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SUMMER THROUGHFALL AND WINTER DEPOSITION IN THE SAN BERNARDINO MOUNTAINS IN SOUTHERN CALIFORNIA

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Abstract—Summer throughfall and year-round precipitation chemistry were studied for three years at Barton Flats (BF), a low to moderate pollution site in the San Bernardino Mountains (SBM) in southern California. Winter fog plus dry deposition, and bulk deposition were also measured during one season at three sites traversing an atmospheric deposition gradient in the SBM. Throughfall N (NO_3^- + NH_4^+) inputs during the growing season in 1993 were 4.0 kg ha^{-1} compared to 0.4 kg ha^{-1} for S. Deposition of N and S in summer 1994 was 50% of that in 1993, and precipitation in summer 1994 was 31% as high as in 1993. Summer throughfall concentrations were highest in 1994, the summer with the lowest precipitation. Ionic concentrations in rain and throughfall at BF during the summer, particularly NO_3^-, were generally as high or higher than values reported for forests in Europe and eastern North America with much higher atmospheric deposition inputs. The high throughfall concentrations at BF were apparently due to the washoff of accumulated dry pollutants from mature trees with large surface areas during infrequent low-volume rain events. White fir, the species with the greatest foliar surface area, had the highest throughfall concentrations and the lowest throughfall volumes. Canopy effects of ponderosa and Jeffrey pine on precipitation chemistry and volume were intermediate, while California black oak throughfall was less modified chemically than the throughfall of the conifer species. Ionic deposition (mg m^{-2} land area) was highest under fir and pine, intermediate under oak, and lowest in rainfall. During the winter, peaks in wet deposition inputs at BF were associated with high monthly rain volumes (11–44 cm), while similar wet deposition peaks in August occurred with only a few light rains (1.4–3.4 cm). Winter (13 December 1993 to 11 April 1994) bulk deposition of N and S at Camp Paivika, a western high-deposition site, was 7.7 and 1.7 kg ha^{-1}, respectively, compared to 0.9 and 0.3 kg ha^{-1} of N and S at BF. Winter deposition of NO_3^-, NH_4^+ and SO_4^{2-} to passive nylon line collectors (fog plus dry deposition) was 15-, 18- and 6-times greater at Camp Paivika than at BF. Winter deposition in both wet and dry forms in the SBM was greater than previously estimated from precipitation data for other forest sites in southern California. Published by Elsevier Science Ltd

Key word index: Atmospheric deposition, nutrient cycling, ion concentrations, air pollution, tree species, forest canopy.

INTRODUCTION

Estimates of dry deposition of N in some areas of the San Gabriel and San Bernardino Mountains (SBM) near Los Angeles, California are among the highest in North America (Bytnerowicz *et al.*, 1987b; Fenn and Bytnerowicz, 1993; Grosjean and Bytnerowicz, 1993), and have resulted in N saturation of some mixed conifer and chaparral stands (Riggan *et al.*, 1985; Fenn *et al.*, 1996). However, stand-level estimates of atmospheric inputs of N and other nutrients to mixed conifer forests in southern California are limited to values based on branch rinse data, which entail considerable uncertainty because of insufficient data on stand leaf area index and seasonal trends in N deposition (Fenn and Bytnerowicz, 1993; Bytnerowicz and Fenn, 1996). Throughfall data and information on stand structure and seasonal deposition trends are needed to quantify nutrient deposition to southern California forests exposed to chronic air pollution.

Typically, about 85% of the annual precipitation occurs during the winter in the Mediterranean climate of California (Aschmann, 1973). Little data on winter deposition of pollutants in the mountains of southern California are available, except for National Atmospheric Deposition Program (NADP) precipitation data from Tanbark Flat and fog deposition data from Henninger Flats (Waldman *et al.*, 1985), both in the San Gabriel mountains; and snow and rime ice chemistry data from Strawberry Peak in the western SBM (Berg *et al.*, 1991). It has previously been assumed that winter deposition was insignificant even in forested sites with high dry deposition of

N and ozone exposures in the summer (Fenn and Bytnerowicz, 1993). However, ionic concentrations in fog at a pine forest in the San Gabriel Mountains were highly concentrated (Waldman *et al.*, 1985), and some areas in the SBM also experience seasonal fog with potentially high pollutant loadings. Nitrate concentrations in rime ice at a western high-pollution site in the SBM were higher than at forested sites in central and northern California (Berg *et al.*, 1991). Ionic deposition to southern California forests during winter may be equally dependent on processes which transport highly concentrated forms of precipitation such as fog, cloudwater and rime ice (Waldman *et al.*, 1985; Collett *et al.*, 1990; Berg *et al.*, 1991), in addition to deposition in rain and snow.

