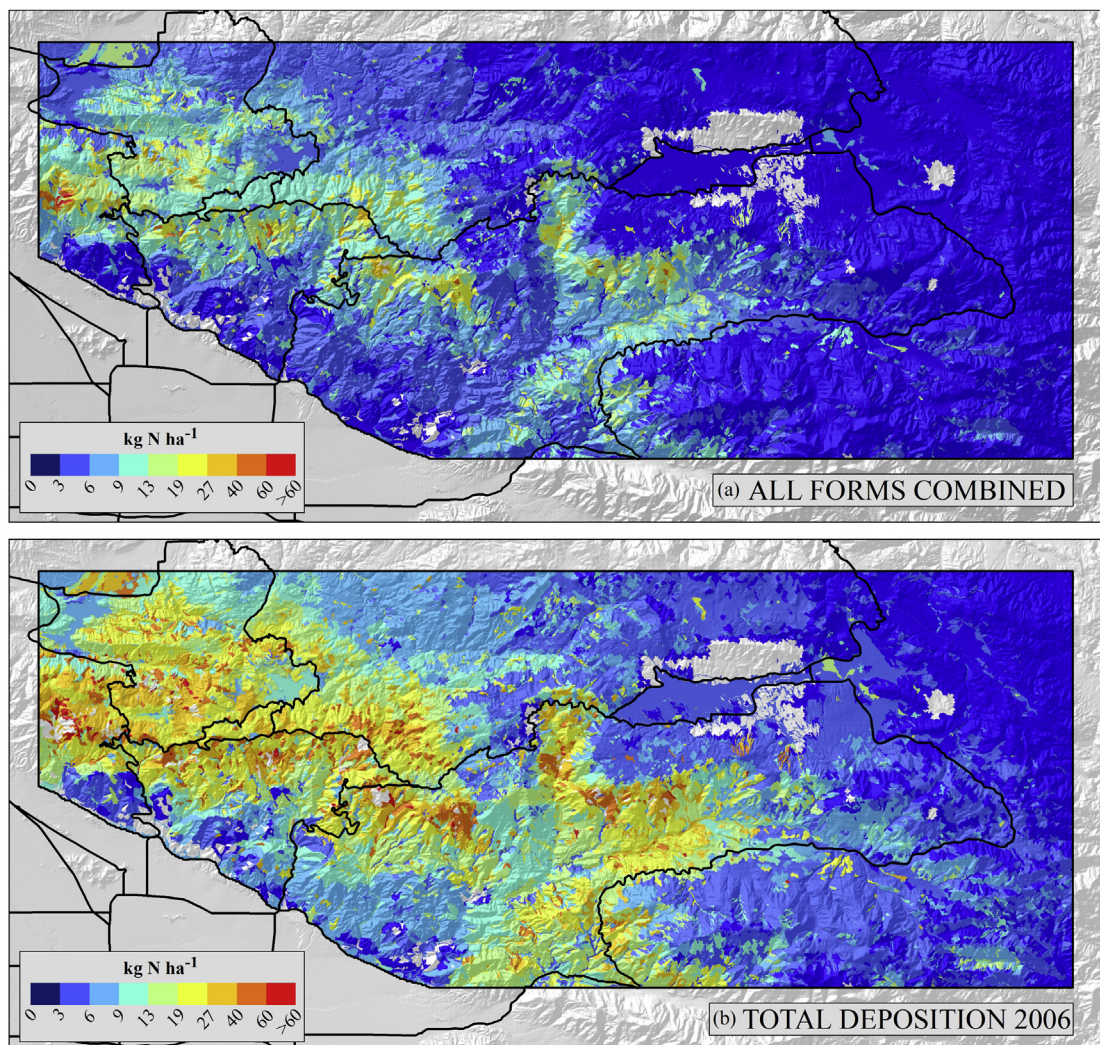


Fig. 3. N deposition in the SBM: (a) dry deposition in summer 2006 estimated by the EIM approach, and (b) annual total deposition (dry and wet) extrapolated from the summertime EIM estimated deposition to the entire year in 2006 based on comparison with CMAQ modeled deposition.

Table 3

Apportionment (%) of N dry deposition for the entire SBM domain in 2006 during the highest pollution 14-day period and entire summer season.

Source	August 24 – September 6	June 1 – September 30
NH ₃ stomatal	15.2	13.9
NO stomatal	10.0	12.5
NO ₂ stomatal	6.5	8.1
HNO ₃ stomatal	3.6	3.6
NH ₄ ⁺ surface	20.1	18.1
NO ₃ ⁻ surface	44.5	43.8
total	100.0	100.0

Table 4

Annual averages for total (dry + wet) and summer dry-deposited inorganic N calculated for the entire SBM domain (kg N ha⁻¹). Annual total N calculations were based on the June–September dry-deposited N: annual total N deposition ratio of 0.436 calculated from the 2002 CMAQ simulations (Tonnesen et al., 2007).

Year	2002	2003	2004	2005	2006
Summer dry-deposition	4.5	5.2	4.4	4.3	5.0
Annual total N	10.2	12.0	10.1	9.8	11.4

over large portions of the western side of the SBM exceeded 17.5 kg N ha⁻¹ (Figs. A-2a and A-2b, respectively). Stomatal uptake during the summer of 2006 also showed a pronounced decrease for all measured gases from west-to-east. However, absolute values of stomatal N uptake were much lower than those for surface deposition. Stomatal uptakes of NH₃ (Fig. A-3a) and NO (Fig. A-3b) were much higher than those of NO₂ (Fig. A-3c) and HNO₃ (Fig. A-3d).

Summer N dry deposition (sum of all combined forms of deposition) is presented in Fig. 3a, while annual total N deposition (dry and wet) based on a comparison with CMAQ is presented in Fig. 3b. Both figures show a strong west-to-east gradient with the highest values exceeding 40 kg N ha⁻¹ for the surface-only, and 60 kg N ha⁻¹ for total dry deposition in the western portion of the SBM. On the low end of the gradient the surface-only and total deposition values were very low, ~1 kg N ha⁻¹ and below 3 kg N ha⁻¹, respectively.

Apportionment of various N deposition components for the most polluted period (August 24 – September 6) and the entire summer 2006 were similar. There was a much higher contribution of surface deposition than deposition as stomatal uptake. Surface deposition of HNO₃ + NO₃⁻ constituted about 44–45% of total deposition, surface deposition of NH₃ + NH₄⁺ about 18–20%, while stomatal uptake of NH₃, the highest among the measured pollutants, was about 14–15% of total deposition (Table 3).

Total annual N deposition (dry + wet) values for the entire SBM domain were extrapolated from the summer EIM-derived dry

deposition values (all formed combined) based on a comparison with CMAQ simulated N deposition for 2002. These results calculated as averages for the entire SBM domain for all years were similar both for total annual (9.8–12.0 kg N ha⁻¹) and summer dry (4.3–5.2 kg N ha⁻¹) N deposition (Table 4).

The annual averages of the EIM 2002–2005 dry + wet N deposition estimates were similar to the IER throughfall analyses for most of the compared sites (Table 5). A comparison of the EIM estimates of dry deposition with those obtained by the big leaf model approach for summer 2006 revealed that values from both models were highly similar at the low-pollution sites (such as Green Valley, Heart Bar, Holcomb Valley, and Onyx Summit), but the EIM method gave deposition values that were about 2–3 fold higher than the big leaf model for the high pollution sites (Camp Paivika, Miller Canyon and Rim of the World). The EIM results for Camp Paivika and Rim of the World also include values with NH₃ stomatal uptake removed since at these two sites the NH₃ compensation points were exceeded (Table 6).

3.3. Exceedance of critical loads

We present exceedance maps for a few selected CL indicators of nutritional effects of N deposition. In 2006, the CL established for changes in lichen communities in chaparral ecosystems (5.5 kg N ha⁻¹ yr⁻¹) were exceeded mostly in the western and northern portions of the study domain, while exceedances for mixed conifer forest (3.1 kg N ha⁻¹ yr⁻¹) covered a much larger area that included large portions of the eastern SBM. The least conservative CL, stream nitrate leaching (14.0 kg N ha⁻¹ yr⁻¹ and 17.0 kg N ha⁻¹ yr⁻¹ for chaparral and mixed conifers, respectively) were exceeded for both ecosystems mostly in the western SBM while in the eastern part of the domain this CL generally was not exceeded (Fig. 4).

3.4. Analysis of uncertainty of predictions

By using a Monte-Carlo based approach we propagated the uncertainty of the dominant components of the N deposition model to the final mapped estimate of total N. In the selected example for HNO₃ surface deposition, uncertainty in ambient concentration measurements contributed minimally to the uncertainty of N deposition estimates. In contrast, uncertainty in the deposition conductance and LAI terms were substantial components of total uncertainty (Appendix B, Table B-4). Uncertainty was not randomly distributed but decreased along the west-east transect for each of the deposition components, with the highest uncertainty caused by surface deposition conductance (Fig. A-4).

Table 5

Comparison of N deposition (kg ha⁻¹) estimates from EIM, throughfall and TDEP for 2002–2005 period.^a

Site	Throughfall (annual)	TDEP ^b (2004 annual)	EIM (surface only) <i>June – September</i>	EIM (surface only) <i>Extrapolated to Annual</i>	EIM (surface & stomatal)	EIM (surface, stomatal and wet)
Angeles Oaks	12.8	10.5	4.3	8.1	8.4	19.3
Camp Paivika	71.1	9.9	10.1	18.9	18.0	41.3
Green Valley	8.7	11.1	2.2	4.1	3.4	7.8
Heaps Peak	36.4	11.3	7.2	13.4	13.2	30.4
Holcomb Valley	6.1	8.1	1.3	2.4	2.2	5.0
Rim of the World ^c	33.4	10.8	8.1	15.3	14.2	32.6
Converse Flats ^d	10.6	10.8	4.0	7.5	7.4	16.9

^a Throughfall fluxes were measured with ion exchange resin samplers (Fenn et al., 2008).

