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DRY DEPOSITION OF NITROGEN AND SULFUR TO PONDEROSA AND JEFFREY PINE IN THE SAN BERNARDINO NATIONAL FOREST IN SOUTHERN CALIFORNIA

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Abstract

*Little is known about the concentrations, deposition rates, and effects of nitrogenous and sulfurous compounds in photochemical smog in the San Bernardino National Forest (SBNF) in southern California. Dry deposition of NO_3^- and NH_4^+ to foliage of ponderosa pine (*Pinus ponderosa *Laws.) and Jeffrey pine (*Pinus jeffreyi *Grev. & Balf.) was correlated (R = 0·83–0·88) with historical average hourly O_3 concentrations at 10 sites across an O_3 gradient in the SBNF. Mean deposition fluxes of NO_3^- to ponderosa and Jeffrey pine branches were 0·82 nmol m^{-2} s^{-1} at Camp Paivika (CP), a high-pollution site, and 0·19 nmol m^{-2} s^{-1} at Camp Osceola (CAO), a low- pollution site. Deposition fluxes of NH_4^+ were 0·32 nmol m^{-2} s^{-1} at CP and 0·17 nmol m^{-2} s^{-1} at CAO, while mean values for SO_4^{2-} were 0·03 at CP and 0·02 nmol m^{-2} s^{-1} at CAO. Deposition fluxes to paper and nylon filters were higher in most cases than fluxes to pine branches at the same site. The results of this study suggest that an atmospheric concentration and deposition gradient of N and S compounds occurs along with the west–east O_3 gradient in the SBNF. Annual stand-level dry deposition rates for S and N at CP and CAO were estimated. Further studies are needed to determine if high N deposition loads in the SBNF significantly affect plant/soil nutrient relations, tree health, and the response of ponderosa pine to ozone.*

INTRODUCTION

Damage to ponderosa pine (*Pinus ponderosa* Laws.) caused by oxidant air pollution has been reported in the San Bernardino National Forest (SBNF) in southern California since the 1960s (Cobb & Stark, 1970; Miller, 1973, 1983). An ozone (O_3) gradient has been defined in the mixed conifer forest in the SBNF, with concentrations decreasing from west to east (Miller *et al.*, 1986, 1989). While most studies of the impact of air pollution on the mixed conifer forest in the SBNF have emphasized the effects of O_3, other compounds also occur in the pollutant mixture (Coyne & Bingham, 1977; Miller & Ryan, 1977).

Recent studies on atmospheric deposition in the San Gabriel Mountains near Los Angeles have demonstrated that high levels of nitrogenous (N) compounds in dry forms are deposited in mountainous areas downwind of Los Angeles (Bytnerowicz *et al.*, 1987*a,b*). Inorganic N in canopy throughfall in the San Gabriel Mountains was 2·5–16 times that for forests nationally (Riggan *et al.*, 1985). In a study at the Rancho Santa Ana Botanic Garden in Claremont, California (approximately 50 km inland from downtown Los Angeles), precipitation, canopy throughfall, and bulk deposition (wet and dry) were analyzed for major cations and anions. High levels of N accumulated in bulk collectors and on canopies between precipitation events. Nitrate was the dominant ion measured, and pine canopies accumulated the highest levels of ions, presumably due to their greater surface area compared with broad-leaved chaparral and oak species (Reid, 1988).

The available data indicate that dry deposition loads of N pollutants are several fold higher than for S pollutants in mountainous areas of California influenced by urban centers (Bytnerowic *et al.*, 1987*a*, 1991; Young *et al.*, 1988). Nevertheless, the S component of the dry deposition load in the SBNF has not been quantified and warrants further investigation. The reason for high deposition of N compounds in the South Coast (Los Angeles) Air Basin is that levels of N pollutants are high in this area (Grosjean, 1983; Bytnerowicz *et al.*, 1987*b*; Pierson & Brachaczek, 1988; Reid, 1988). In eastern North America and in Germany, levels of S pollutants generally are higher than levels of N pollutants (Mollitor & Raynal, 1983; Lindberg & Lovett, 1985).

Information on rates of N and S deposition in the SBNF is important considering the possible effects of elevated deposition levels on forest ecosystems (Swank, 1984; Aber *et al.*, 1989). Nitrogen is frequently the rate-limiting nutrient for plant growth, while S levels in forest soils are infrequently limiting for tree growth (Fernandez, 1985; Rasmussen & Kresge, 1986). Deposition of high concentrations of N in natural ecosystems is likely to increase plant growth rates if the deposited