Precipitation chemistry is often modified considerably as it passes through the canopy, especially in areas of high atmospheric dry deposition inputs (Lovett and Lindberg, 1993). Because of the difficulty in measuring dry deposition inputs, throughfall measurements are often used as an estimate of atmospheric deposition inputs to forests. In many instances throughfall S fluxes have been shown to effectively estimate total atmospheric deposition to forests, as most of the dry-deposited S is removed by precipitation and little S is leached from the canopy (Joslin and Wolfe, 1992; Lindberg and Lovett, 1992; Butler and Likens, 1995). For N deposition, however, it is common for 20–40% of the deposited N to be retained by the canopy (Johnson and Lindberg, 1989; Marshall and Cadle, 1989; Schulze, 1989; Cadle *et al.*, 1991; Friedland *et al.*, 1991; Hanson and Garten, 1992; Lovett, 1992; Lovett and Lindberg, 1993). Extensive data from the twelve sites of the Integrated Forest Study indicated that approximately 40% of the N deposited to the forest was consumed in the canopy (Lovett and Lindberg, 1993). Thus, atmospheric deposition of N from throughfall is underestimated, although Butler and Likens (1995) reported that throughfall estimates of N deposition in an eastern hardwood stand agreed with dry deposition estimates based on the inferential method. Leaching from internal plant tissues of the more leachable ions (most notably K^+) can also complicate the estimation of atmospheric deposition from throughfall data (Parker, 1983).

This paper presents data from a study of summertime deposition measured in rainfall and throughfall from the major overstorey species at Barton Flats (BF), a low to moderate pollution site in the SBM. Data are also presented on winter and early spring bulk deposition, and fog plus dry deposition of N and S at three sites across an air pollution gradient in the SBM (including BF). This study was part of a larger study on the effects of acidic deposition and ozone on conifer forests in the SBM. The primary objectives of the study were to: (1) determine growing season throughfall deposition at BF, (2) compare throughfall ionic composition in pine, fir and oak at BF, (3) compare throughfall ion concentrations in this summer dry climate with forests receiving higher precipitation during the growing season, and (4) measure winter bulk deposition and fog deposition at sites traversing a deposition gradient in the SBM.

METHODS

Study sites

Atmospheric deposition was studied in the mixed conifer zone in the SBM east of Los Angeles. Pollutant concentrations are greatest in the western end of the range, adjacent to the urban centers east of Los Angeles. Winter wet and bulk deposition were collected for one season at Camp Paivika (1600 m elevation), a western high-pollution site, and at two relatively low-deposition eastern sites, BF (1976 m) and Heart Bar (2160 m; Fig. 1a). Throughfall and precipitation data were collected during the growing season from 1992 to 1994 in three vegetation plots established in 1991 near BF (Fig. 1b). The three plots are located within a 3.2 km radius of a complete air monitoring station at BF. Precipitation samples were collected and meteorological data were measured year-round at the monitoring station at BF. The forest is of the mixed conifer type with four dominant overstorey species, ponderosa pine (*Pinus ponderosa* Laws.), Jeffrey pine (*Pinus jeffreyi* Grev. & Balf.), white fir (*Abies concolor* Gord. & Glend.) and California black oak (*Quercus kelloggi* Newb.). The forest stands in the plots are relatively open, with canopy cover over ca. 67% of the stands.