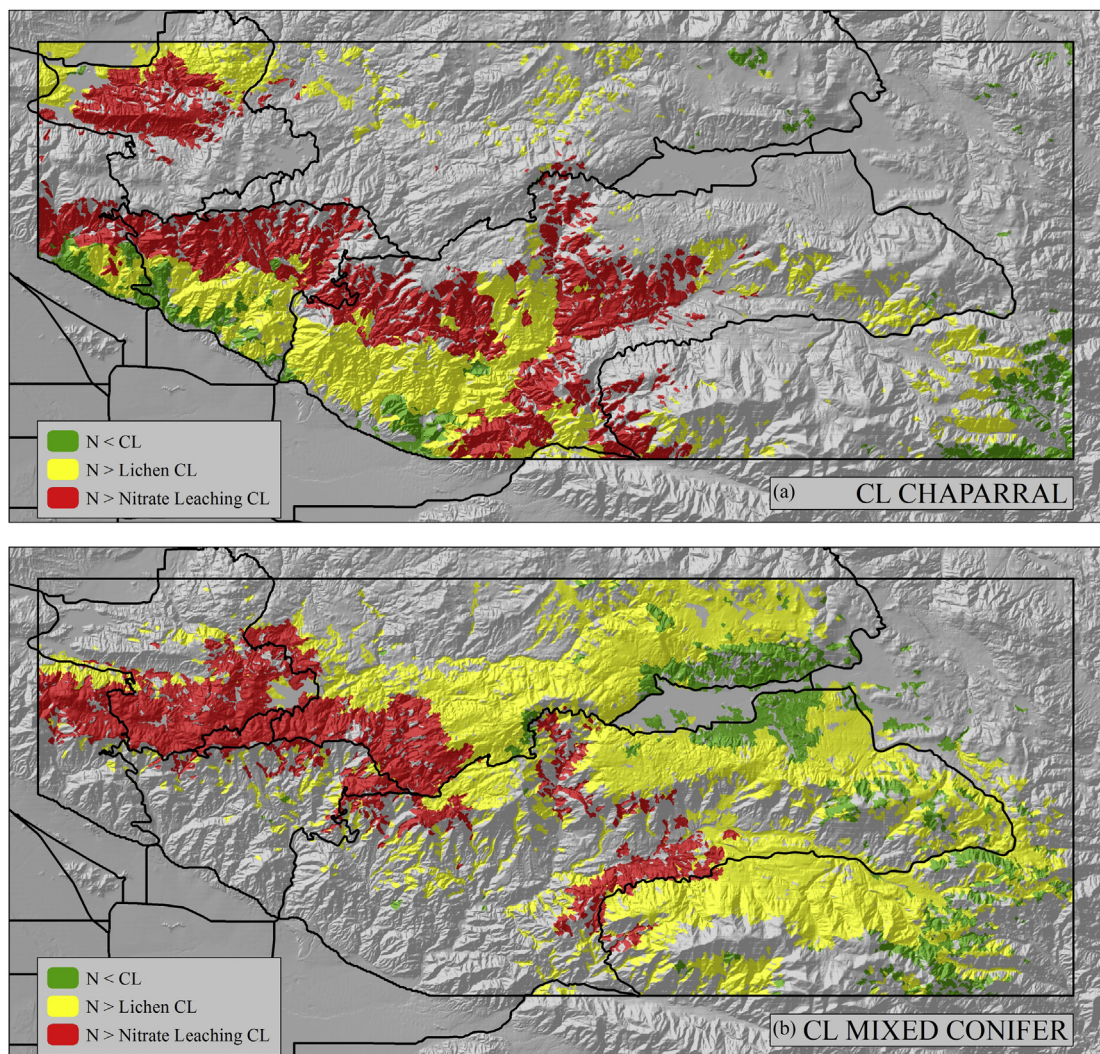
^b Data obtained from <ftp://ftp.epa.gov/castnet/tdep>.

^c Throughfall data was obtained from the nearby Dogwood site.

^d Unpublished data for throughfall.

Table 6Comparison of N dry deposition estimated by the EIM and big-leaf model during summer 2006 (kg N ha^{-1}).^{a,b}

Sampler location	HNO_3		NH_3		NO_2		Combined	
	Big- leaf	EIM	Big- leaf	EIM	Big- leaf	EIM	Big-leaf	EIM
Angeles Oaks	1.9	3.9	1.2	2.9	0.65	0.7	3.8	7.5
Arctic Circle	1.5	2.4	0.7	1.8	0.4	0.35	2.65	4.6
Camp Paivika	3.8	10.6	1.6	5.4 (2.6)	1.2	1.8	6.7	17.9 (15.0)
Converse Flats	1.4	3.3	0.95	2.5	0.6	0.7	3.0	6.4
Green Valley	1.75	1.9	1.0	1.4	0.5	0.2	3.2	3.5
Heaps Peak	2.7	7.0	1.2	4.2	0.9	1.3	4.8	12.4
Heart Bar	1.05	1.0	0.7	0.9	0.4	0.1	2.2	2.0
Holcomb Valley	1.0	0.9	0.5	0.9	0.25	0.1	1.8	1.9
Keller Peak	0.9	2.5	0.7	1.8	0.4	0.3	2.1	4.7
Lake Arrowhead	2.1	3.1	1.2	2.2	0.8	0.6	4.0	5.9
Miller Canyon	1.35	3.2	0.9	3.2	0.8	1.35	3.1	8.0
Onyx Summit	1.2	0.6	0.6	0.6	0.2	0.05	2.1	1.3
Rim of the World	2.4	6.1	1.3	4.1 (2.1)	1.4	1.5	5.1	12.0 (9.6)

^a For this comparison stomatal uptake of NO was not included in the EIM estimates.^b Numbers in parentheses are corrected values with stomatal uptake of NH_3 removed. Camp Paivika and Rim of the World are sites where the NH_3 compensation point was exceeded and vegetation acted as an NH_3 source.**Fig. 4.** Exceedance of N Critical Loads in 2006 for: (a) chaparral; and (b) mixed conifer forests. Exceedances are based on the CL for effects on epiphytic lichen communities and nitrate runoff in streamwater and estimates of total annual N deposition as shown in Fig. 3b.

4. Discussion

4.1. Air quality

Compared with the 1992–1994 measurements performed at Barton Flats, a site in the middle of the SBM, concentrations of HNO_3 increased in 2002–2006 while those of NH_3 , NO and NO_2 were similar (Bytnerowicz et al., 1999; Watson et al., 1999). Generally, concentrations of the N pollutants measured in the SBM were higher than background levels for North American forests: $0.3\text{--}1.0\ \mu\text{g m}^{-3}$ for HNO_3 (Ashbaugh et al., 1991; Bytnerowicz and Fenn, 1996; Legge and Krupa, 1989) and $0.2\text{--}0.5\ \mu\text{g m}^{-3}$ for NH_3 (Bytnerowicz and Fenn, 1996; Langford and Fehsenfeld, 1992; Legge and Krupa, 1989). Ammonia concentrations in the SBM were similar, while HNO_3 values were ~2 fold higher than those on the western slopes of Sequoia National Park (Bytnerowicz et al., 2002). Concentrations of NO and NO_2 in our study were higher than those typically measured in other forests in California (Bytnerowicz and Fenn, 1996; Bytnerowicz et al., 2002). Concentrations of the measured N pollutants showed a sharp west-to-east gradient indicating a strong effect of the Los Angeles Basin source area. These trends held during all individual exposures periods in all study years. Similar to the 1992–1994 study at Barton Flats (Bytnerowicz et al., 1999), levels of the measured pollutants were similar between individual summer exposure periods during the summers from 2002 to 2006. Strong west-to-east gradients of N pollutant concentrations influenced the distribution of N deposition in the SBM. Similar deposition patterns, with very high levels on the western side of the SBM and very low values in their eastern side, were also determined with throughfall measurements (Fenn et al., 2008; Fenn and Poth, 2004; Fenn and Bytnerowicz, 1997).

4.2. Atmospheric deposition

Elevated concentrations of NH_3 and HNO_3 and their high conductance values are the main determinants of high summer N deposition to forests and other ecosystems in the SBM. The other factor are high LAI values for some land cover categories, such as chaparral or mixed conifer forests compared to low-elevation scrub or grasslands, and at the same time the openness of their canopies; similar to edge effects in more closed forests canopies (Weathers et al., 2001). Total N deposition reached values $>60\ \text{kg N ha}^{-1}\ \text{yr}^{-1}$ in the most affected western slopes while the lowest values $<3\ \text{kg N ha}^{-1}\ \text{yr}^{-1}$ were typical in the eastern portion of the range. Average total N deposition for the entire domain during several years of this study was about $9.8\text{--}12.0\ \text{kg N ha}^{-1}\ \text{yr}^{-1}$. Such values compare well with the CMAQ and TDEP estimates for this general area (e.g., TDEP annual deposition in 2004 for the seven sites listed in Table 5 were relatively flat, ranging from 8.1 to $11.3\ \text{kg N ha}^{-1}\ \text{yr}^{-1}$). This agrees with a previous study in which N deposition in the high deposition sites in the San Bernardino Mountains and in the Sierra Nevada was underestimated by CMAQ (Fenn et al., 2010). TDEP grossly underestimates N deposition in the western SBM with values ranging from 10 to $11\ \text{kg N ha}^{-1}\ \text{yr}^{-1}$ for the year 2004 (Table 5). In the region most exposed to N air pollution on the far western end of the SBM the highest annual throughfall deposition is $\sim 70\ \text{kg N ha}^{-1}\ \text{yr}^{-1}$ (Fenn et al., 2008). Results of our estimates confirm that the highest N deposition in the US and California occur on the western slopes of the SBM (Aber et al., 2003; Fenn and Poth, 2004; Fenn et al., 1998, 2008). Most of the N dry deposition (~65%) resulted from deposition $\text{HNO}_3 + \text{NO}_3^-$ and $\text{NH}_3 + \text{NH}_4^+$ to plant surfaces while the stomatal uptake of N gases (~35%) was much lower (Table 3).

Values determined with the EIM compared relatively well with

the big-leaf model for the low deposition sites (Table 6). Differences increased at the high deposition sites where much higher deposition fluxes from HNO_3 and NH_3 were determined with the EIM. These differences could be because the estimates of surface deposition of HNO_3 and NH_3 by the big-leaf model were too conservative, or excessively high surface deposition conductance values were used for these pollutants at high deposition areas in the EIM approach. The latter seems unlikely considering that throughfall deposition fluxes were much higher than the EIM values for surface deposition (Table 5). In respect to NH_3 , calculations of its compensation point showed that two sites on the high end of the N pollution gradient, Camp Paivika and Rim of the World, acted as NH_3 sources. While that does not change surface NH_3 deposition, the removal of stomatal NH_3 uptake at those sites resulted in reduced combined N deposition values (Table 6). In regard to the EIM, more complete data on N deposition to foliar surfaces of key plant species typical for the SBM is needed. Such data collected together with ambient concentrations of NH_3 and HNO_3 would allow for calculation of surface deposition conductances for more plant species increasing the accuracy of the model. Similarly, measurements performed throughout the entire dry season (May–October) should allow for more accurate estimates of $F_{\text{HNO}_3 + \text{NO}_3^-}$ and $F_{\text{NH}_3 + \text{NH}_4^+}$ throughout the dry season.

