Predicting Nitrogen Flux Along a Vertical Canopy Gradient in a Mixed Conifer Forest Stand of the San Bernardino Mountains in California[1]

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Abstract

*A 3-year study of nitrogenous (N) air pollution deposition to ponderosa pine (*Pinus ponderosa *Dougl. ex. Laws.) seedlings along a mature tree vertical canopy gradient was conducted in the mixed conifer forest of the San Bernardino Mountains of southern California. Concentrations of nitric acid vapor (HNO_3), particulate nitrate (NO_3^-), and ammonium (NH_4^+) were measured, as well as dry surface deposition of NO_3^- and NH_4^+. By using this data, along with meteorological information, a series of simple models were developed that predict the vertical gradient of foliage-rinse surface deposition for NO_3^-, NH_4^+, and total N. Individual models for NO_3^- and NH_4^+ were calculated by using deposition data, air concentrations at the top of the canopy, and wind speed. These models explained 80 percent of the variation between deposition values at the lower canopy positions. Examination of model coefficients indicated that the two models were not significantly different, and a single model was developed to estimate total N deposition. This model explained less variation than the individual models (R^2_N = 0.69) but is a simpler description of the system. All models have two parameters (a_0 and a_1) that are estimated by nonlinear regression. Independent data indicates that the a_1 parameter depends only on the rate of decline in wind speed vertically down the canopy. The a_0 parameter reflects the difference between foliage rinse surface deposition at the top of the canopy and that at lower canopy positions. It indicates that about 20 percent less dry surface deposition occurs at lower canopy positions than expected from wind speed alone for all nitrogenous compounds, most likely because decreased turbulence within the canopy results in increased quasi-laminar boundary layer resistance at lower canopy positions.*

Introduction

Dry deposition is one of the major mechanisms of nitrogenous (N) transfer from the atmosphere to plant surfaces in arid California mountains (Bytnerowicz and Fenn 1996, Rundell and Parsons 1977). High dry deposition fluxes of N pollutants have been reported in exposed areas of the San Gabriel and San Bernardino Mountains (Bytnerowicz and others 1987, Fenn and Bytnerowicz 1993), and in lesser amounts in the southern and western portions of the Sierra Nevada Mountains (Bytnerowicz and others 1991).

Foliage rinsing techniques (Bytnerowicz and others 1987, Lindberg and Lovett 1985) have been successfully used for determinations of atmospheric deposition of various ions to trees. The technique is especially valuable in dry climates of southern California where in summer and fall periods precipitation is scarce, which limits collecting throughfall measures of deposition.

Extensive foliage rinse sampling requires considerable time and expense to analyze. Seedlings must be obtained and stored in greenhouses before field exposure. A scaffold tower must be erected at the remote site, and periodic watering and rinsing must be done for groups of seedlings at different tower heights to obtain sufficient information to quantify the vertical deposition profile. This extensive sampling reduces the number of sample locations and times that can be directly measured using this approach.

Expanding limited foliage rinse measurements to larger areas and longer time periods has been accomplished in some systems by using inferential models that have been developed over the last decade (Hicks and Meyers 1988, Meyers and Baldocchi 1988). These models estimate deposition flux (F_d) from air concentration measurements (C) and deposition conductance (K_1) by using air concentrations and micrometeorological information. To use inferential models, aerodynamic transport, boundary layer transport, and physiochemical surface interactions must be estimated for model input. This model approach works best when ecosystems

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have uniform canopy and vegetation and when atmospheric conditions are stable and predictable.

The mixed conifer forest of the San Bernardino Mountains is quite different (*fig. 1*) from these systems. This forest type is comprised of several species including, ponderosa pine (*Pinus ponderosa* Dougl. ex. Laws) or Jeffrey pine (*Pinus jeffreyi* Grev & Balf.) (in transition zones both species are found), sugar pine (*Pinus lambertiana*), white fir (*Abies concolor*), incense cedar (*Calocedrus decurrens*), California black oak (*Quercus kelloggii*), and a herbaceous or shrubby understory. The forest often has a discontinuous canopy that results in increased atmospheric mixing and edge effects that seldom result in a significant vertical air pollutant concentration gradient (Bytnerowicz and others, this volume). However, equal deposition does not occur over the canopy. These conditions reduce the ability to apply inferential models to this system, and can result in excessive estimates of N by inferential models (Taylor and others 1996) compared with empirical estimates.