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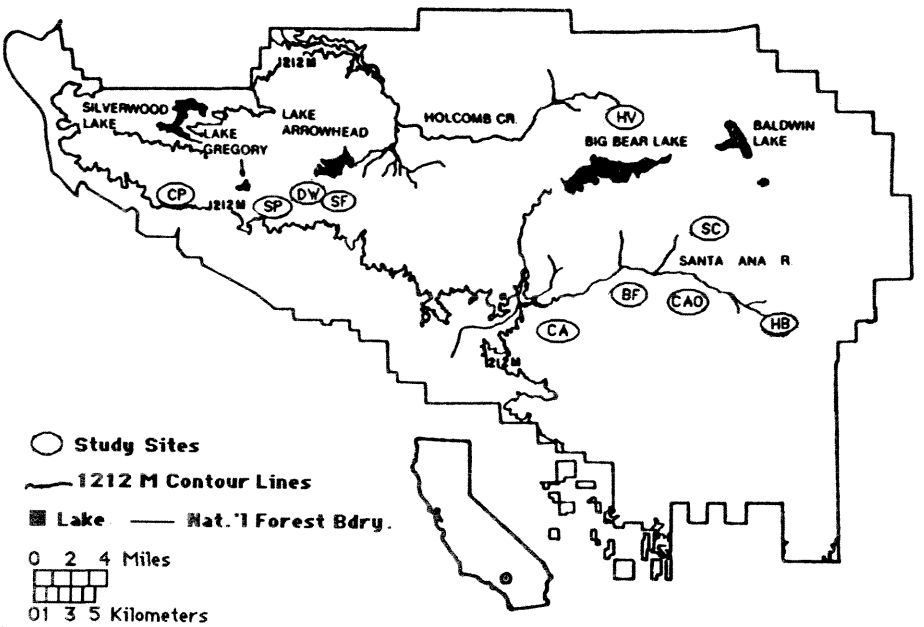

Fig. 1. Location of the 10 study plots in the San Bernardino Mountains. From west (high-pollution) to east (low-pollution) the plots are: CP (Camp Paivika), SP (Strawberry Peak), DW (Dogwood), SF (Sky Forest), CA (Camp Angelus), BF (Barton Flats), HV (Holcomb Valley), CAO (Camp Osceola), SC (Sand Canyon), and HB (Heart Bar). Modified from Miller *et al.* (1986).

N is available for plant uptake, and if other nutrients, water, competition, or environmental factors are not limiting. Higher N levels have resulted in nutrient imbalances (Schulze, 1989), increased litter decomposition rates (Aber *et al.*, 1989; Fenn, 1991; Fenn & Dunn, 1989), and may also result in higher water demand. When increased growth of ponderosa pine causes higher water stress, reduced stomatal uptake of O_3 will likely result in less O_3 injury (Temple *et al.*, 1992). Under conditions of sufficient available water and high ozone exposure, increased plant growth and metabolism due to N enrichment would likely result in greater uptake of O_3 and foliar damage in sensitive species like ponderosa pine. Growth of current-year foliage of loblolly pine (*P. taeda* L.) was more sensitive to elevated O_3 concentrations when seedlings were grown in soil with higher levels of N (Tjoelker & Luxmoore, 1991).

To determine if a deposition gradient of N and S compounds occurs along with the west–east O_3 gradient in the SBNF, we measured dry deposition to pine foliage at 10 sites across the air-pollution gradient, and to foliage and surrogate surfaces at a high- and a low-pollution site. The objective of this study was to estimate the dry deposition flux of N and S in the SBNF in order to evaluate the potential for impacts of N and S deposition on the forest.

MATERIALS AND METHODS

Rinsing foliage across the pollution gradient

To measure dry deposition to needle surfaces, we rinsed ponderosa or Jeffrey pine (*P. jeffreyi* Grev. & Balf.) foliage from 10 plots across the air-pollution gradient (Fig. 1) in October 1988. The 10 plots were chosen to include the range of air-pollution exposures which occur within the mixed conifer zone in the San Bernardino Mountains. A preliminary leaf-washing experiment at the 10 plots had been done in early July. Of the 10 plots 9 were initially selected in 1972 and 1973 as part of an interdisciplinary study of the effects of air pollution on the mixed conifer forest in the SBNF (McBride & Miller, 1977). The area containing the plots spans a distance of 55 km. From west to east along the gradient the dominant pine species shifts from ponderosa to the closely related Jeffrey pine. The last precipitation in the western plots before needle-rinsing was 7·1 mm of rainfall over a 2-day period, measured at the Lake Arrowhead weather station, 27–28 days before sampling. At the Big Bear Lake weather station, on the eastern, low-pollution side of the SBNF, 22·9 mm of rain fell 53 days before we collected samples.