Criteria for plot site selection were largely those prescribed by Miller *et al.* (1996) and included: the presence of at least 40 dominant, codominant or intermediate ponderosa and Jeffrey pine trees within or contiguous to the boundary of a 40 m × 120 m area, no more than 250 m difference in elevation between the three plots, minimal site disturbance, and similar soil, slope, aspect, vegetation species and age composition. Barton Flats is within a transition zone in the SBM for yellow pine, where a mixture of the closely related ponderosa and Jeffrey pines occurs. For purposes of this study, data on ponderosa and Jeffrey pine throughfall are combined and not differentiated. Little Jeffrey pine was found in plot 1, basal area of ponderosa pine was 2.8 times greater than Jeffrey pine in plot 3, and Jeffrey pine basal area was 1.6 times greater than for ponderosa pine in plot 2.

Rainfall and throughfall

Throughfall and rainfall were collected in the three plots at BF using the flip-top collectors described by Glaubig and Gomez (1994). The diameter of the throughfall collection cylinders was 10 cm (cross-sectional area = 79 cm^2). The throughfall collectors were designed to remain closed until a slight amount of precipitation collected in a small funnel wet a narrow strip of dissolvable "magic" paper (Magic World, Chatsworth, CA). When the paper dissolved, a counter weight was released causing the lid of the collector to flip open. Collection efficiency of the flip-top collectors in field trials was equal to that of a constantly open Belfort gravimetric rain gauge (Glaubig and Gomez, 1994). Rain was collected using the flip-top collectors in stand openings free of canopy influences, but adjacent to throughfall collector trees. Throughfall collectors were placed 0.85–1.05 m from the trunk of mature dominant Jeffrey or ponderosa pine, white fir, or California black oak trees. Trees free of canopy interference from neighboring trees were chosen for throughfall collection. The number of collectors under each species and ions measured in each of the three years are given in Table 1.