We also found good agreement between the EIM estimates of total annual N deposition and throughfall deposition fluxes in most of the monitoring sites. An exception was the very high deposition value at Camp Paivika determined with the throughfall method (Table 6). This difference can be largely attributed to the frequent fog episodes that occur at the site during favorable conditions and the high concentrations of NO_3^- and NH_4^+ in fogwater at Camp Paivika (Fenn et al., 2000; Fenn and Poth, 2004; Fenn and Bytnerowicz, 1997). Such fogwater deposition dripping from tree canopies is captured by the IER samplers used to collect throughfall. Fogwater deposition is not well characterized by TDEP or by the CMAQ estimates that were used for the extrapolation of the summer EIM results to the annual wet + dry deposition values. Considering that N deposition in fog in the SBM can represent as much as one-third of the total N deposition in some sites (Fenn et al., 2000), the inability of CMAQ to account for this can be an impediment in being able to extrapolate our summer values from the EIM approach to annual total N deposition values. The EIM values for surface deposition fluxes (based on branch rinsing) extrapolated to annual values were much lower than throughfall deposition. This is in large measure likely because throughfall deposition also includes N inputs from wet deposition and fogwater. It is also possible that the EIM surface deposition fluxes are underestimated or that throughfall captured by the IER collectors also included NO_3^- and NH_4^+ leached from the foliar interior, possibly as a result of stomatal uptake of NH_3 , NO , NO_2 , and HNO_3 .

4.3. Exceedance of CL for nutrient N

A number of ecological impacts have been documented in the mixed conifer forest zone in the SBM and in the Sierra Nevada in locations where the respective CL has been exceeded (Fenn et al., 2011). Prominent examples of effects include shifts in functional groups of epiphytic lichens over large portions of the SBM. Where the CL for streamwater nitrate leaching is exceeded, elevated nitrate levels in streams and groundwater reduce the quality of water supplied to local populations (Fenn and Poth, 1999). Communities of ectomycorrhizal fungi and understory vegetation appear to also be affected and fine root biomass of ponderosa pine is strongly reduced, while the trees are more susceptible to bark beetle attack and mortality (Fenn et al., 2011; Grulke et al., 2009). Acidification of chaparral and forest soils in high N deposition regions has also been

documented (Fenn et al., 2011).

4.4. Uncertainties and potential improvements of the method

Uncertainty analysis of complex models allows for improved understanding of scaling transformations and can help evaluate sources of uncertainty across a model (Wu et al., 2005; Jenerette et al., 2009; Arieira et al., 2011). By using a Monte-Carlo based approach we propagated the uncertainty of dominant components of the N deposition model to the final mapped estimate of summer dry N deposition. Uncertainty from atmospheric N pollutant concentration measurements, as shown for HNO_3 , contributed minimally to uncertainty in surface N deposition confirming that performance of the atmospheric sampling network was appropriate for mapping atmospheric N deposition. In contrast, uncertainties caused by the MODIS-derived LAI, surface deposition conductance and stomatal conductance were much higher and similar to each other. The distribution of uncertainty decreased along a strong west-to-east gradient and was related to the magnitude of pollutant concentration and deposition values. Although the LAI uncertainty was high, it was not surprising for the complex mountain terrain and no recommendations for reducing its contribution to the overall uncertainty of our methodology are suggested. A clear outcome from the uncertainty analysis is the need for improved quantification of surface deposition and stomatal conductances. Especially this latter component could vary seasonally with changing phenology and physiological activity of plants, in addition to meteorological conditions (Watanabe et al., 2008; Kirchner et al., 2014). Accordingly, datasets for both types of conductance should be expanded to include updated information for more tree and shrub species and be coordinated with simultaneous air pollution monitoring throughout the summer season. In the future, consideration could also be given to other approaches for calculating stomatal N uptake. In this study we show that results of the EIM compared well with the inferential big-leaf micrometeorological model (Jarvis, 1976). Other approaches such as photosynthesis-based Ball-Berry stomatal conductance models (Anav et al., 2012; Val Martin et al., 2014) could also be considered. However, these models require extensive amounts of meteorological and plant response data (e.g., photosynthetically active solar radiation, air temperature, CO_2 concentrations, relative humidity or soil moisture, and phenology for multiple plant species) and therefore may be impractical for many potential applications. Such data-intensive and complex models would also defeat the purpose of our empirical approach which was designed to be readily applied to a given region without a high data requirement threshold. The data required for those models were unavailable for the SBM making that potential modification of our methodology impossible.

There are many other factors affecting the accuracy of the proposed methodology. The relative contributions of HNO_3 and particulate NO_3^- to the total NO_3^- deposited to plant surfaces, and of NH_3 and particulate NH_4^+ to the total NH_4^+ deposited cannot be determined with branch rinsing. Additionally, no data on ambient particulate NO_3^- and NH_4^+ was available because no simple methods exist for routine measurements of aerosols in contrast to gaseous N pollutants monitored with passive samplers. Therefore we could not calculate fluxes of these aerosol pollutants for individual monitoring locations. The surface deposition conductance values used in this study were based on measurements conducted in the middle of the SBM range, and the assumption was made that these values were representative for the entire study domain. This may be not true for a large portion of the domain resulting in ratios of gaseous to particulate components that differ in time and space. However, we can assume a much higher contribution of gaseous N

pollutants to dry deposition of N to canopy surfaces because HNO_3 and NH_3 have several fold higher conductance values than NO_3^- and NH_4^+ (Hanson and Lindberg, 1991; Petroff et al., 2008), and ambient concentrations of gaseous N pollutants are much higher than for particulate N species as previously determined in the study area (Bytnerowicz et al., 1999).

There are also uncertainties related to uptake of N pollutants at the leaf level. Under certain circumstances, cuticles can act as sources of NH_3 , NO_2 and HNO_3 due to emissions from a drying water layer, re-volatilization of molecules under high leaf temperatures and photochemical reactions at the leaf surface contributing to bi-directional exchange fluxes of these gases (Hanson and Garten, 1992; Hari et al., 2003; Massad et al., 2010). It was also established that at the high end of the N deposition gradient (Camp Paivika and Rim of the World) plants could act as an NH_3 source, and therefore in the western portion of the SBM domain this issue has to be addressed. While in our approach NO stomatal uptake was included in total N deposition (Saxe, 1986; Raivonen et al., 2009), other studies indicate that due to its low water solubility (Hanson and Lindberg, 1991) its contribution to the N flux may be negligible (Hertel et al., 2011; Zhang et al., 2003).

Improvement can also be made in the extrapolation of summer dry deposition values to annual values using CMAQ estimates which were based only on a single year (2002). Clearly, a better understanding of temporal and spatial characteristics of all these factors could significantly improve the accuracy of our methodology.

Generally atmospheric N deposition estimates are characterized by a significantly high level of uncertainty, commonly as large as a factor of ~2 (Flechard et al., 2011; Schwede et al., 2011). Although much lower differences were determined between the EIM, throughfall and big-leaf N deposition estimates, it is recommended that in future applications the EIM be used in conjunction with complementary approaches to assure the most reliable, state-of-science N deposition estimates as suggested by Hanson and Lindberg (1991) and Lovett (1994).

4.5. Advantages of the proposed methodology

Our method offers a new approach for estimating atmospheric N deposition to forests and other ecosystems in Mediterranean environments where wet N deposition constitutes a lower fraction of total atmospheric N inputs. It could also be applied in other dry deposition-dominated ecosystems such as semi-arid shrublands or woodlands. This method is based on simple methodologies for air pollution monitoring (passive samplers) and therefore can be easily applied in complex topography including mountain ranges. Use of passive samplers allows for an establishment of dense monitoring networks that provide air pollution data for generation of reliable surfaces of air pollution distribution. In addition we used experimentally derived conductance values of surface deposition and literature-based stomatal conductance values for native plant species representative of major land use categories in the study area. This approach combined with detailed land cover categories and LAI values within a GIS platform allowed for generation of spatially and temporally-dense deposition fields. Such information is important for detailed understanding of potential effects of N deposition in remote areas, including Class I and II Wilderness areas that require federal protection.

Acknowledgments

Landcover and LAI data are available from the United States Forest Service and National Aeronautics and Space Administration (<https://lpdaac.usgs.gov/>). Gas concentration data are available on

request by contacting the corresponding author. Study was partially funded by the National Science Foundation Biocomplexity Project DEB 04-21530 and DEB 0919006. Ignacio Gonzalez-Fernandez participation was supported by a Fulbright-Schuman grant and the EDEN (CGL2009-13188-C03-02) and FP7 ECLAIRE (EU-FP7-ENV-2011) projects. The authors thank Haiganoush Preisler for

discussion of methodologies used in the project, especially analysis of uncertainty.

Appendix A

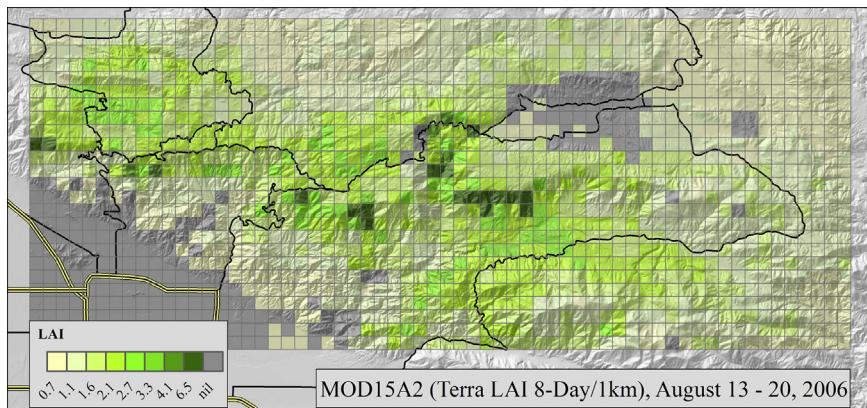


Fig. A-1. Leaf area index during the 8/24–9/6, 2006 period.