At each plot, current-year foliage was rinsed from 20 trees. Our preliminary tests showed that 79–94% of the NO_3^-, 63–82% of the NH_4^+, and 56–74% of the SO_4^{2-} washed from the pine branches were contained in the first 50 ml of branch runoff. For each tree a branch from each of the four geographic quadrants was rinsed with deionized distilled water from a polyethylene spray bottle until 50 ml of runoff was collected into a funnel and graduated cylinder. The rinses from each of the four quadrants per tree were combined to obtain 200 ml of needle rinse for each tree. Samples were placed on ice in the field and placed in a freezer upon returning to the laboratory. All samples in the study were kept frozen until analyzed for NH_4^+ and NO_3^- with a Technicon* (Traacs 800) autoanalyzer (Tarrytown, New York), and the pH determined with a Beckman*

* Mention of trade names or products is for information only and does not imply endorsement by the US Department of Agriculture.

(Irvine, CA) pH meter (model phl-71). To insure reliability of chemistry data, standards and duplicate samples were included in all laboratory analyses according to a strict QA/QC protocol operative in our laboratory.

Total leaf surface areas were calculated for subsamples of ponderosa and Jeffrey pine foliage. A regression equation was computed for determining leaf surface area for ponderosa pine and also for Jeffrey pine based on the dry weight of foliage. Dry weight of all foliage rinsed was determined after drying overnight in an oven at 80°C. The surface area of the stems to which the needles were attached was calculated from stem diameter and length measurements. The surface area of the four stems and of the four annual whorls collected from each tree were combined to determine the stem and leaf surface area rinsed for each tree. The amount of a given ion rinsed from foliage was expressed as milligrams per square meter of leaf and stem.

Regression analysis was used to test the relationship between concentration of NO_3^- and NH_4^+ (log transformed) in branch rinses, and 24-h average O_3 concentrations at the 10 sites 10–14 years earlier. Although O_3 concentrations have decreased slightly in the last 10–15 years (Miller *et al.*, 1989), the geographical pattern of O_3 distribution is likely to have changed little. The 24-h averages of O_3 concentration were measured from a subsample of days from May to October, 1974–78 (Miller *et al.*, 1989). Data on O_3 concentration was not available for Strawberry Peak (SP) and Sand Canyon (SC). The concentration of O_3 at SP was estimated based on a regression equation ($R = 0{\cdot}99$) for the plots located in the Lake Gregory and Lake Arrowhead region (Miller, 1983, Miller *et al.*, 1989), with O_3 concentration as a function of east–west location along the transect. Another regression equation ($R = 0{\cdot}90$) for the plots located along the Santa Ana River transect was used to estimate the 24-h average O_3 concentration at SC.

Measuring deposition to foliage and surrogate surfaces at two sites

Because of the inadequacy of any single method for quantifying dry deposition, we measured deposition to nylon filters, paper filters, and branches. This approach provided a broader data base for comparing relative deposition rates at a high- and a low-pollution site. Thus, data on deposition rates at CP and CAO reflect relative deposition rates to collector surfaces with varying affinities for the N and S pollutants measured. Nylon has a relatively high affinity for NO_3^-, while paper filters are more efficient in accumulating NH_4^+ and SO_4^{2-} (Bytnerowicz *et al.*, 1987*a*, 1991).

Four nylon filter disks (Nylasorb, Gelman Sciences Inc., Ann Arbor Michigan, 1 μm pore size) and four paper filter disks (Whatman no. 41) were set out at Camp Paivika (CP, high-pollution) and at Camp Osceola (CAO, low-pollution) on 17 April 1989. Filters were 47 mm in diameter and were placed in polycarbonate filter holders, which were attached to the stands with wooden clothespins approximately 1·5 m above the ground in a horizontal position. On the same date, current year foliage on five branches of a ponderosa pine tree at CP, and of a Jeffrey pine tree at CAO were washed thoroughly with distilled water. The trees selected for branch rinsing were approximately 12 m from the filter stands. At approximately 2-week intervals the filter disks were changed, and each of the selected branches were rinsed with distilled deionized water until 50 ml of rinse were collected. After exposure to the atmosphere, filter disks were stored in sealed plastic Petri dishes in sealed plastic bags in the freezer along with branch rinses.

After the final rinses were collected on 9 September 1989, the branches were harvested and the surface area of foliage and stems was calculated. Current-year foliage appeared to be of a mature size at the time of the first rinses, but foliage may have increased in surface area between the first rinse (17 April 1989) and the last rinse (9 September 1989). Thus, deposition per unit area (nmoles N m^{-2} leaf area) based on greater foliar surface area in September, may be slightly underestimated on the earlier rinse dates. Sulfate in branch rinses was analyzed with a Dionex Series 4000i high-performance ion chromatograph (Dionex Corp., Sunnyvale, CA). Pollutants were extracted from the filter disks with distilled water, and extracts were analyzed as described for branch rinses. For nylon and paper filter disks a sum of the surface area of the upper and lower surfaces was used to calculate deposition rates.