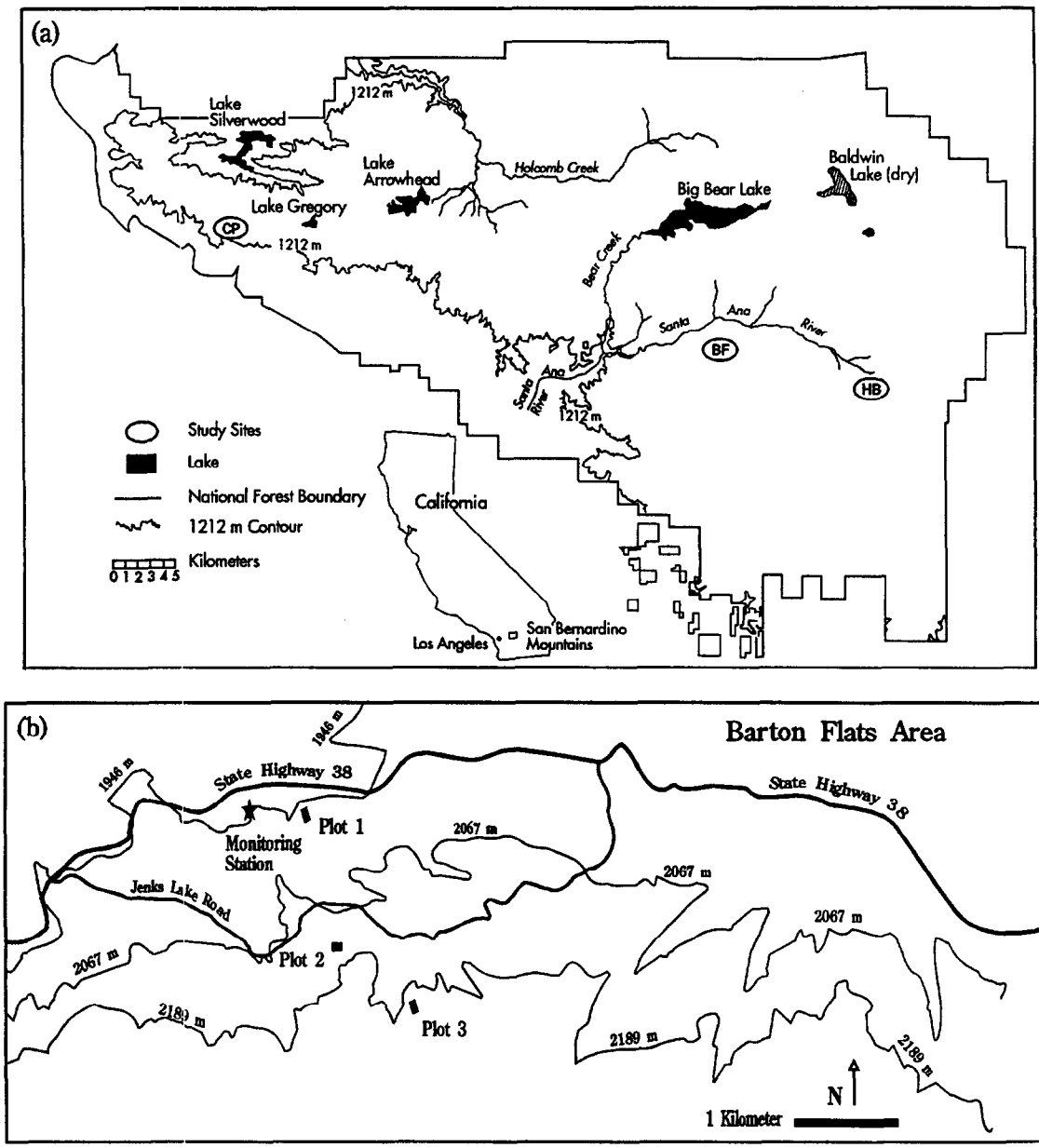

Fig. 1. (a) Map showing sites in the San Bernardino National Forest (CP is Camp Paivika, BF is Barton Flats, and HB is Heart Bar) where precipitation and winter deposition samples were collected. (b) Map showing the location of plots 1–3 and the monitoring station at Barton Flats.

Anion concentrations in rain and throughfall were determined with ion chromatography (Dionex* series 4000i, Sunnyvale, CA), NH_4^+ was determined colorimetrically (Technicon TRAACS 800, Autoanalyzer, Tarrytown, NY), and other cations by atomic absorption spectroscopy (Perkin-Elmer 5000, Norwalk, CT). In each year of the study, throughfall and rainfall were collected at BF with flip-top collectors during the spring, summer and early fall periods. Wet deposition samples were collected year-round only at the monitoring station near plot 1 at BF, with an Aerochem Metrics Model 301 automatic sensing wet/dry precipitation collector (Aerochem Metrics Inc., Bushnell, FL). Although year-round throughfall input data are not available for BF, annual deposition inputs were estimated from branch rinse data and other known deposition parameters (Bytnerowicz *et al.*, 1996). Stand-level throughfall inputs during the growing season were determined in plots 1 and 2 in 1993 and in 1994. Stand-level throughfall deposition was not calculated for 1992 because throughfall was collected only under Jeffrey and ponderosa pine during that year (Table 1). Total throughfall inputs in plots 1 and 2 were determined by extrapolation from deposition to the area covered by the collector openings (using the average of all the replicate collectors) to the total area covered by the canopies of that

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Table 1. Number of throughfall and rain collectors and ions measured in the three plots at Barton Flats during the three-year study

Year	Plot	Rain	Throughfall			Ions measured
			Pine	Fir	Oak	
1992	1	3	22	—	—	All ions[a] and pH
1992	2	3	24	—	—	All ions[a] and pH
1992	3	3	24	—	—	All ions[a] and pH
1993	1	6	22	10	10	All ions[a] and pH
1993	2	6	24	10	10	All ions[a] and pH
1993	3	6	24	—	—	All ions[a] and pH
1994	1	6	10	10	10	NO_3^-, NH_4^+, SO_4^{2-}
1994	2	6	10	10	10	NO_3^-, NH_4^+, SO_4^{2-}

[a] NO_3^-, NH_4^+, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, and PO_4^{3-}.

species. This was done for pine, fir and oak. Data from each rain event in a given season were summed to obtain seasonal totals for rain and throughfall inputs.