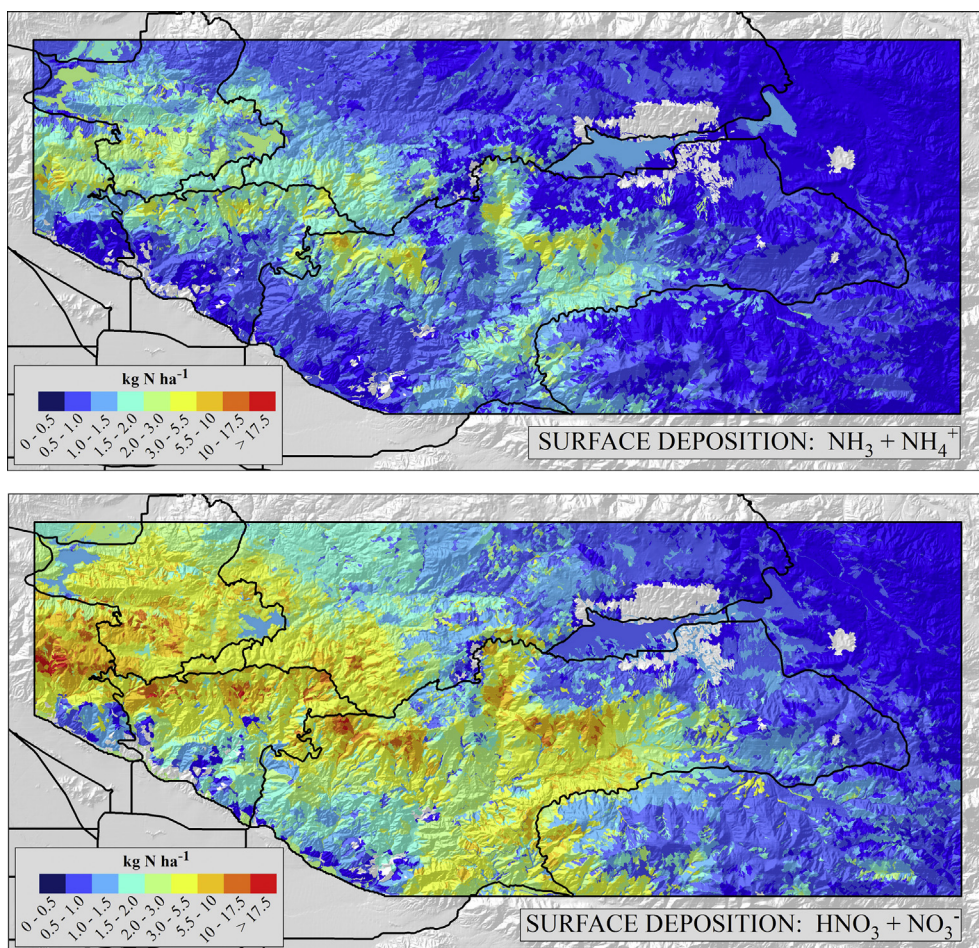


Fig. A-2. Surface N deposition in the SBM in summer 2006: (a) NH_3 and particulate NH_4^+ ; (b) HNO_3 and particulate NO_3^- .

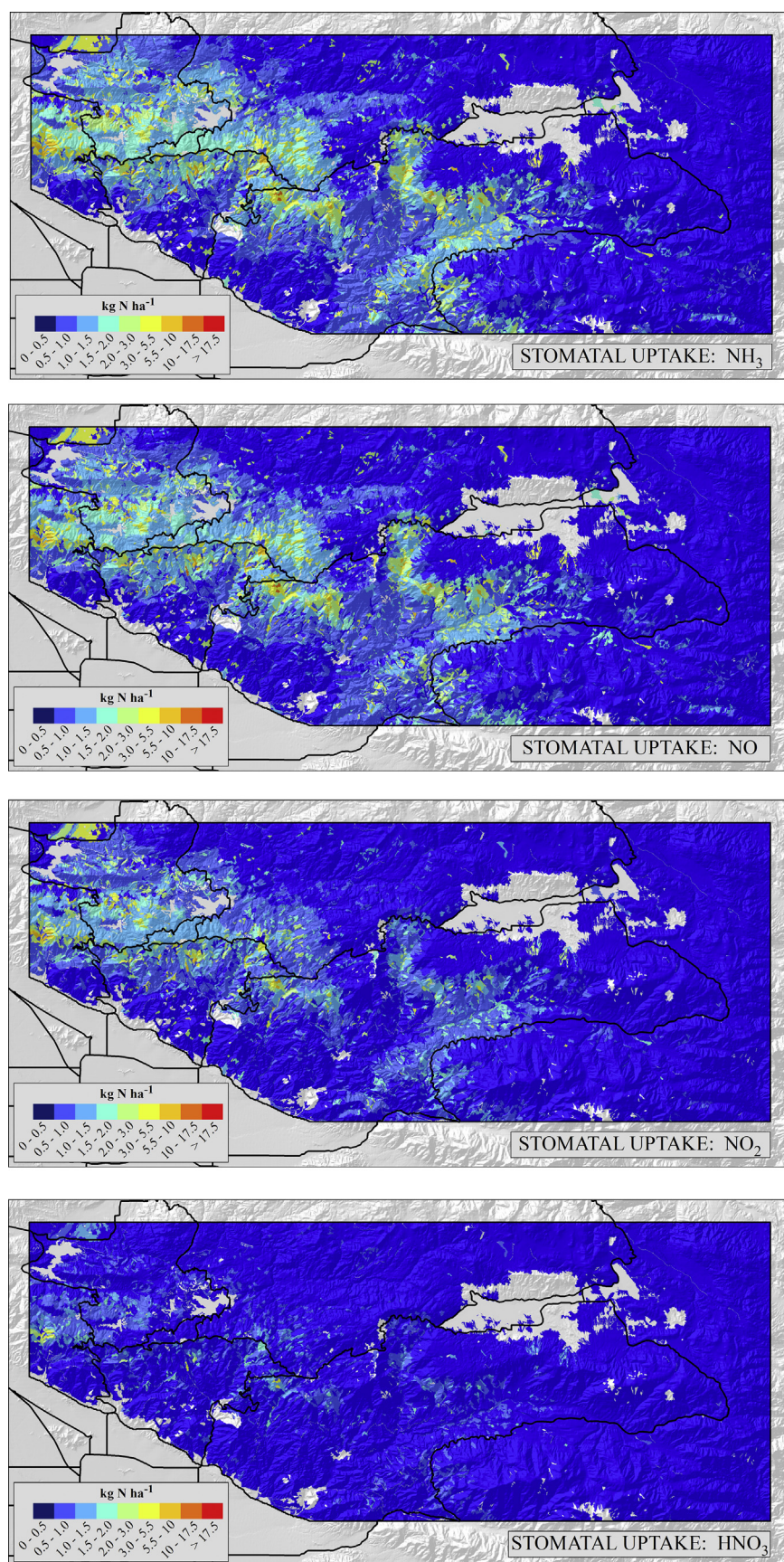


Fig. A-3. Stomatal uptake of N in the SBM in summer 2006: (a) NH_3 ; (b) NO; (c) NO_2 ; (d) HNO_3 .

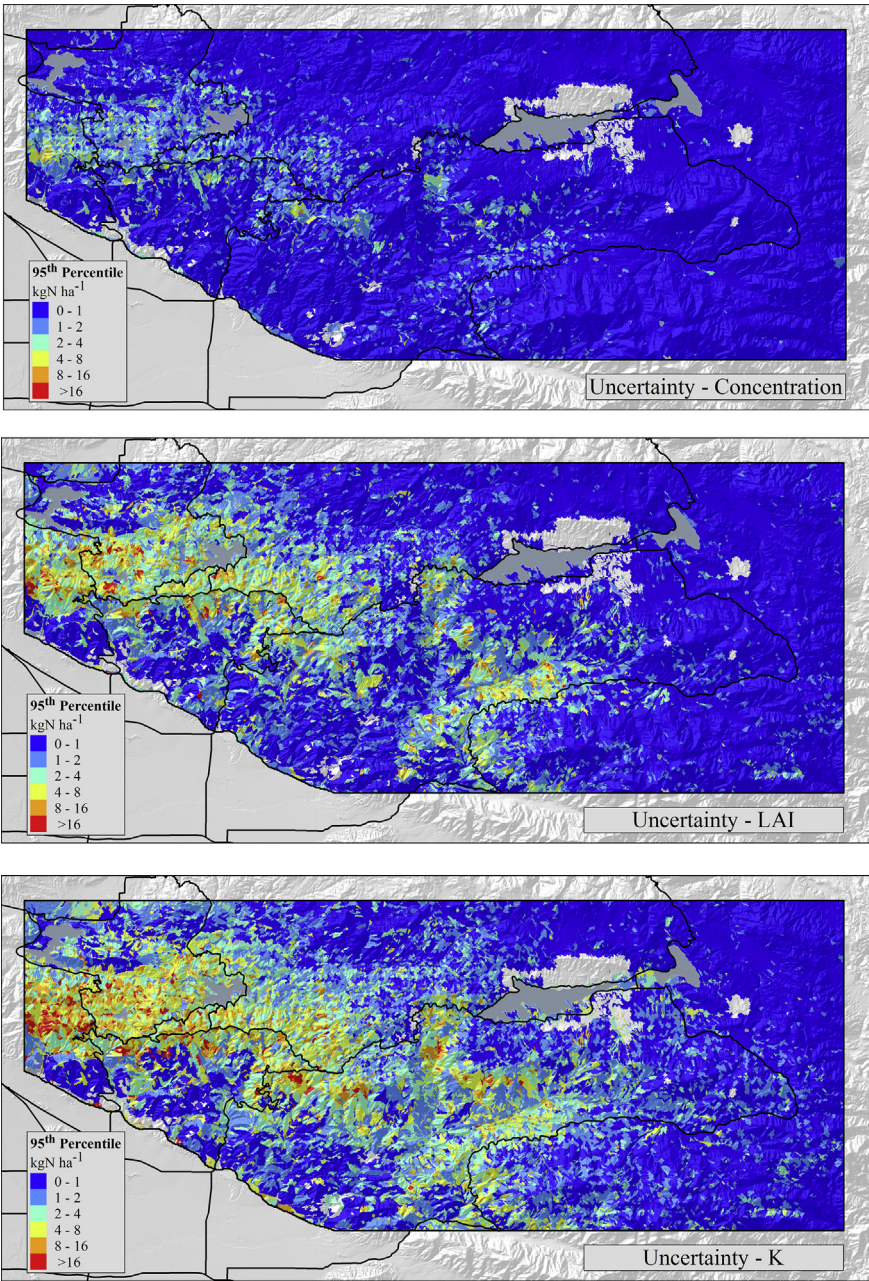


Fig. A-4. Spatial uncertainty of HNO_3 surface deposition predictions related to: (a) ambient HNO_3 concentration; (b) LAI, and (c) conductance (K) for the 8/24–9/6/2006 high-pollution period.