Atmospheric concentrations of N and S species were determined at CP and at CAO for two consecutive 24-h periods, beginning in the afternoon of 7 September 1989. An annular denuder system (Possanzini *et al.*, 1983; Peake & Legge, 1987) was used to measure atmospheric concentrations of NH_3, HNO_3, and SO_2 in the gaseous phase, and of NH_4^+, NO_3^-, and SO_4^{2-} in the particulate phase. Air was pulled through the system at 17 liters min^{-1} with the inlet cyclone providing a 2·2 μm particle diameter cutpoint. Particulate matter larger than 2·2 μm was not analyzed.

RESULTS

Dry deposition across an air-pollution gradient

Levels of NH_4^+ and NO_3^- washed from pine foliage in the 10 plots were positively correlated with historical 24-h average O_3 concentrations in 10 plots across the air-pollution gradient, with correlation coefficients of 0·88 for NH_4^+ and 0·83 for NO_3^- (Fig. 2). The levels of NO_3 were 9–27 times higher than levels of NH_4^+ in foliar rinses. The pH of foliar rinses in 9 of the 10 plots ranged from 5·3 to 5·7. Branch rinses from Holcomb Valley, a low-pollution site located on the northern (desert) side of the SBNF, were unusually alkaline with an average pH of 6·5. Highly alkaline dust from desert soil may have caused this high pH. Another low-pollution site (Heart Bar) had the lowest pH, 5·3. The pH of foliar rinses showed no clear pattern across the air-pollution gradient.

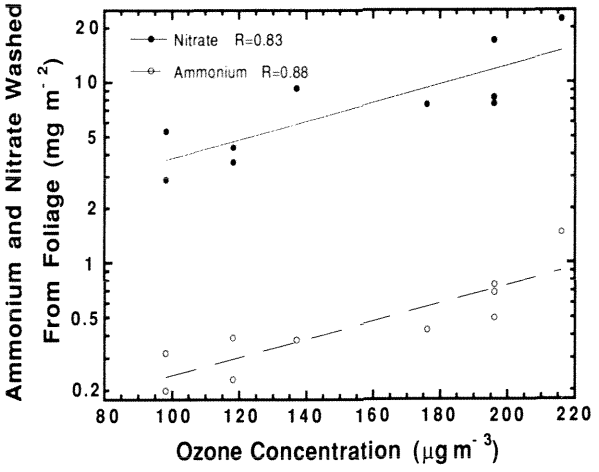

Fig. 2. Historical average hourly O_3 concentration versus concentration of NO_3^- and NH_4^+ (log transformed) washed from foliage, at 10 sites across an air-pollution gradient in the San Bernardino National Forest.

Dry deposition at a high- and a low-pollution site

An average of 3·2 to 3·4 times more NO_3^- was deposited on nylon and paper filters at CP (high-pollution) than at CAO (low-pollution). An average of 3·0 and 7·2 times more NH_4^+ was deposited on paper and nylon filters at CP than at CAO (Table 1).

On nylon filters 2·6 times more NO_3^- than NH_4^+ accumulated at CP, and 5·8 times more NO_3^- than NH_4^+ accumulated at CAO (Table 1). Although deposition of SO_4^{2-} was low at both sites, it was lowest at CAO. Sulfate was not detectable at CAO (low-pollution site) on three out of five sampling dates with paper filters, and on two out of five sampling dates with nylon filters.

Levels of NO_3^- in branch rinses averaged 4·3 times higher at the high-pollution site (CP) than at the low-pollution site (CAO). Concentrations of NH_4^+ in branch rinses averaged 1·9 times higher at CP than at CAO, and concentrations of SO_4^{2-} averaged 1·5 times higher. The concentration of NO_3^- in branch rinses at CP averaged 2·6 times higher than the concentration of NH_4^+, and 27 times higher than SO_4^{2-} . However, the nitrate : sulfate ratio may be artificially high, as SO_4^{2-} levels were near detection limits (Table 1).

Table 1. Average deposition fluxes to foliage and surrogate surfaces at a low-pollution (CAO) and high-pollution (CP) site in the San Bernardino National Forest.

Plot	Dry deposition (nmol m^{-2} s^{-1})		
	Paper[a]	Nylon[a]	Branch[b]
NO_3^-			
CP–	1·04 (0·074)[c]	1·13 (0·148)	0·82 (0·108)
CAO	0·31 (0·053)	0·35 (0·038)	0·19 (0·018)
NH_4^+			
CP	0·93 (0·121)	0·43 (0·048)	0·32 (0·034)
CAO	0·31 (0·059)	0·06 (0·015)	0·17 (0·019)
SO_4^{2-}			
CP	0·05 (0·017)	0·10 (0·025)	0·04 (0·010)
CAO[d]	0·003 (0·002)	0·02 (0·009)	0·02 (0·005)

[a] Average of five 2-week deposition periods from April to August 1989.
[b] Average of six 2-week deposition periods from April to September 1989.
[c] Numbers in parentheses represent 1 standard error of the mean.
[d] Sulfate levels from nylon and paper filters at CAO were below, or nearly below, detectable limits in many samples.