Rainfall inputs were calculated in a similar manner to throughfall: The content (concentration × volume) of each ion in the open collectors was determined and averaged. Rain deposition per land area was determined by extrapolation from deposition to the land area covered by the collector openings to the open area of the plot. The percent of the plot which was open or uncovered by canopy was determined by subtracting the total drip areas of all the trees in the plot from the total plot ground area, and also from image analysis of aerial photographs. Both methods were in close agreement. Combining the value for rainfall deposition in the open portion of the forest with gross throughfall deposition under the canopy areas provided an estimate of total atmospheric deposition in the plot during the sampling period. Net throughfall was calculated as total deposition in the plot minus deposition in rain for the entire plot.

Winter deposition at three San Bernardino mountain sites

Winter and early spring deposition of air pollutants in the form of rain, snow, fog and dry deposition was monitored at three sites across a west to east atmospheric deposition gradient in the SBM (Fig. 1a; Fenn and Bytnerowicz, 1993). Flip-top throughfall and rainfall collectors (Glaubig and Gomez, 1994) were modified for collecting winter/spring wet deposition. Modifications included replacing the butyrate plastic inner and outer collection cylinders with a polyvinylchloride (PVC) capped tube; this tube was approximately 75 cm deep to allow for heavy snowfall collection. In addition, the triggering papers for the winter/spring deposition collectors were lightly sprinkled with NaCl which hastened the melting of snow necessary for triggering the collectors to open. Three replicate wet-only collectors at each site remained closed with a flip-top lid until a precipitation event. Three bulk collectors without lids were also located adjacent to the wet-only collectors at each site. Samples were collected for analysis shortly after each storm event. Wet deposition samples were collected at Camp Paivika (CP), BF and Heart Bar (HB) on eleven dates from 13 December 1993 through 11 April 1994. Samples were collected on four additional dates at CP only, with the last collection on 1 June 1994. Samples were analyzed for SO_4^{2-}, NH_4^+, and NO_3^- as described for the analysis of throughfall and rainfall.

A passive line collector design was used to collect fog/dry deposition during the same period that winter wet deposition was collected at CP, BF and HB. Nylon lines arranged in parallel constituted the collection surface for dry deposition and fog condensation. The frame of the collectors consisted of büchner funnel bases (11.8 cm i.d.) at each end which were connected with three tri-sided plexiglass rods. Using the existing holes in the büchner funnels, 108 nylon lines 50 cm in length were strung between the funnels. The collectors in the field were covered with a 1.2 m × 1.2 m roof of polyethylene sheeting to exclude rain and snow from contacting the collectors. The fog condensate collected by the nylon lines ran down the lines through a funnel and into a polypropylene bottle. The nylon lines were also rinsed with purified distilled water at the time of sample collection. Fog condensate and line rinse samples were collected approximately every 14 d. Both the condensate and rinse water were saved for chemical analysis as described above. Sample collection at CP, BF and HB occurred from 3 December 1993 until 6 April 1994. Sample collection continued at CP until 1 June 1994.

Statistical analyses

Data analysis was performed using SigmaStat™ statistical software from Jandel Scientific Software (San Rafael, CA). Because of the variability inherent in throughfall, differences were considered statistically significant at $P < 0.10$. Differences in concentrations of ions in rain and throughfall were tested by two-way ANOVA, with plots as blocking factors and rain or throughfall plant species as the second factor. Bonferroni's all pairwise multiple comparison procedures were used to test for differences among species. When data failed the normality test, the Kruskal–Wallis two way analysis of variance on ranks test was used, followed by Dunn's all pairwise multiple comparison procedures (Fox *et al.*, 1994). All statistical tests on pH results were performed with the data expressed as hydrogen ion concentrations (H^+). Likewise, average pH values were determined from average H^+ concentrations.