In this study we measured atmospheric concentrations and foliar deposition in the San Bernardino Mountains to determine relationships between atmospheric concentrations, meteorological factors, and deposition. The primary data consists of annular denuder and foliage-rinse data gathered at several heights on a scaffolding tower erected between the canopies of three trees (Miller and others 1996). Filter pack data (Chow and Watson 1996) that continuously monitored air pollution and meteorology at a location about 5 kilometers from the tower location was used to corroborate the results of the annular denuder data.

Figure 1 — The Barton Flats Tower site in a mixed conifer forest in the San Bernardino Moutnains in southern Califronia photographed aerially to illustrate the diverse canopy structure of the study site. Canopy diameters vary and are interspersed with large open areas. The arrow points to the location of the scaffold tower where data was gathered for this study.

Our goal was to develop a predictive model for foliage rinse flux along a vertical canopy profile that minimizes the number of flux measurements needed to estimate N deposition flux to mature pine canopies. The model developed is intended to reduce the amount of time and expense to determine deposition vertically along the canopy, and enable estimates of total N dry deposition to the forest.

Methods

Modeling and Analysis Data

As part of a multi-disciplinary study (Miller and others 1996), foliar rinse data were gathered to determine the effect of canopy position on deposition of nitrogenous and sulfurous pollutants, to compare deposition to branches of mature trees and seedlings, and to compare deposition to three tree species (ponderosa/Jeffrey pine, white fir, and California black oak). Measurement of nitrate, ammonium, and sulfate deposition to branches of seedlings and mature trees of ponderosa pine at various levels of the canopy were performed during three photochemical smog seasons (1992, 1993 and 1994). Fluxes of NO_3^- and NH_4^+ to branches of ponderosa pine seedlings were determined on a tower located in a stand of mature ponderosa/Jeffrey pines. Four seedlings were located at each of four different levels of the tower (29 m at the top of the canopy; 24 m and 16 m in the middle of the canopy; and 12 m at the canopy bottom).

In the beginning of each collection period branches about 10 cm long were thoroughly rinsed with double deionized water. The branches were re-rinsed at the end of the collection period with about 100 mL of double deionized water and the rinses were collected in 250 mL Nalgene bottles. Bottles were placed on ice, immediately transferred to the laboratory and placed at -18 °C. Concentrations of nitrate were determined with ion chromatography (Dionex 4000i ion chromatograph)[3] and concentrations of ammonium colorimetrically with a Technicon TRAACS Autoanalyzer.

The filter pack dry deposition sampling system (Chow and others 1993) was equipped with an acid-washed PFA (perfluoralkoxy) sampling surface with PFA Teflon-coated Bendix-Sensidyne Model 240 cyclone. Particles and gases were drawn through the Teflon-coated $PM_{2.5}$ inlet at a constant flow rate of 113 l/min. A total of

[3] Mention of trade names or products is for information only and does not imply endorsement by the U.S. Department of Agriculture

62 l/min was drawn through four filter packs simultaneously. In routine operation, air was drawn through the filter pack for NO_2 sampling at a flow rate of 2 l/min and through the remaining three filter packs at a flow rate of 20 l/min apiece. Four additional ports were provided for field blanks that were used to evaluate filter loadings during passive sampling periods and during filter handling.

Daytime (0600 to 1800 PST) and nighttime (1800 to next day 0600 PST) measurements were taken every sixth day between 11/02/91 and 09/28/93 and between 06/01/94 and 08/30/94 for ammonia (NH_3) and nitric acid (HNO_3) gases on absorbing substrates, and ammonium (NH_4+) and nitrate (NO_3-) particulates on filter substrates.