Table 2. Atmospheric concentrations of gaseous pollutants and ions in the fine particulate fraction at a low-pollution (CAO) and high-pollution (CP) site in the San Bernardino National Forest[a]

Pollutant	Atmospheric concentration (μg m^{-3})	
	CP	CAO
O_3	216[b]	118[b]
HNO_3	8·9	1·1
NO_3^-	5·1	2·1
NH_3	1·2	0·7
NH_4^+	0·9	0·1
SO_2	2·9	0·7
SO_4^{2-}	1·4	0·2

[a] Average of 2 consecutive days, 7–9 September 1989.
[b] Ozone data, shown for comparison, was collected from 1974 to 1978 (Miller *et al.*, 1989).

Average atmospheric concentrations of N and S gases, and ions in the fine particulate fraction, were much higher at CP compared with CAO during 2 consecutive days in September (Table 2). Pollutant concentrations were higher on the second day at both sites; probably due to Santa Ana wind conditions, which prevailed on the first day. Santa Ana winds originate over the deserts of eastern southern California and descend through mountain passes to the coastal plain, arriving as a hot, dry, gusty wind.

In a previous study at Tanbark Flat in the San Gabriel Mountains northeast of Los Angeles, 40% of the particulate NO_3^- and approximately 10% of the particulate NH_4^+ and SO_4^{2-} were in the coarse fraction (particles > 2·5 μm; John *et al.*, 1985). Since we did not analyze the coarse fraction, total particulate NO_3^- in our study may be underestimated by approximately 40%, and total particulate NH_4^+ and SO_4^{2-} may be underestimated by approximately 10%.

DISCUSSION

N and S deposition gradient

The high correlation between levels of NO_3^- and NH_4^+ washed from pine foliage, and historical O_3 concentrations, in 10 plots traversing the air-pollution gradient, suggests that N pollutants are transported with O_3 from urban centers and deposited onto tree canopies and other surfaces in the SBNF. This conclusion is based on the relatively safe assumption that current O_3 levels across the O_3 concentration gradient in the SBNF are proportional to O_3 levels measured in 1974–78. Average foliar deposition rates for NO_3^- (foliage exposed

for 14 days) was 0·19 nmol m^{-2} s^{-1} at CAO (low-pollution), and 0·82 nmol m^{-2} s^{-1} at CP (high-pollution). In a study conducted near Claremont, California, 50 km east of Los Angeles, the foliar deposition flux of NO_3^- to potted Canary Island pine (*P. canariensis* Chr. Sweet ex Spreng.) was 1·40 nmol m^{-2} s^{-1} during a 12-day exposure (Wu *et al.* 1992; Yee-Lin Wu, pers. comm.).

Dry deposition of N and S compounds to nylon filters at CP in this study was slightly lower than levels measured at Tanbark Flat in the San Gabriel Mountains, about 35 km northeast of central Los Angeles (Bytnerowicz *et al.*, 1987*a*). Deposition flux of NO_3^- to nylon filters at CP averaged 1·13 nmol m^{-2} s^{-1} compared with 1·68 nmol m^{-2} s^{-1} at Tanbark Flat; while NH_4^+ deposition to nylon filters averaged 0·43 nmol m^{-2} s^{-1} at CP and 0·66 nmol m^{-2} s^{-1} at Tanbark Flat. Sulfate deposition to nylon filters at CP was 0·10 nmol m^{-2} s^{-1} and 0·23 nmol m^{-2} s^{-1} at Tanbark Flat (Bytnerowicz *et al.*, 1987*a*). Atmospheric concentrations of N and S compounds at CP were similar to concentrations at Tanbark Flat (Bytnerowicz *et al.*, 1987*b*, and unpublished data). However, because measurement of atmospheric concentrations of N and S pollutants at CP and CAO was limited to only 2 days in September 1989, undue emphasis cannot be placed on these results. Nonetheless, higher atmospheric concentrations of N and S pollutants in the western site (CP) compared to the eastern site (CAO) support the existence of a west-to-east deposition gradient for N and S in the SBNF.

Relative deposition levels of N and S

Our results confirm that in California and in some other parts of the western United States, dry deposition of nitrogenous compounds to vegetation is much greater than dry deposition of sulfurous compounds. This result is in contrast to the eastern United States and Europe where deposition of S is generally greater than that of N (Mollitor & Raynal, 1983; Lindberg & Lovett, 1985).