RESULTS

Rain and throughfall volumes

Total annual precipitation at the BF monitoring station near plot 1 was 59 cm in 1992, 89 cm in 1993, and 38 cm in 1994. Precipitation inputs were mainly as winter snow. Average summer rainfall in the three plots, and the percent of annual precipitation occurring during the summer collection periods, were

Table 2. Total summertime (late May to mid-November) rain and throughfall volumes (cm precipitation) and average pH at Barton Flats

		Throughfall		
Year	Rain	Oak	Pine	Fir
Precipitation and throughfall (cm)				
1992	9.37 (0.46) a	—	5.13 (0.18) b	—
1993	5.93 (0.20) a	5.65 (0.27) ab	5.17 (0.12) b	3.97 (0.32) c
1994	1.82 (0.09) a	0.52 (0.05) b	0.37 (0.04) c	0.20 (0.03) d
pH				
1992	4.28 b	—	4.11 a	—
1993	4.57 b	4.89 b	4.23 a	4.44 b

Note: Letters following numbers indicate significant differences between rain and throughfall within a given year (across the row; $p \leq 0.10$). Values in parentheses are standard errors of the plot mean

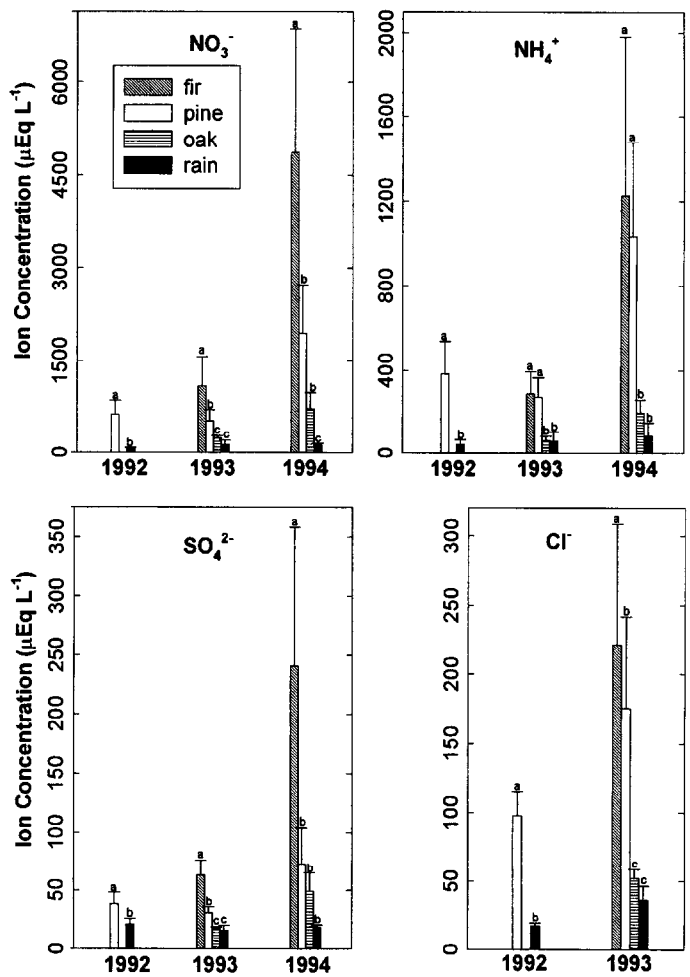

Fig. 2. Volume-weighted mean concentrations of NO_3^-, NH_4^+, SO_4^{2-} and Cl^- in rain and throughfall of three species at Barton Flats in summer 1992–1994 (data from all plots combined). Note the varying scales for the *y*-axes. Letters above bars indicate significant differences between rain and throughfall of the three species within a given year ($p \leq 0.10$). Standard error bars are also presented.

9.37 cm (15.8%) in 1992, 5.93 cm (6.6%) in 1993 and 1.82 cm (4.8%) in 1994 (data for only plots 1 and 2 in 1994). Rainfall volumes were usually greater than throughfall volumes except under occasional conditions of persistent fog. Rain and throughfall volumes generally decreased in the following order: rain > oak > pine > fir throughfall (Table 2).

Ionic concentrations in rain and throughfall of three species

Ionic concentrations in throughfall and rainfall generally decreased in the following order: fir > pine > oak and rain (Figs 2 and 3). Ionic concentrations in throughfall were usually higher in 1994 than the previous two years, while ion concentrations in rain differed little from year to year (Figs 2 and 3). Passage through pine canopies resulted in throughfall that was more acidic than precipitation. Interaction with oak and fir canopies had no significant effect on throughfall pH (Table 2).