Appendix B. Miscellaneous tables.

Table B-1
Characteristics of cover types in the San Bernardino Mountains.

Cover type	Area (ha)	Designated species for deposition estimates
Agriculture	162	Crops
Alpine Grassland	7	Short grass
Barren Land	1004	Soil
Basin Big Sagebrush	1446	Hoary-leaved ceanothus
Bitterbrush	8	Hoary-leaved ceanothus
Blackbush	919	Hoary-leaved ceanothus
California Black Oak	2943	California black oak
California Coast Live Oak	381	California black oak
California Mixed Subalpine	2786	Ponderosa pine/white fir
Canyon Live Oak	6582	California black oak

Table B-1 (continued)

Cover type	Area (ha)	Designated species for deposition estimates
Ceanothus Mixed Chaparral	3620	Hoary-leaved ceanothus
Chamise Chaparral	1349	Hoary-leaved ceanothus
Chokecherry-Serviceberry-Rose	5725	Hoary-leaved ceanothus
Coastal Sage Scrub	2163	Hoary-leaved ceanothus
Cottonwood - Willow	347	California black oak
Creosote Bush Scrub	837	Creosote bush
Curlleaf Mountain-Mahogany	795	Hoary-leaved ceanothus
Interior Ponderosa Pine	11,714	Ponderosa pine
Jeffrey Pine	4010	Ponderosa pine
Knobcone Pine	475	Ponderosa pine
Limber Pine	268	Ponderosa pine
Lodgepole Pine	3	Ponderosa pine
Mesquite	169	Creosote bush
Montane Meadows	354	Short grass
Montane Shrubland	3757	Hoary-leaved ceanothus
Mountain Big Sagebrush	2068	Hoary-leaved ceanothus
Non-Native Hardwood Forest	36	California black oak
Pacific Douglas-Fir	2710	White fir
Pacific Ponderosa Pine	943	Ponderosa pine
Pinyon – Juniper	16,502	Pinyon pine
Salt Desert Shrub	50	Hoary-leaved ceanothus
Scrub Oak Mixed Chaparral	27,874	Hoary-leaved ceanothus
Sierra Nevada Mixed Conifer	15,327	Ponderosa pine/white fir/California black oak
Urban	3196	Urban
Valley Grassland	1269	Short grass
Water	2362	Water
Western Juniper	250	Pinyon pine
White Fir	16,216	White fir

Table B-2Surface deposition conductances (K) for NO_3^- and NH_4^+ and their coefficients of variation (CV).

Cover type	NH_4^+ (cm s^{-1})	NH_4^+ CV (%)	NO_3^- (cm s^{-1})	NO_3^- CV (%)	Reference
Agriculture	0.515	—	1.300	—	Zhang et al., 2003
Alpine Grassland	0.425	—	1.190	—	Zhang et al., 2003
Barren Land	0.275	—	0.850	—	Zhang et al., 2003
Basin Big Sagebrush	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Bitterbrush	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Blackbush	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
California Black Oak	0.241	26.8	1.446	34.4	Bytnerowicz et al., 1999
California Coast Live Oak	0.241	26.8	1.446	34.4	Bytnerowicz et al., 1999
California Mixed Subalpine	0.134	26.8	0.491	34.4	Bytnerowicz et al., 1999
Canyon Live Oak	0.241	26.8	1.446	34.4	Bytnerowicz et al., 1999
Ceanothus Mixed Chaparral	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Chamise Chaparral	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Chokecherry-Serviceberry-Rose	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Coastal Sage Scrub	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Cottonwood – Willow	0.241	26.8	1.446	34.4	Bytnerowicz et al., 1999
Creosote Bush Scrub	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Curlleaf Mountain-Mahogany	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Interior Ponderosa Pine	0.200	26.8	0.615	34.4	Bytnerowicz et al., 1999
Jeffrey Pine	0.200	26.8	0.615	34.4	Bytnerowicz et al., 1999
Knobcone Pine	0.200	26.8	0.615	34.4	Bytnerowicz et al., 1999
Limber Pine	0.200	26.8	0.615	34.4	Bytnerowicz et al., 1999
Lodgepole Pine	0.200	26.8	0.615	34.4	Bytnerowicz et al., 1999
Mesquite	0.040	—	0.220	—	Bytnerowicz, unpublished
Montane Meadows	0.425	—	1.190	—	Zhang et al., 2003
Montane Shrubland	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Mountain Big Sagebrush	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Non-Native Hardwood Forest	0.241	26.8	1.446	34.4	Bytnerowicz et al., 1999
Pacific Douglas-Fir	0.069	26.8	0.367	34.4	Bytnerowicz et al., 1999
Pacific Ponderosa Pine	0.200	26.8	0.615	34.4	Bytnerowicz et al., 1999
Pinyon – Juniper	0.095	—	0.420	—	Bytnerowicz, unpublished, 2005
Salt Desert Shrub	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Scrub Oak Mixed Chaparral	0.170	27.2	0.940	34.3	Bytnerowicz et al., 1987
Sierra Nevada Mixed Conifer	0.170	26.8	0.809	34.4	Bytnerowicz et al., 1999
Urban	0.270	—	1.455	—	Zhang et al., 2003
Valley Grassland	0.425	—	1.190	—	Zhang et al., 2003
Water	0.770	—	0.885	—	Zhang et al., 2003
Western Juniper	0.095	—	0.420	—	Bytnerowicz, unpublished
White Fir	0.069	26.8	0.367	34.4	Bytnerowicz et al., 1999

Table B-3Stomatal conductance (c_s) for HNO_3 , NH_3 , NO_2 and NO and their coefficients of variation (CV).

Cover type	NH_3 (cm s^{-1})	NO (cm s^{-1})	NO_2 (cm s^{-1})	HNO_3 (cm s^{-1})	CV (%)	Reference
Agriculture	1.286	0.969	0.783	0.668	37.3	Knapp, 1993
Alpine Grassland	1.729	1.302	1.051	0.897	37.3	Knapp, 1993
Barren Land	0.000	0.000	0.000	0.000	—	
Basin Big Sagebrush	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Bitterbrush	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Blackbush	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
California Black Oak	0.562	0.423	0.342	0.292	21.7	Gulke et al., 2005
California Coast Live Oak	0.562	0.423	0.342	0.292	21.7	Gulke et al., 2005
California Mixed Subalpine	0.044	0.033	0.027	0.023	35.5	Gulke et al., 2003
Canyon Live Oak	0.562	0.423	0.342	0.292	21.7	Gulke et al., 2005
Ceanothus Mixed Chaparral	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Chamise Chaparral	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Chokecherry-Serviceberry-Rose	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Coastal Sage Scrub	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Cottonwood – Willow	0.562	0.423	0.342	0.292	21.7	Gulke et al., 2005
Creosote Bush Scrub	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Curlleaf Mountain-Mahogany	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Interior Ponderosa Pine	0.104	0.078	0.063	0.054	30.7	Beyers et al., 1992; Gulke et al., 2003
Jeffrey Pine	0.044	0.033	0.027	0.023	35.5	Gulke et al., 2003
Knobcone Pine	0.104	0.078	0.063	0.054	30.7	Beyers et al., 1992; Gulke et al., 2003
Limber Pine	0.104	0.078	0.063	0.054	30.7	Beyers et al., 1992; Gulke et al., 2003
Lodgepole Pine	0.104	0.078	0.063	0.054	30.7	Beyers et al., 1992; Gulke et al., 2003
Mesquite	0.031	0.023	0.019	0.016	16.5	Roberts, 1982
Montane Meadows	1.729	1.302	1.051	0.897	37.3	Knapp, 1993
Montane Shrubland	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Mountain Big Sagebrush	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Non-Native Hardwood Forest	0.562	0.423	0.342	0.292	21.7	Gulke et al., 2005
Pacific Douglas-Fir	0.080	0.060	0.049	0.042	41.3	Takemoto and Bytnerowicz, 1992
Pacific Ponderosa Pine	0.104	0.078	0.063	0.054	30.7	Beyers et al., 1992; Gulke et al., 2003
Pinyon – Juniper	0.079	0.060	0.049	0.041	34.5	De Lucia et al., 1988, 1989
Salt Desert Shrub	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Scrub Oak Mixed Chaparral	0.221	0.167	0.135	0.115	16.5	Roberts, 1982
Sierra Nevada Mixed Conifer	0.249	0.187	0.151	0.129	31.2	Gulke et al., 2003, 2005; Beyers et al., 1992; Takemoto and Bytnerowicz, 1992
Urban	0.000	0.000	0.000	0.000	—	
Valley Grassland	1.729	1.302	1.051	0.897	37.3	Knapp, 1993
Water	0.000	0.000	0.000	0.000	—	
Western Juniper	0.031	0.023	0.019	0.016	48.3	De Lucia et al., 1988
White Fir	0.080	0.060	0.049	0.042	41.3	Takemoto and Bytnerowicz, 1992

Table B-4Monte Carlo test results of uncertainty for estimates of N deposition caused by HNO_3 during the August 24 to September 6, 2006 period.

	Stomatal uptake			Surface deposition		
	Domain total kg N	kg N/ha	% of baseline	Domain total kg N	kg N/ha	% of baseline
Baseline	2887.1	0.023	100.0	21,665.2	0.163	100.0
<i>Concentration</i>						
Mean minimum	2709.7	0.021	93.9	20,333.9	0.153	93.9
Mean maximum	3064.5	0.024	106.1	22,996.5	0.173	106.1
Baseline +/-	177.4	0.001	6.1	1331.3	0.010	6.1
<i>LAI</i>						
Mean minimum	2336.0	0.019	80.9	17,777.4	0.134	82.1
Mean maximum	3441.0	0.027	119.2	25,570.8	0.193	118.0
Baseline +/-	552.5	0.004	19.1	3896.7	0.029	18.0
<i>K</i>						
Mean minimum	2326.1	0.018	80.6	15,740.8	0.119	72.7
Mean maximum	3449.3	0.027	119.5	27,604.7	0.208	127.4
Baseline +/-	561.6	0.004	19.5	5932.0	0.045	27.4
<i>All 3 Combined</i>						
Mean minimum	1768.1	0.014	61.2	12,123.4	0.091	56.0
Mean maximum	4364.6	0.035	151.2	34,586.9	0.261	159.6
Baseline +/-	1298.3	0.010	45.0	11,231.7	0.085	51.8

Appendix C. NH₃ compensation point estimation methods

The NH₃ compensation points for the monitoring sites in the SBM during summer 2006 have been calculated based on summertime daylight average air temperature (K) and N deposition (kg N ha⁻¹ yr⁻¹) following different methods available in the literature. Daily maximum and minimum air temperatures at the monitoring sites were extracted from PRISM 800 m resolution climate model estimates (Daly et al., 2008). Daylight averages were calculated using T_{max} and T_{min} based on the equation of Goudriaan and Laar (1994). The compensation point is related to leaf temperature, but we used air temperature as a simplification due to the difficulties of estimating leaf temperature.