Concentrations of NO_3^- washed from foliage and surrogate surfaces at CP were higher than concentrations of NH_4^+ or SO_4^- . Dry deposition rates and atmospheric concentrations of HNO_3 and NO_3^- in the San Gabriel Mountains near Los Angeles were also much greater than that of NH_3, NH_4^+, SO_2, and SO_4^{2-} (Bytnerowicz *et al.*, 1987*a,b*). High levels of NO_3^- , and to a lesser degree, of NH_4^+ and SO_4^{2-} , were also measured in bulk collectors, in throughfall of chaparral, oak, and pine species, and in leaf washes at sites in and near Claremont, California, 50 km east of Los Angeles (Reid, 1988; Wu *et al.*, 1992). Compared with SO_4^{2-} much higher levels of NO_3^- and NH_4^+ were deposited on native pines and surrogate surfaces in the western Sierra Nevada (Bytnerowicz *et al.*, 1991). Similarly, at a mountain site near Boulder, Colorado, dry deposition of NO_3^- to foliage of Rocky Mountain lodgepole pine (*Pinus contorta* Dougl. var. *latifolia Engelm.*) was three to four times higher than deposition of SO_4^{2-} over a 2-year period (Sievering *et al.*, 1989).

Decrease in concentration and deposition of O_3, N and S between a high- and a low-pollution site

Comparing the results from this study on N and S pollutants with historical values for O_3 concentrations in the SBNF, suggests that the concentration and deposition of most N and S pollutants decreased proportionately more than did the concentration of O_3 between a western high-pollution plot (CP) and an eastern low-pollution plot (CAO). However, the limited data available do not allow precise comparisons between concentrations of O_3, and of N and S pollutants. Data on O_3 concentration at CP and CAO were collected 11–15 years earlier (Miller *et al.*, 1989) than were the data on N and S pollutants, which were limited to only 2 days in September 1989.

Nitric acid was the dominant compound measured at both sites, and the concentration of HNO_3 at CAO was only 12% of that at CP. The sharp reduction in HNO_3 between CP and CAO is probably due to the high deposition velocity characteristic of HNO_3 (Meyers *et al.*, 1989; Murphy & Sigmon, 1990). Ammonia generally has a deposition velocity similar to that of O_3 (Cadle & Mulawa, 1988; Meyers & Hicks, 1988), which may explain why the concentration of O_3 and NH_3 decreased in similar proportions between CP and CAO.

Estimation of stand-level N and S deposition rates

We estimated landscape-level deposition rates for N (as NH_4^- and NO_3^-) and for S (as SO_4^{2-}) at CP and CAO based on our results for deposition fluxes to pine foliage (Table 1). These estimates entailed a high degree of uncertainty due to a number of assumptions (Table 3), and can be considered only as crude estimates at best. Nonetheless, these rough estimates may indicate the potential for significant biological effects due to chronic deposition of N and S in the SBNF.

Table 3. Assumptions made in estimating stand-level N and S deposition rates at CP and CAO in the San Bernardino National Forest

A. Dry deposition
   1. Total LAI (all sides) of 5·2 for ponderosa and Jeffrey pine in the SBNF was used in calculating deposition rates. Based on the lowest LAI reported for ponderosa pine in the literature.
   2. Deposition to oak trees was considered to be equal to pine trees; as if these were pure pine stands, except for the lack of foliage during 6 months of the year. An LAI of 1·0 was used for oak during the 6 leafless months.
   3. Deposition fluxes to fern foliage occurs during 6 months of the year. LAI of fern is 5·0 during the 6 months of the growing season, and zero in the remaining 6 months.
   4. N and S dry deposition rates from November through April are 40% as high as during the May through October 'smog' season, based on year-round O_3 data from Tanbark Flat.

B. Wet deposition
   1. The ratio of wet deposition of N and S at CP versus Tanbark Flat is equal to the ratio of dry deposition at CP versus Tanbark Flat.
   2. Wet deposition of N at CAO if 0·2 times that at CP, based on 0·2 times as much dry deposition of N at CAO. Similarly, dry deposition and wet deposition of S at CAO is 0·3 times that at CP.

Values of stand leaf area or leaf area index (LAI) are not available for the SBNF. Total LAI (all-sided) values for ponderosa pine stands, or mixed conifer stands dominated by ponderosa pine, ranged from 5·2 to 8·4 in Montana (McLeod & Running, 1988), and from 7 to 20 on the eastern slopes of the Cascades in Oregon (Grier & Running, 1977; Gholz, 1982). We have conservatively used an LAI of 5·2 (the lowest value reported for ponderosa pine) for estimating stand-level deposition to the overstory at CP and CAO. However, 43% of the stand at CP and 11% of the stand at CAO are composed of California black oak (*Quercus kelloggii* Newb.). In our calculations we considered deposition to oak trees to be equal to pine trees, except that the LAI of 43% of the stand at CP and 11% of the stand of CAO was reduced from 5·2 to 1·0 for the 6 months of the year when the oak canopy is devoid of foliage.