Stand-level throughfall and rainfall deposition

Total inorganic N (NH_4^+ plus NO_3^-) deposition at BF from rain and throughfall in summer 1993 was 4.0 kg ha^{-1}, and deposition of SO_4–S was 0.4 kg ha^{-1}. Nitrogen and S deposition in summer 1994 were 1.9 and 0.2, respectively. The proportion of total summer throughfall N and S deposition as net throughfall was 1.4–2.1 times greater in 1994 (1.82 cm summer precipitation) than in 1993 (5.93 cm summer precipitation; Fig. 4).

Monthly trends in precipitation volumes and wet deposition of N and S at the monitoring station near plot 1 at BF indicated that peaks in wet deposition during the winter were associated with high monthly precipitation volumes (11–44 cm; Fig. 5). However, similar peaks in wet deposition inputs during August in these same years occurred with only 1.4–3.4 cm of rain. Total annual wet deposition of NO_3–N, NH_4–N and SO_4–S at the BF monitoring station was low, ranging from 0.33 to 0.98 kg ha^{-1} in 1992–1994 (Table 3).

Winter deposition at three sites traversing the San Bernardino Mountains

Winter and early spring deposition of N and S is clearly minimal at HB and BF compared to the western site at CP (Fig. 6). The molar ratio of

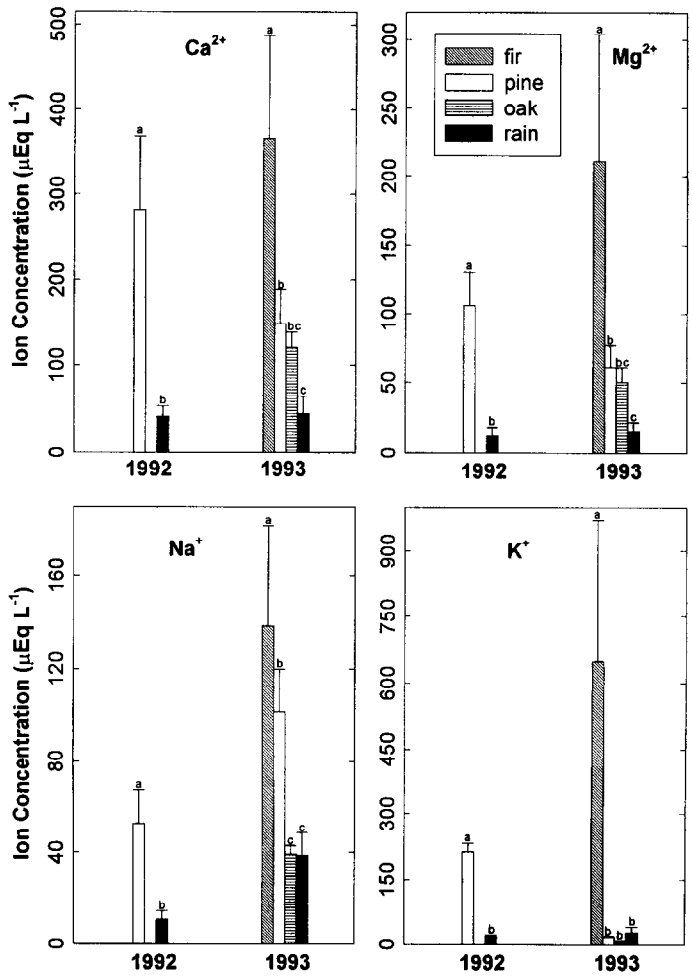

Fig. 3. Volume-weighted mean concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ in rain and throughfall of three species at Barton Flats in summer 1992 and 1993 (data from all plots combined). Note the varying scales for the *y*-axes. Letters above bars and error bars are as described in Fig. 2.