Model Development

Empirical relationships are subject to spurious correlations and relationships, especially when limited numbers of locations and sampling times are available. To reduce this effect, we based our model upon simplified theoretical relationships rather than observed ones. We chose the equilibrium relationship between aerosol and gaseous concentrations as the basis for model formulation:

$$NH_4NO_3 <=> HNO_3 + NH_3$$

If it is assumed that all particulates are deposited as NH_4NO_3, then it can be assumed that:

$$K_{NO3p} = K_{NH4p} = K_{NH4NO3}$$

in which:

K = conductance of N to the plant surface (cm s^{-1})

NO_{3p} = N from particulate NO_3-

NH_{4^+p} = N from particulate NH_4+

Expressing atmospheric concentrations (C) as µg m^{-3} N, then

$$C_{NO3p} = C_{NH4p}$$

These relationships implicitly assume that NH_4+_p deposition to plant surfaces is caused by NH_4+ rather than NH_3. Several studies that have linked diurnal patterns of NH_3 deposition to stomatal aperture (Aneja and others 1986, Hutchinson and others 1972, Rogers and Aneja 1980) found that little NH_4+ is absorbed cuticularly (Van Hove and others 1987), and that NH_3 deposition contributes little to surface deposition (Van Hove and others 1987).

The equilibrium relationship is also only valid if the majority of particulates are in the range of 0.1 µm to 2 µm diameter. Wall and others (1988) found nitrate and ammonium particulate sizes vary between 0.52 µm and about 2.0 µm in a study conducted in Claremont, California. Similar results were found by Lundgren and others (1979) in a study conducted in Riverside, California, which is about 50 km from our study site.

Both the annular denuder and filter pack data were used to examine model assumptions. High significant correlations were found by both systems between particulate NO_3^- and particulate NH_4^+ concentrations (r=0.92 and r=0.93, respectively) during foliage wash periods, indicating that the majority of particulates were in the form of NH_4NO_3. Average NO_3^- concentrations were 1.80 mg N/m^3 ± 0.98 mg N/m^3 compared to 1.98 mg N/m^3 ± 0.74 mg N/m^3 estimated from NH_4^+. The two estimates are not significantly different (paired t-test, p = 0.05).

By using these relationships, flux (F) and atmospheric concentration (C) data can be expressed as:

$$F_{NO3p} = F_{NH4p}$$

and

$$F_{HNO3} = F_{NO3t} - F_{NH4p}$$

in which F is flux (µg N m^{-2} s^{-1}).

Fluxes at lower canopy positions can be estimated for nitrate deposition as:

$$F_{NO3h} = a_0 e[a_1(1- H_h/H_t)](F_{HNO3t} + F_{NO3t}) + e_h$$

for ammonium deposition as:

$$F_{NO3h} = a_0 e[a_1(1- H_h/H_t)](F_{NH4t}) + e_h$$

or for either type of deposition as:

$$F_{Nh} = a_0 e[a_1(1- H_h/H_t)](F_{Nt}) + e_h$$

in which:
h = vertical height along canopy (H)
t = max(h) = top of canopy
F_{Nt} = flux to leaves from either nitrate and nitric acid or ammonium
a_0, a_1 = constant terms estimated from nonlinear regression
e_h = independently and identically Gaussian distributed errors.

The model was fitted with a nonlinear regression procedure, NLIN (SAS 1990), by using the derivative-free multivariate secant method. The starting value of wind speed parameter a_1 = - 1.2 was estimated as:

$$\text{Wind speed} = e[a_1(1- H_t/H_h)],$$

from wind speed information gathered during 1994 at the tower location (Miller and others 1996). A grid search was used to identify a starting value of a_0. Graphical and analytical analyses of residuals were conducted to determine if any model assumptions were violated.

Results

Model results indicate that deposition estimated at the top of the canopy is strongly related to deposition at lower canopy positions for individual ion models (*table* 1). Nonlinear R^2 (analogous but not equal to linear R^2) was high for both pollutants, indicating that conductance for both compounds at lower levels of the canopy is also strongly linked to conductance at the top of the canopy (*figs. 2a, 3a*).

The observed decline in flux is dominated by declines in wind speed from the top to the bottom of the canopy. Neither NO_3^- or NH_4^+ model a_1 parameters were significantly different from a_1 developed from wind speed information. The a_1 parameters from both models are lower than those reported for other systems (Davidson and Wu 1990), indicating that wind speed declines more linearly in this open forest relative to closed canopy forests.