Total N deposition for each of the monitoring sites was based on an estimate of total dry N deposition for the summer (June 1 – September 30) for the landcover polygon in which the passive samplers were located in 2006. These values were extrapolated to annual deposition based on a comparison of the CMAQ summer dry deposition with CMAQ annual total wet and dry deposition values for 2002 (Tonnesen et al., 2007).

The following methods classified into two groups were used to estimate the NH₃ compensation point:

1. The simplest approaches only consider the influence of temperature on the compensation point (Langford and Fehsenfeld, 1992; Tarnay et al., 2001; Neiryck and Ceulemans, 2008). These approaches vary in their NH₃ emission potential (ratio of NH₄⁺/H⁺ in the leaf interior). The summertime NH₃ emission potential described by Neiryck and Ceulemans (2008) was selected. The average NH₃ compensation point obtained using this method is provided as the 'type 1' estimate in Table C-1.
2. The second method group considers both the effects of temperature and N deposition (Massad et al., 2010). Two different calculations for estimating the compensation point were done using this method, identified as 'type 2'. The first estimates the year-round total N deposition as extrapolated from EIM summertime estimates for 2006, and the second estimates total N deposition as in the first method but excludes stomatal uptake of NH₃. The average NH₃ compensation points obtained are provided as the 'type 2' estimates in Table C-1.

(considers the effect of temperature and N deposition), with and without stomatal uptake of NH₃.

The classification of sites as net NH₃ emitters or sinks depends on the atmospheric NH₃ concentration and whether the method for estimating the NH₃ compensation point considers N deposition or not. The exclusion or inclusion of stomatal uptake of NH₃ into compensation point estimates based on N deposition does not change the classification of a site as a net NH₃ emitter or sink.

Considering that the current consensus on NH₃ deposition and emission to/from vegetation canopies acknowledges that the N status of the vegetation affects the NH₃ compensation point, we chose the type 2 method for estimating the compensation point. In this case, Rim of the World and Camp Paivika (shown in bold font) act as net emitters of NH₃ (their type 2 χ NH₃ values were higher than ambient NH₃ concentrations), thus the stomatal deposition pathway for NH₃ was excluded from estimates of their total N deposition. The analysis was repeated on a monthly basis at these two sites with consistent results. The rest of the sites acted as net sinks for NH₃ and the stomatal deposition pathway contributes to their total N deposition. It is important to bear in mind that the model to estimate the NH₃ compensation point based on total N input is still uncertain. This uncertainty results from insufficient field data from warm and dry climates (Massad et al., 2010).

Appendix D. GIS platform description.

The approach requires calculating a time-series of N mass values for each annual collection season that considers each form of deposition in each patch of land cover and for each sampler measurement period. The information required for each value calculation includes: type of cover, surface area where N accumulates, N gaseous pollutant concentrations, period of pollutant exposure, type of N compound, and a surface or stomatal conductance (K value) specific for each cover type for each measured N compound (Tables B-2 and B-3). Surface area of vegetated types varied with each of the 53 collector periods as a function of the leaf area index value provided by the MODIS data. Gas concentration levels were provided by the passive samplers and varied each period. Pollutant exposure periods were continuous for calculation of surface deposition of NH₄⁺ and NO₃⁻ calculated for HNO₃ and NH₃, respec-

Table C-1

Variables considered per site, measured NH₃ concentration, the average of estimated NH₃ compensation points type 1 χ NH₃ and the estimated compensation point of type 2 method with and without stomatal uptake of NH₃.^a

Site	T (K)	N dep (kg N ha ⁻¹ yr ⁻¹)	NH ₃ (μg m ⁻³)	Type 1 χ NH ₃ (μg m ⁻³)	Type 2 χ NH ₃ ^b (μg m ⁻³)	Type 2 χ NH ₃ ^c (μg m ⁻³)
Angeles Oaks	294.4	15.7	2.97	2.76	1.54	1.37
Heart Bar	292.8	6.9	1.87	2.31	1.00	1.00
Converse	296.2	8.3	2.24	3.41	1.50	1.49
Keller Peak	293.6	13.9	2.15	2.52	1.29	1.20
Onyx Summit	290.8	2.1	1.80	1.81	0.77	0.77
Rim of the World	295.4	49.3	4.24	3.10	24.83	13.87
Heaps Peak	294.4	19.4	3.58	2.78	1.95	1.75
Camp Paivika	297.8	60.9	4.17	4.09	67.66	38.61
Arctic Circle	293.8	11.6	2.21	2.58	1.21	1.17
Green Valley	293.6	5.6	2.65	2.53	1.09	1.09
Lake Arrowhead	296.5	14.7	3.74	3.52	1.87	1.72
Holcomb Valley	292.8	4.8	1.56	2.30	0.99	0.99
Miller Canyon	300.7	12.3	3.11	5.65	2.72	2.60

^a Sites shown in bold font act as net emitters of NH₃.

^b Total N.

^c Excludes stomatal uptake of NH₃.

Table C-1 specifies the variables considered per site: measured NH₃ concentration, the average of estimated NH₃ compensation points (type 1 χ NH₃ —considers only the effect of temperature), and the estimated compensation point based on the type 2 method

tively. However, calculations were limited to daylight hours for foliar uptake of NH₃, NO, NO₂ and HNO₃ via stomata. The value for daylight hours was set as the average for the period of June 1 through September 30 in San Bernardino, California (13.571).

The basics of the N mass calculations can be portrayed for each gaseous compound as:

$$\begin{aligned} \text{N mass per polygon per period} &= \text{deposition conductance} \\ & * \text{gas concentration} * \text{days in period} * \text{exposure time per day} \\ & * \text{N proportion of compound molecular weight} * \text{surface area.} \end{aligned} \quad (\text{D-1})$$

To accomplish this, two spatial relations between three contributing spatial datasets are required: (1) between land cover and LAI values, and (2) between land cover and the gas concentration. The first establishes a relationship between each patch and the discrete 1 km² areas (cells) that provides time-series LAI values. Where a patch straddled more than one LAI cell, the patch was split into portions with each resulting patch fragment in its related cell. Gaseous pollutant concentration values were tied to the same geography of cells as the LAI values and so were spatially related to land cover in the same manner. Pollutant concentration values were provided at 13–17 point locations within the study area. This number of locations provides an inadequate statistical basis for Kriging so Inverse Distance Weighting (IDW) was employed to predict concentration values throughout. Pollutant distribution maps were developed with the Geostatistical Analyst, extension of Arc-GIS software (ESRI, Redlands, CA). All IDW calculations used a power setting of 2 for an inverse distance squared interpolation and were based on the eight nearest passive sampler locations within a slightly elliptical neighborhood. This neighborhood was oriented with long axis at 115° azimuth and parallel to the southwest edge of the mountains. Eight sampler locations were used in all calculations. Locations outside the elliptical neighborhood were used if all eight locations were not within the neighborhood. Gas concentration estimates were calculated for all N forms in all sampling periods at a resolution of 60 m. The value at the center of each cell was used as the value for the entire cell area.

All spatial and non-spatial data were assembled into related tables and values were calculated using Python scripts. The resulting deposition values were aggregated from the fragmented patch portions distributed across different LAI cells back to the original configuration of land cover patch areas. These aggregated values were used for displaying various deposition distributions and calculating critical loads.

Spatial analyses, data storage, data processing, and cartography were carried out primarily with ESRI's ArcGIS software packages. Parameter values were extracted from spatial data and stored in tabular format within an ArcGIS 9.3.1 file geodatabase (ESRI, 2009). All data extraction and final processing were scripted and run under Python 2.5.1. ArcGIS 10.0 Geostatistical Analyst and Python 2.6.5 (ESRI, 2010) were used exclusively for production of gaseous pollutant concentration prediction surfaces. The MODIS Reprojection Tool version 4.0 (USGS, 2008) was used to convert LAI data from their standard distribution format.