Total site LAI at CP was also adjusted according to the understory vegetation. We assumed that deposition flux to understory vegetation is equal to deposition flux to pine foliage. In the spring and summer the understory layer at CP is dominated by a dense fern (*Pteridium aquilinum* var. *pubescens* Underw.) layer, which often reaches 2 m high. At CAO the understory vegetation is mainly a sparse shrub community, and the surface litter layer is thin compared with that at CP. For estimating deposition fluxes at CP we included an LAI of 5·0 for the 6 months of the year when the fern layer is physiologically active, based on typical LAI values of 4–8 for herbaceous crops (Larcher, 1980; Meyers & Hicks, 1988).

Data on dry deposition of N and S in the SBNF and in other forests in the region, are available only for April through October. We estimated, based on monthly 24-h average O_3 concentrations taken year-round from Tanbark Flat in the San Gabriel Mountains, that dry deposition rates for N and S from November through April were 40% as high as during the May through October 'smog' season. Using the data, rationale, and procedure described above, we estimated the annual N load from dry deposition to be 29·1 kg ha^{-1} at CP and 5·7 kg ha^{-1} at CAO. Corresponding values for S were 2·0 kg ha^{-1} at CP and 0·6 at CAO. Our estimate of dry deposition fluxes to a ponderosa pine stand at CP (29·1 kg N ha^{-1} year^{-1}) is similar to N levels in the throughfall of *Ceanothus* chaparral canopies (23·3 kg N ha^{-1} year^{-1}) following periods of accumulation of dry deposition in the San Dimas Experimental Forest in the San Gabriel Mountains northeast of Los Angeles (Riggan *et al.*, 1985). Nitrogen input from bulk precipitation in the same study was 8·2 kg ha^{-1} year^{-1}.

Although the objective of this study was to quantify dry deposition of N and S, including an estimate of wet deposition demonstrates the magnitude of wet versus dry deposition, and allows for an estimate of total atmospheric input. Wet deposition likely contributes appreciable amounts of N and S in the SBNF. Concentrations of NO_3^- and SO_4^{2-} were virtually identical in rime ice, and also in snow at Strawberry Peak (a western site in the SBNF) during the winter of 1987–88; and concentrations were 2–8 times higher than at mountain sites in central and northern California (Berg *et al.*, 1991). Average annual wet deposition of N at Tanbark Flat in the SDEF from 1982 to 1989 was 2·4 kg ha^{-1}, while S averaged 1·4 kg ha^{-1} (NADP, 1982–89).

Table 4. Estimates of dry, wet and total annual deposition rates at CP and CAO in the SBNF, and S:N ratios of pollutants

Pollutant form	Deposition (kg ha^{-1} year^{-1})	
	Camp Paivika	Camp Osceola
Nitrogen		
Dry	29·1	5·7
Wet	1·6	0·3
Total	30·7	6·0
Sulfur		
Dry	2·0	0·6
Wet	0·9	0·3
Total	2·9	0·9
S:N ratio		
Dry	0·07	0·11
Wet	0·56	1·00
Total	0·09	0·15

Dry deposition of NH_4^+ and NO_3^- to nylon filters was 65 and 67% as high at CP as at Tanbark Flat (Bytnerowicz *et al.*, 1987*a*). Assuming a similar relationship for wet deposition of N between CP and Tanbark Flat, we estimate total (wet plus dry) annual deposition of N at CP to be 30·7 kg ha^{-1}. Assuming that wet deposition of N at CAO is 0·20 times that of CP (based on 0·20 times as much dry deposition of N at CAO), we estimate total annual deposition of N at CAO to be 6·0 kg ha^{-1}. Dry deposition of SO_4^{2-} to nylon filters at CP was 43% of that at Tanbark Flat (Bytnerowicz *et al.*, 1987*a*). Using the procedure described above for N, we estimate total annual deposition of S to be 2·9 kg ha^{-1} at CP and 0·9 kg ha^{-1} at CAO. Estimates of wet, dry, and total deposition of N and S, and S : N ratios at CP and CAO are summarized in Table 4.

The assumption of a similar relationship between dry deposition and wet deposition at CP versus Tanbark Flat is untested. Our estimates of wet deposition of N and S in the SBNF are therefore highly uncertain, and in fact, probably greatly underestimate actual wet deposition inputs from rain, clouds, snow, fog and rime ice in the SBNF. Typical levels of wet deposition in rural areas of the western US fall between 0·7 and 2·5 kg N ha^{-1} year^{-1} and 1·0–2·0 kg S ha^{-1} year^{-1} (Young *et al.*, 1988), compared to our estimates of 1·6 and 0·9 kg ha^{-1} year^{-1} for N and S at CP. Considering the high level of emissions, and high ionic content of fogwater (Young *et al.*, 1988), rime ice, and snow (Berg *et al.*, 1991) in the South Coast Air Basin, we expect that our estimates are possibly several orders of magnitude lower than actual wet deposition values.