***Table 1** — Model parameters and summary statistics for individual ion and combined ion deposition models.*[1]

Model	n	Mean	Std [2]	a_0	(SE) [3]	a_1	(SE)	RMSE [4]	R^2_N
NO_3^-	33	6.79	0.98	0.761	(0.05)	-1.39	(0.17)	1.03	0.81
NH_4^+	33	6.25	0.77	0.853	(0.05)	-1.04	(0.15)	1.28	0.80
N_{either}	66	6.52	0.88	0.791	(0.04)	-1.26	(0.14)	1.27	0.69

[1] All models use the equation: $F_h = a_0 e[a_1(1-H_t/H_h)](F_t) + e_{hj}$.
All ion values are expressed as mg N/m^2/hr.
[2] Standard deviation.
[3] Standard error.
[4] Root mean square error.

Coefficients were not significantly different (at p = 0.05) for the NO_3^- and NH_4^+ models, indicating that it might be possible to develop a combined model. A single model was parameterized using NO_3^- and NH_4^+ expressed as mg N. Model results indicate that the single model, although marginally poorer for explaining variation, may be a simpler representation of the system. The combined ion model a_1 parameter estimate was nearly identical to that estimated using wind speed information (a_1 = -1.2). Individual model differences (*table 1*) may be due to smaller data sets used in the analysis.

Interpretation of a_0 is more difficult for these models. The parameter reflects a proportional reduction in the estimated foliar deposition at lower canopy positions relative to the canopy top. This constant reduction does not depend on canopy position and is similar to the proportion of total deposition retained on foliage after rinsing or throughfall occurs (Friedland and others 1991, Lovett and Lindberg 1993). Model differences are not, however, the result of canopy retained N; rather, the parameter may reflect an additional resistance to deposition in the canopy not present at the more open areas of the canopy top. Although data is sparse, this resistance may result from reduced turbulence occurring in the canopy interior that results in increased quasi-laminar layer depth and stability, which increases diffusive and interception resistance. Detailed measurements are needed, however, to confirm this interpretation.

Residual distribution was best for the combined model (*figs. 2b, 3b, 4b*). No significant heteroscadisticity or serial correlation was found for the models, nor was there any apparent relationship between canopy position and residual distribution. Analysis of residuals did suggest that individual ion models may overestimate deposition at low air concentrations (*figs. 2b, 3b*). This may be due to reductions in the ion concentrations near the ground caused by reduced atmospheric mixing. This overestimation was lessened in the combined model (*fig. 4b*).