References

- Aber, J.D., Goodale, C.L., Ollinger, S.V., Smith, M.L., Magill, A.H., Martin, M.E., Hallett, R.A., Stoddard, J.L., 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *BioScience* 53, 375–389.
- Allen, A.G., Machado, C.M.D., Cardoso, A.A., 2011. Measurements and modeling of reactive nitrogen deposition in southeast Brazil. *Environ. Pollut.* 159, 1190–1197.
- Anav, A., Menut, L., Khvorostyanov, D., Viovy, N., 2012. A comparison of two canopy conductance parameterizations to quantify the interactions between surface ozone and vegetation over Europe. *J. Geophys. Res. Biogeosci.* 117 (G03027) <http://dx.doi.org/10.1029/2012JG001976>.
- Arieira, J., Karssenber, D., de Jong, S.M., Addink, E.A., Couto, E.G., Nunes da Cunha, C., Skoien, J.O., 2011. Integrating field sampling, geostatistics and remote sensing to map wetland vegetation in the Pantanal, Brazil. *Biogeosciences* 8, 667–686.
- Ashbaugh, L.L., Chow, J.C., Watson, J.D., 1991. Atmospheric acidity data quality and measurement characteristics for California's acid deposition monitoring program. In: Presented at 84th Annual Meeting and Exhibition of the Air & Waste Management Association, Vancouver, BC, June 16–21.
- Baldocchi, D.D., Hicks, B.B., Meyers, T.P., 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. *Ecology* 69, 1331–1340.
- Beyers, J.L., Riechers, G.H., Temple, P.J., 1992. Effects of long-term ozone exposure and drought on the photosynthetic capacity of ponderosa pine (*Pinus ponderosa* Laws.). *New Phytol.* 122, 81–90.
- Brook, J.R., Zhang, L., Franco, D., Padro, J., 1999. Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part I. Model development. *Atmos. Environ.* 33, 5037–5052.
- Bytnerowicz, A., Fenn, M.E., 1996. Nitrogen deposition in California forests: a review. *Environ. Pollut.* 92, 127–146.
- Bytnerowicz, A., Miller, P.R., Olszyk, D.M., 1987. Dry deposition of nitrates, sulfates and ammonium to a *Ceanothus crassifolius* canopy and surrogate surface. *Atmos. Environ.* 21, 1749–1757.
- Bytnerowicz, A., Fenn, M.E., Miller, P., Arbaugh, M., 1999. Wet and dry pollutant deposition to the mixed conifer forest. In: Miller, P.R., McBride, J. (Eds.), *Oxidant Air Pollution Impacts in the Montane Forests of Southern California: the San Bernardino Mountains Case Study*, Ecological Series, vol. 134. Springer, New York, pp. 235–269.
- Bytnerowicz, A., Carroll, J.J., Takemoto, B.K., Miller, P.R., Fenn, M.E., Musselman, R.C., 2000. Distribution and transport of air pollutants to vulnerable California ecosystems. In: Scow, K.M., Fogg, G.E., Hinton, D.E., Johnson, M.L. (Eds.), *Integrated Assessment of Ecosystem Health*. Lewis Publishers, Boca Raton, pp. 93–118.
- Bytnerowicz, A., Tausz, M., Alonso, R., Jones, D., Johnson, R., Grulke, N., 2002. Summer-time distribution of air pollutants in Sequoia National Park, California. *Environ. Pollut.* 118, 187–203.
- Bytnerowicz, A., Sanz, M.J., Arbaugh, M.J., Padgett, P.E., Jones, D.P., Davila, A., 2005. Passive sampler for monitoring ambient nitric acid (HNO₃) and nitrous acid (HNO₂) concentrations. *Atmos. Environ.* 39, 2655–2660.
- Bytnerowicz, A., Fraczek, W., Schilling, S., Alexander, D., 2010. Spatial and temporal distribution of ambient nitric acid and ammonia in the Athabasca Oil Sands Region. *J. Limnol.* 69 (Suppl. 1), 11–21.
- Daly, C., Halbleib, M., Smith, J.L., Gibson, W.P., Doggett, M.K., Taylor, G.H., Curtis, J., Pasteris, P.P., 2008. Physiographically sensitive mapping of climatological temperature and precipitation across the conterminous United States. *Int. J. Clim.* 28, 2031–2064.
- Dasch, J.M., 1989. Dry deposition of sulfur dioxide or nitric acid to oak, elm and pine leaves. *Environ. Pollut.* 59, 1–6.
- De Lucia, E.H., Schlesinger, W.H., Billings, W.D., 1988. Water relations and the maintenance of Sierran conifers on hydrothermally altered rock. *Ecology* 69, 303–311.
- De Lucia, E.H., Schlesinger, W.H., Billings, W.D., 1989. Edaphic limitations to growth and photosynthesis in Sierran and Great Basin vegetation. *Oecologia* 78, 184–190.
- Dentener, F., Vet, R., Dennis, R.L., Du, E., Kulshrestha, U.C., Galy-Lacaux, C., 2014. Progress in monitoring and modelling estimates of nitrogen deposition at local, regional and global scales (Chapter 2). In: Sutton, M.A., Mason, K.E., Sheppard, L.J., Sverdrup, H., Haeuber, R., Hicks, W.K. (Eds.), *Nitrogen Deposition, Critical Loads and Biodiversity* (Proceedings of the International Nitrogen Initiative Workshop, Linking Experts of the Convention of Long-range Transboundary Air Pollution and the Convention on Biological Diversity). Springer, Dordrecht, The Netherlands, pp. 7–22, 564 pp.
- Draaijers, G.P.J., Erismann, J.W., Van Leeuwen, N.F.M., Römer, F.G., Te Winkel, B.H., Veltkamp, A.C., Vermeulen, A.T., Wyers, G.P., 1997. The impact of canopy exchange on differences observed between atmospheric deposition and throughfall fluxes. *Atmos. Environ.* 31, 387–397.
- ESRI, 2009. ArcGIS 9.3.1. Environmental Systems Research Institute, Redlands California.
- ESRI, 2010. ArcGIS 10.0. Environmental Systems Research Institute, Redlands California.
- Fenn, M.E., Bytnerowicz, A., 1997. Summer throughfall and winter deposition in the San Bernardino mountains of southern California. *Atmos. Environ.* 31, 673–683.
- Fenn, M.E., Poth, M.A., 1999. Temporal and spatial trends in streamwater nitrate concentrations in the San Bernardino Mountains, southern California. *J. Environ. Qual.* 28, 822–836.
- Fenn, M.E., Poth, M.A., 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: a field test in the San Bernardino Mountains. *J. Environ. Qual.* 33, 2007–2014.
- Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F., Stottlenmyer, R., 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecol. Applic.* 8, 706–733.
- Fenn, M.E., Poth, M.A., Schilling, S.L., Grainger, D.B., 2000. Throughfall and fog deposition of nitrogen and sulfur at an N-limited and N-saturated site in the San Bernardino Mountains, southern California. *Can. J. For. Res.* 30, 1476–1488.
- Fenn, M.E., Poth, M.A., Terry, J.D., Blubaugh, T.J., 2005. Nitrogen mineralization and nitrification in a mixed conifer forest in southern California: controlling factors, fluxes, and nitrogen fertilization response at a high and low nitrogen deposition site. *Can. J. For. Res.* 35, 1464–1486.
- Fenn, M.E., Jovan, S., Yuan, F., Geiser, L., Meixner, T., Gimeno, B.S., 2008. Empirical