Data from seven National Acid Deposition Program/National Trends Network (NADP/NTN) sites in California (including Tanbark Flat; NADP, 1982–89), from Strawberry Peak in the SBNF (Berg *et al.*, 1991),

and at sites throughout the West (Young *et al.*, 1988), support our estimation that the S:N ratio for wet deposition is much higher than for dry deposition fluxes to foliage in the SBNF (Table 4). The S : N ratio may be higher in wet deposition than in dry because of more rapid dry deposition of N compared to S, and/or more effective S scavenging in clouds and precipitation (Young *et al.*, 1988).

Potential effects of chronic N deposition

In previous studies in the SBNF the concentration of N in soil, foliage, and litter of three conifer species, the rate of litter decomposition, and the diversity of fungal decomposers were higher in the high-pollution sites than in the low- and moderate-pollution sites (Fenn & Dunn, 1989; Fenn, 1991). Phosphorus concentrations in soil, foliage and litter did not follow a similar trend across the pollution gradient. Treating litter from CP with NH_4NO_3 did not stimulate litter decomposition, suggesting that decomposition at CP is not N-limited. It was concluded that greater site fertility in the western, high-pollution sites resulted in more nutrient-rich litter (Fenn, 1991). A significant portion of the annual N (and possibly of other elements) requirements for plant growth in the SBNF is likely supplied via processes of atmospheric dry deposition, and to a lesser extent, wet deposition. Even in the relatively wet climate of Tennessee, dry deposition contributed significantly to the N and S requirements for annual woody increment of an oak-hickory forest (Lindberg *et al.*, 1986).

The effect of chronic N deposition on the mixed conifer forest in the SBNF depends on the capacity of the ecosystem to absorb, process, and retain atmospherically deposited N. The 'critical load' of a pollutant has been defined as 'the highest load that will not cause chemical changes leading to long-term harmful effects on most sensitive ecological systems' (Nilsson, 1987). The critical load concept has been applied to forests dominated by wet deposition inputs, but should also be applicable to forests where dry deposition loading predominates. Critical loads of N deposition estimated for most temperate coniferous ecosystems range from 10 to 20 kg N ha^{-1} $year^{-1}$; although in highly productive forests it might be as high as 20–45 kg N ha^{-1} $year^{-1}$ (Nilsson, 1987). Schulze *et al.* (1989) calculated critical loads for N deposition, based on the assumption that the stability of an ecosystem is maintained at a constant exchangeable base cation pool. Critical loads calculated for granitic soils ranged from 3 to 14 kg N ha^{-1} $year^{-1}$ (Schulze *et al.*, 1989). Soils in the SBNF are of granitic parent material (Fenn & Dunn, 1989).

Theoretically, when N deposition exceeds the critical load for a given forest ecosystem, the forest becomes N saturated. Further additions of N do not increase primary production, other resources limit plant and microbial growth, and the forest converts atmospheric N to groundwater nitrate and to nitrous oxide, a greenhouse gas (Nilsson, 1987; Aber *et al.*, 1989). Further studies in the SBNF on potential impacts of N deposition are certainly warranted based on our estimate of total N deposition at CP (30·7 kg N ha^{-1} $year^{-1}$). Sulfur deposition levels do not appear to be of sufficient magnitude to have major effects on the SBNF. However, more information is especially needed on N and S inputs from wet deposition, including input from fog, clouds, rain, snow, and rime ice.

CONCLUSIONS

High correlation between historical 24-h average O_3 concentrations and dry deposition of N to pine branches at 10 sites, suggests that a deposition gradient of N occurs along with the west–east decreasing O_3 gradient in the SBNF. The hypothesis of a deposition gradient of N and S is further supported by high deposition fluxes and atmospheric concentrations of N, and—to a much lesser degree—S compounds, at a western site (high-pollution); and relatively low deposition fluxes and concentrations at an eastern site (low-pollution). Gaseous HNO_3^- and particulate NO_3 were much more abundant than NH_3, NH_4^+, SO_2, or SO_4^{2-} in air samples. High concentrations of HNO_3 and NO_3^- in the air resulted in high deposition of NO_3^- to branches and surrogate surfaces.

Year-round deposition measurements of the major wet and dry N and S pollutants are needed in order to quantify and characterize total ecosystem loading from the atmosphere. The high values for deposition of N compounds in the SBNF indicate the need to investigate ecosystem processing of deposited N compounds. Studies are also needed on the effects of N deposition on tree growth and nutrient status, plant nutrient ratios, nutrient cycling processes and pools, production and consumption of greenhouse gases, leaching of N from soil, plant water demand, growth and composition of understory communities, and of possible interactions between N deposition and O_3 stress of sensitive species, such as ponderosa pine.

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