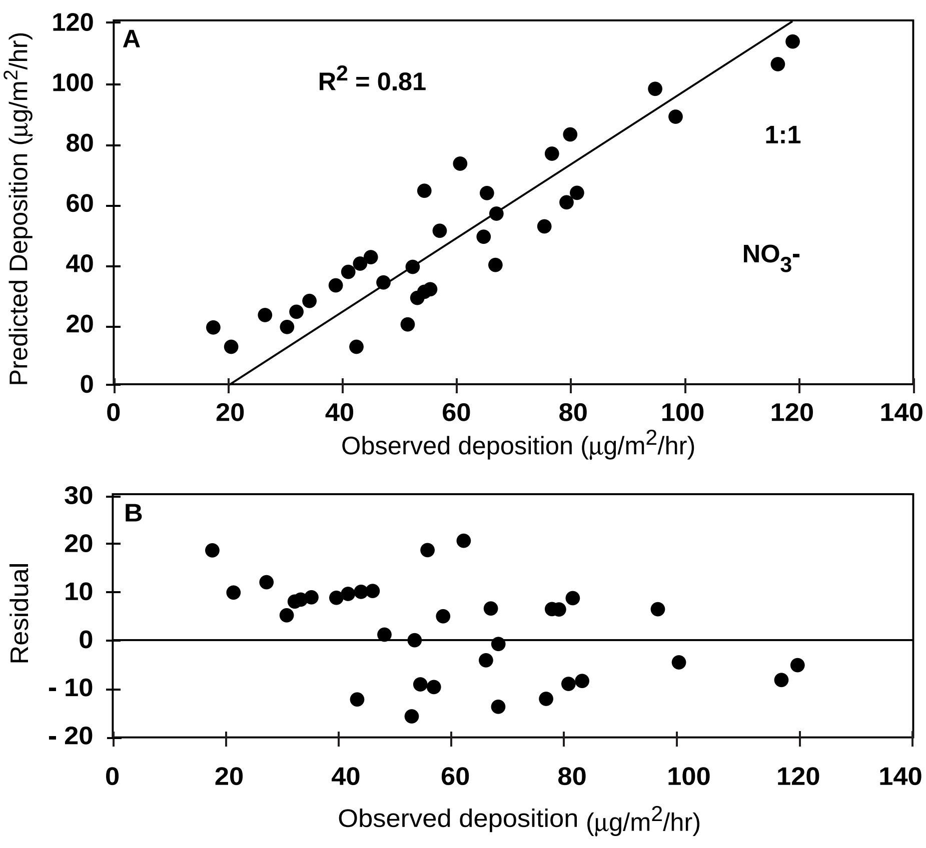

Figure 2 — Model results for predicting NO_3^- deposition at 24 m, 16 m, and 12 m on the canopy. Predicted deposition is compared with observed; the line represents a perfect model fit (1:1) and corresponds to deposition calculated at 29 m (A). Model residuals lack any pattern that would indicate poor model fit (B).

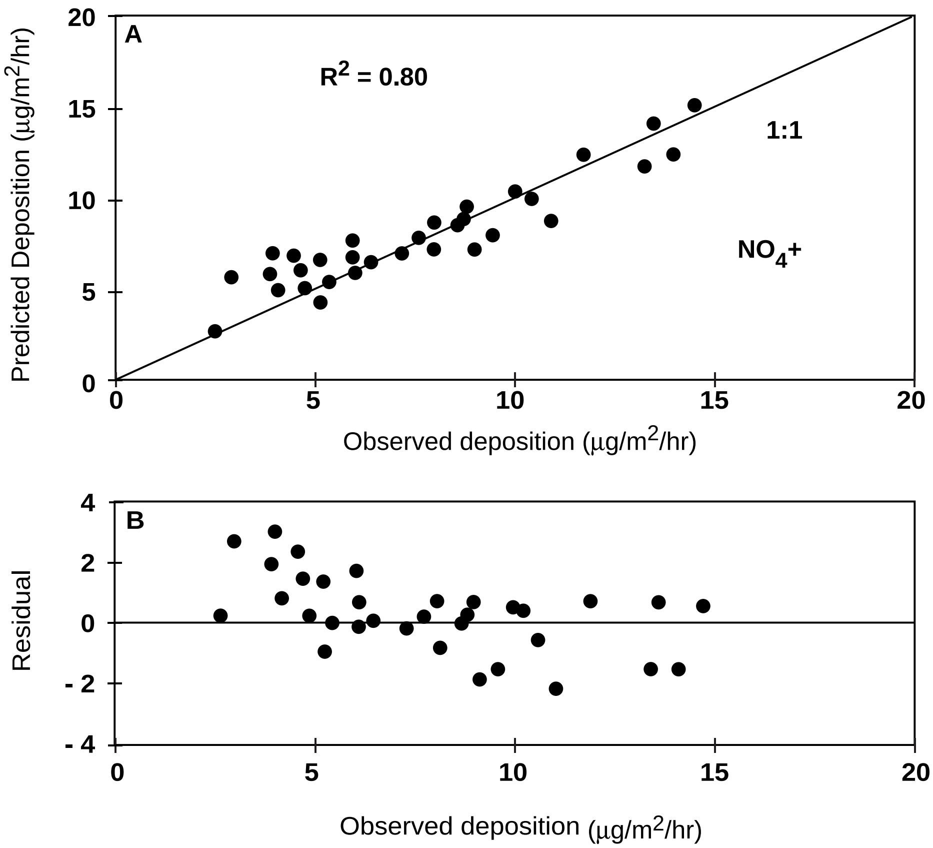

Figure 3 — Model results for predicting NH_4^+ deposition at 24 m, 16 m, and 12 m on the canopy. Predicted deposition is compared with observed; the line represents a perfect model fit (1:1) and corresponds to deposition calculated at 29 m (A). Model residuals lack any pattern that would indicate poor model fit (B).