- and simulated critical loads for nitrogen deposition in California mixed conifer forests. *Environ. Pollut.* 155, 492–511.
- Fenn, M.E., Sickman, J.O., Bytnerowicz, A., Clow, D.W., Molotch, N.P., Pleim, J.E., Tonnesen, G.S., Weathers, K.C., Padgett, P.E., Campbell, D.H., 2009. Methods for measuring atmospheric nitrogen deposition inputs in arid and montane ecosystems of western North America. In: Legge, A.H. (Ed.), *Developments in Environmental Science, Air Quality and Ecological Impacts: Relating Sources to Effects*, vol. 9. Elsevier, Amsterdam, pp. 179–228.
- Fenn, M.E., Allen, E.B., Weiss, S.B., Jovan, S., Geiser, L., Tonnesen, G.S., Johnson, R.F., Rao, L.E., Gimeno, B.S., Yuan, F., Meixner, T., Bytnerowicz, A., 2010. Nitrogen critical loads and management alternatives for N-impacted ecosystems in California. *J. Environ. Manag.* 91, 2404–2423.
- Fenn, M.E., Allen, E.B., Geiser, L.H., 2011. Mediterranean California (Chapter 13). In: Pardo, L.H., Robin-Abbott, M.J., Driscoll, C.T. (Eds.), *Assessment of Nitrogen Deposition Effects and Empirical Critical Loads of Nitrogen for Ecoregions of the United States*. Gen. Tech. Rep. NRS-80. Department of Agriculture, Forest Service, Northern Research Station, Newtown Square, PA: U.S., pp. 143–169, 291 pp.
- Flechar, C.R., Nemitz, E., Smith, R.L., Fowler, D., Vermeulen, A.T., Bleeker, A., Erisman, J.W., Simpson, D., Zhang, L., Tang, Y.S., Sutton, M.A., 2011. Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network. *Atmos. Chem. Phys.* 11, 2703–2728.
- Fowler, D., Pilegaard, K., Sutton, M.A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J.K., Granier, C., Neftel, A., Isaksen, I.S.A., Laj, P., Maione, M., Monks, P.S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechar, C., Tuovinen, J.P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T.N., Ro-Poulsen, H., Cellier, P., Cape, J.N., Horváth, L., Loreto, F., Niinemets, Ü., Palmer, P.I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M.W., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M.C., de Leeuw, G., Flossman, A., Chaumerliac, N., Erisman, J.W., 2009. Atmospheric composition change: ecosystems–Atmosphere interactions. *Atmos. Environ.* 43, 5193–5267.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The nitrogen cascade. *BioScience* 53, 341–356.
- Garten, C.T., Hanson, P.J., 1990. Foliar retention of 15N-nitrate and 15N-ammonium by red maples (*Acer rubrum*) and white oak (*Quercus alba*) leaves from simulated rain. *Environ. Exp. Bot.* 30, 333–342.
- Goudriaan, J., Laar, H.H., 1994. Modeling Potential Crop Growth Processes. Series. In: *Current Issues in Production Ecology*, vol. 2. Springer, 239 pp.
- Greaver, T.L., Sullivan, T.J., Herrick, J.D., Barber, M.C., Baron, J.S., Cosby, B.J., Deerpake, M.E., Dennis, R.L., Dubois, J.J.B., Goodale, C.L., Herlihy, A.T., Lawrence, G.B., Liu, L.L., Lynch, J.A., Novak, K.J., 2012. Ecological effects of nitrogen and sulfur air pollution in the US: what do we know? *Front. Ecol. Environ.* 10, 365–372.
- Gulke, N.E., Johnson, D., Esperanza, A., Jones, D., Nguyen, T., Posch, S., Tausz, M., 2003. Canopy transpiration of Jeffrey pine in mesic and xeric microsites: O₃ uptake and injury response. *Trees* 17, 292–298.
- Gulke, N.E., Dobrowski, W., Mings, P., Fenn, M.E., 2005. California black oak response to nitrogen amendment at a high O₃, nitrogen-saturated site. *Environ. Pollut.* 137, 536–545.
- Gulke, N.E., Minnich, R.A., Paine, T.D., Seybold, S.J., Chavez, D.J., Fenn, M.E., Riggan, P.J., Dunn, A., 2009. Air pollution increases forest susceptibility to wildfires: a case study in the San Bernardino Mountains in southern California. In: Bytnerowicz, A., Arbaugh, M., Riebau, A., et al. (Eds.), *Wildland Fires and Air Pollution*, Developments in Environmental Science, vol. 8. Elsevier, Oxford.
- Hanson, P., Garten, C.T., 1992. Deposition of H¹⁵NO₃ vapour to white oak, red maple and loblolly pine foliage: experimental observations and a generalized model. *New Phytol.* 122, 329–337.
- Hanson, P.J., Lindberg, S.E., 1991. Dry deposition of reactive nitrogen compounds: a review of leaf, canopy and non-foliar measurements. *Atmos. Environ.* 25A, 1615–1634.
- Hari, P., Raivonen, M., Vesala, T., Munger, J.W., Pilegaard, K., Kumala, M., 2003. Ultraviolet light and leaf emission of NO_x. *Nature* 422, 134.
- Hertel, O., Reis, S., Skjoth, C.A., Bleeker, A., Harrison, R., Cape, J.N., Fowler, D., Skiba, U., Simpson, D., Jickells, T., Baker, A., Kumala, M., Gyldenkaene, S., Sorensen, L.L., Erisman, J.W., 2011. Nitrogen processes in the atmosphere. In: The European nitrogen assessment. In: Sutton, M.A., Howard, C.M., Erisman, J.W., et al. (Eds.). Cambridge University Press, pp. 177–207.
- Jarvis, P.G., 1976. The interpretation of the variations in leaf water potential and stomatal conductance found in canopies in the field. *Philos. Trans. B. R. Soc.* 927, 593–610.
- Jenerette, G.D., Scott, R.L., Barron-Gafford, G.A., Huxman, T.E., 2009. Gross primary production variability associated with meteorology, physiology, leaf area, and water supply in contrasting woodland and grassland semiarid riparian ecosystems. *J. Geophys. Res. Biogeosci.* 114, G04010. <http://dx.doi.org/10.1029/2009JG001074>.
- Kirchner, M., Fegg, W., Rommelt, H., Leuchner, M., Ries, L., Zimmerman, R., Michalke, B., Wallasch, M., Maguhn, J., Faus-Kessler, T., Jakobi, G., 2014. Nitrogen deposition along differently exposed slopes in the Bavarian Alps. *Sci. Total Environ.* 470–471, 895–906.
- Knapp, A.K., 1993. Gas exchange dynamics in C3 and C4 grasses: consequences of differences in stomatal conductance. *Ecology* 74, 113–123.
- Krupa, S.V., Legge, A.H., 2000. Passive sampling of ambient, gaseous air pollutants: an assessment from an ecological perspective. *Environ. Pollut.* 107, 31–45.
- Langford, A.O., Fehsenfeld, F.C., 1992. Natural vegetation as a source or sink for atmospheric ammonia: a case study. *Science* 255, 581–583.
- Legge, A.H., Krupa, S.V., 1989. Air quality at a high elevation, remote site in western Canada. In: Olson, R.K., Lefohn, A.S. (Eds.), *Transactions of the Symposium on Effects of Air Pollution on Western Forests*, Anaheim, CA, 29–30 June, 1989. Air and Waste Management Association, Pittsburgh, PA, pp. 193–206.
- Lovett, G.M., 1994. Atmospheric deposition of nutrients and pollutants in North America: an ecological perspective. *Ecol. Appl.* 4, 629–650.
- Lovett, G.M., Lindberg, S.E., 1984. Dry deposition and canopy exchange in a mixed oak forests as determined by analysis of throughfall. *J. Appl. Ecol.* 21, 1013–1027.
- Lovett, G.M., Lindberg, S.E., 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. *Can. J. For. Res.* 23, 1603–1616.
- Massad, R.S., Nemitz, E., Sutton, M.A., 2010. Review and parameterization of bi-directional ammonia exchange between vegetation and the atmosphere. *Atmos. Chem. Phys.* 10, 10359–10386.
- Massman, W.J., 1998. A review of the molecular diffusivities of H₂O, CO₂, CH₄, CO, O₃, SO₂, NH₃, N₂O, O, and NO in air, O₂ and N₂ near STP. *Atmos. Environ.* 32, 1111–1127.
- Neirynck, J., Ceulemans, R., 2008. Bidirectional ammonia exchange above a mixed coniferous forest. *Environ. Pollut.* 154, 424–438.
- NASA, 2010. NASA Land Processes Distributed Active Archive Center (LP DAAC). MODIS 15A2. USGS/Earth Resources Observation and Science (EROS) Center, Sioux Falls, South Dakota.
- Ogawa USA Inc, 2006. NO, NO₂, NO_x and SO₂ Sampling Protocol Using the Ogawa Sampler. Pompano Beach, FL, 30 pp.
- Padgett, P.E., Cook, H., Bytnerowicz, A., Heath, R.L., 2009. Foliar loading and metabolic assimilation of dry deposited nitric acid air pollutants by trees. *J. Environ. Monit.* 11, 75–84.
- Pardo, L.H., Fenn, M.E., Goodale, C.L., Geiser, L.H., Driscoll, C.T., Allen, E.B., Baron, J.S., Bobbink, R., Bowman, W.D., Clark, C.M., Emmett, B., Gilliam, F.S., Greaver, T.L., Hall, S.J., Lilleskov, E.A., Liu, L., Lynch, J.A., Nadelhoffer, K.J., Perakis, S.S., Robin-Abbott, M.J., Stoddard, J.L., Weathers, K.C., Dennis, R.L., 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecol. Appl.* 21, 3049–3082.
- Petroff, A., Mailliat, A., Amielh, M., Anselmet, F., 2008. Aerosol dry deposition on vegetative canopies. Part I: review of present knowledge. *Atmos. Environ.* 42, 3625–3653.
- Raivonen, M., Vesala, T., Pirjola, L., Altimir, N., Keronen, P., Kulmala, M., Hari, P., 2009. Compensation point of NO_x exchange: net result of NO_x consumption and production. *Agric. For. Meteorol.* 149, 1073–1081.
- Roadman, M.J., Scudlark, J.R., Meisinger, J.J., Ullman, W.J., 2003. Validation of Ogawa passive samplers for the determinations of gaseous ammonia concentrations in agricultural settings. *Atmos. Environ.* 37, 2317–2325.
- Roberts, S.W., 1982. Some Recent Aspects and Problems of Chaparral Plant Water Relationships. Gen. Tech. Rep., PSW-58. Pacific Southwest Research Station, USDA Forest Service, Berkeley, CA, pp. 351–357.
- SAF, 1980. In: Eyre, F.H. (Ed.), *Forest Cover Types of the United States and Canada*. Society of American Foresters.
- Saxe, H., 1986. Effects of NO, NO₂ and CO₂ on net photosynthesis, dark respiration and transpiration of pot plants. *New Phytol.* 103, 185–197.
- Schmitt, M., Thöni, L., Waldner, P., Thimonier, A., 2005. Total deposition of nitrogen on Swiss long-term forest ecosystem research (LWF) plots: comparison of the throughfall and the inferential method. *Atmos. Environ.* 39, 1079–1091.
- Schwede, D.B., Lear, G.G., 2014. A novel hybrid approach for estimating total deposition in the United States. *Atmos. Environ.* 92, 207–220.
- Schwede, D.B., Zhang, L., Vet, R., Lear, G., 2011. An intercomparison of the deposition models used in the CASTNET and CAPMoN networks. *Atmos. Environ.* 45, 1337–1346.
- SRM, 1994. Rangeland Cover Types of the United States. In: Shiflet, Thomas N. (Ed.). Society for Range Management, Denver, Colorado.
- Takemoto, B.K., Bytnerowicz, A., 1992. Effects of acidic fog on seedlings of *Pinus ponderosa* and *Abies concolor*: foliar injury, physiological and biochemical responses. *Environ. Pollut.* 79, 235–241.
- Tarnay, L., Gertler, A.W., Blank, R.R., Taylor Jr., G.E., 2001. Preliminary measurements of summer nitric acid and ammonia concentration in the Lake Tahoe Basin Airshed: implications for dry deposition of atmospheric nitrogen. *Environ. Pollut.* 113, 145–153.
- Tonnesen, G., Wang, Z., Omary, M., Chien, C.J., 2007. Assessment of Nitrogen Deposition: Modeling and Habitat Assessment. California Energy Commission, PIER Energy-Related Environmental Research. CEC-500-2005-032.
- USFS, 2008. EvgTile54_03_09_24k_v1 & EvgTile44C_03Part_v2. USDA Forest Service - Pacific Southwest Region - Remote Sensing Lab, McClellan, CA. <http://www.fs.usda.gov/detail/r5/landmanagement/resourcemanagement/?cid=stelprdb5347192>.
- USGS, 2008. MODIS Reprojection Tool (MRT). Version 4.0, February 2008, Land Processes Distributed Active Archive Center.
- Val Martin, M., Heald, C.L., Arnold, S.R., 2014. Coupling dry deposition to vegetation phenology in the community Earth system model: implications for the simulation of surface O₃. *Geophys. Res. Lett.* 41, 2988–2996. <http://dx.doi.org/10.1002/2014GL059651>.
- Watanabe, M., Takamatsu, T., Koshikawa, M.K., Yamamura, S., Inabushi, K., 2008. Dry deposition of acidic air pollutants to tree leaves, determined by a modified leaf-washing technique. *Atmos. Environ.* 42, 7339–7747.
- Watson, J.G., Chow, J.C., Frazier, C.A., Hinsvark, B., Green, M., 1999. Ambient air quality at Barton flats and other California Forests. In: Miller, P.R., McBride, J.

- (Eds.), *Oxidant Air Pollution Impacts in the Montane Forests of Southern California: the San Bernardino Mountains Case Study*, Ecological Series, vol. 134. Springer, New York, pp. 81–105.
- Weathers, K.C., Cadenasso, M.L., Pickett, S.T.A., 2001. Forest edges as nutrient and pollutant concentrators: potential synergism between fragmentation, forest canopies, and the atmosphere. *Conserv. Biol.* 15, 1506–1514.
- Wu, J., Jones, B., Li, H., Loucks, O.L., 2005. *Scaling and Uncertainty Analysis in Ecology: Methods and Applications*. Springer, Dordrecht, The Netherlands.
- Zhang, L., Moran, M.D., Makar, P.A., Brook, J.R., Gong, S.L., 2002. Modelling gaseous dry deposition in AURAMS— a Unified regional air-quality modelling system. *Atmos. Environ.* 36, 537–560.
- Zhang, L., Brook, J.R., Vet, R., 2003. A revised parameterization for gaseous dry deposition in air-quality models. *Atmos. Chem. Phys.* 3, 2067–2082.
- Zhang, L., Vet, R., O'Brien, J.M., Mihele, C., Liang, Z., Wiebe, A., 2009. Dry deposition of individual nitrogen species at eight Canadian rural sites. *J. Geophys. Res. Atmos.* 114, D02301.