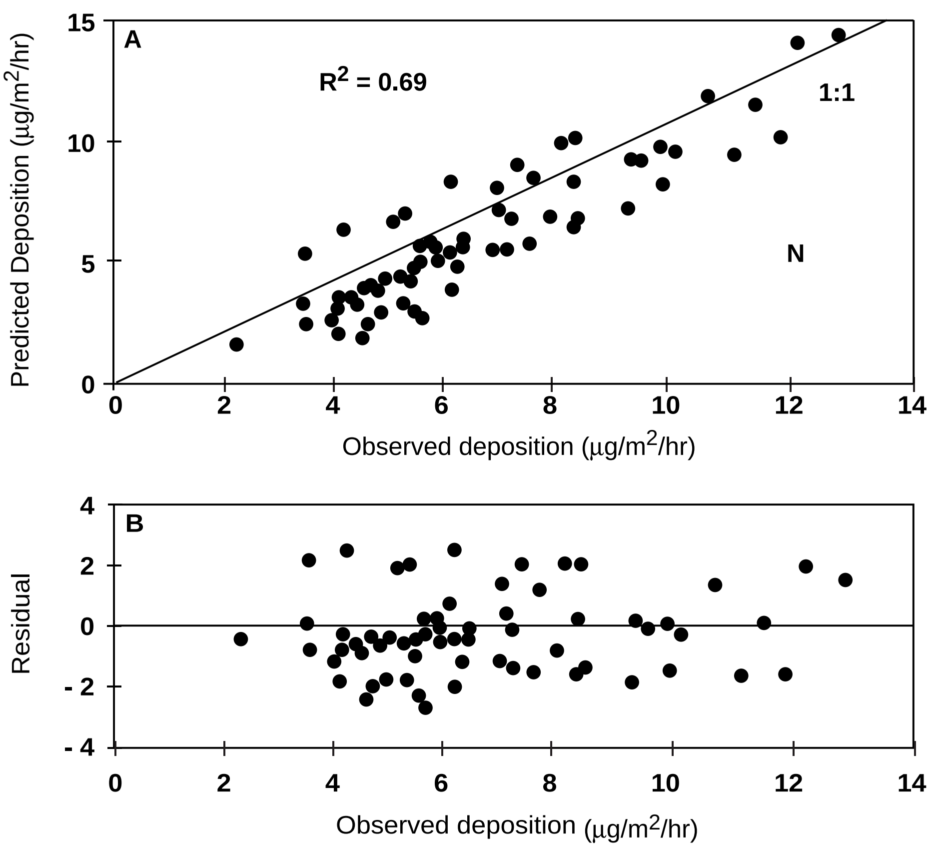

Figure 4 — Single model results for N deposition from ammonium and nitrate. Predicted deposition is compared with observed; the line represents a perfect model fit (1:1) and corresponds to deposition calculated at 29 m (A). Model residuals lack any pattern that would indicate poor model fit (B).

Conclusions

The estimators developed in this study have potential for reducing the necessary work in future studies to obtain estimates of whole canopy flux. The physically based models used in this study have high R^2, favorable residual properties, and interpretable parameters. Study results indicate that the models are applicable over a range of concentration values and pollution exposure seasons. The models need to be tested at other locations and for other tree species to verify their predictive ability. The scaffold tower data used for the analysis represents only a single point, and the foliage extraction information is most relevant for only two species, ponderosa and Jeffrey pine. Additional locations, especially in the western San Bernardino Mountains and the southern Sierra Nevada, need to be examined.

A single combined model may have application throughout the Transverse Ranges in southern California and the southern Sierra Nevada, since the chemical composition of N pollutants and forest types are similar for these areas. It may also have application to other open montane systems that lack vertical concentration gradients of pollutants and where the dominate form of aerosol N pollution is NH_4NO_3. Such systems may include coastal sage scrub, oak-grasslands, and chapparal.

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