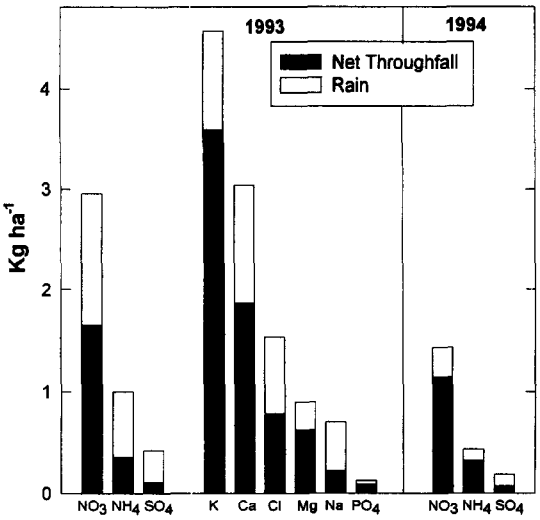

Fig. 4. Net throughfall (total throughfall-deposition–rainfall-deposition) and rain deposition at Barton Flats during the summer of 1993 (5/17–11/15) and 1994 (8/12–10/18; data combined for plots 1 and 2).

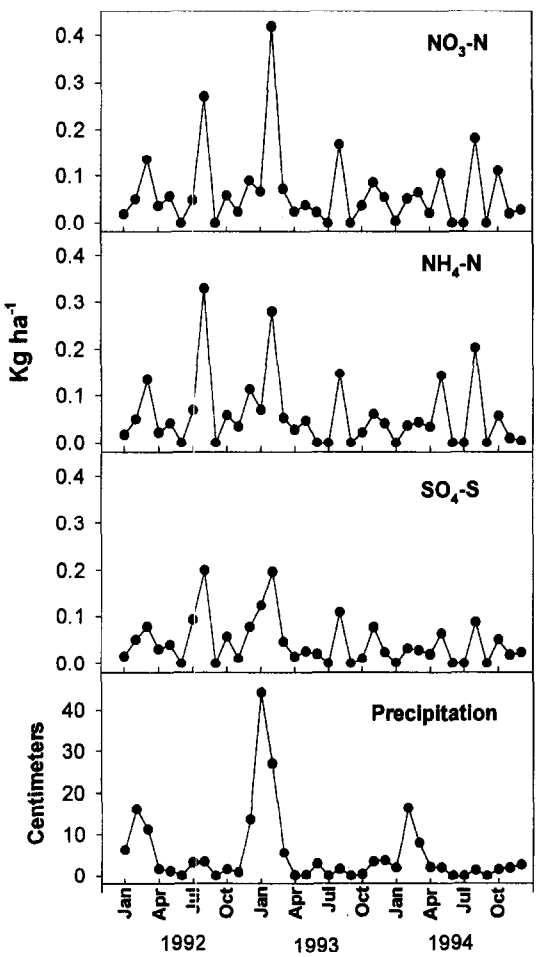

Fig. 5. Monthly precipitation and wet deposition of N and S for 1992–1994 at the Barton Flats monitoring station.

NO_3:NH_4:SO_4 in bulk deposition at CP was 5.6:4.6:1.0. Dry deposition of NO_3^- appears to be greater than NH_4^+ if we assume the difference in deposition between the bulk deposition vs wet-only samples is an indication of dry deposition. Dry deposition in winter/spring caused a noticeable increase in cumulative N deposition, and to a lesser degree, of S deposition at CP (Fig. 6). The cumulative total of bulk deposition of NH_4–N at CP from 11 precipitation events was 3.37 kg ha^{-1}, but only 0.38 and 0.19 kg ha^{-1} at BF and HB, respectively. Analogous values for NO_3–N at CP were 4.32 kg ha^{-1} compared to 0.49 and 0.35 kg ha^{-1} at BF and HB (Fig. 6). After 11 collection dates, cumulative SO_4–S deposition at CP totaled 1.73 kg ha^{-1} compared to 0.32 and 0.19 kg ha^{-1} at BF and HB. Total inorganic N ($NH_4^+ + NO_3^-$) and S deposition to the modified

Table 3. Annual wet deposition (kg ha^{-1}) of inorganic N and S at the monitoring station near plot 1 at Barton Flats

Year	Precipitation (cm)	NO_3–N	NH_4–N	SO_4–S
1992	59.3	0.78	0.87	0.65
1993	89.3	0.98	0.75	0.65
1994	37.9	0.58	0.53	0.33

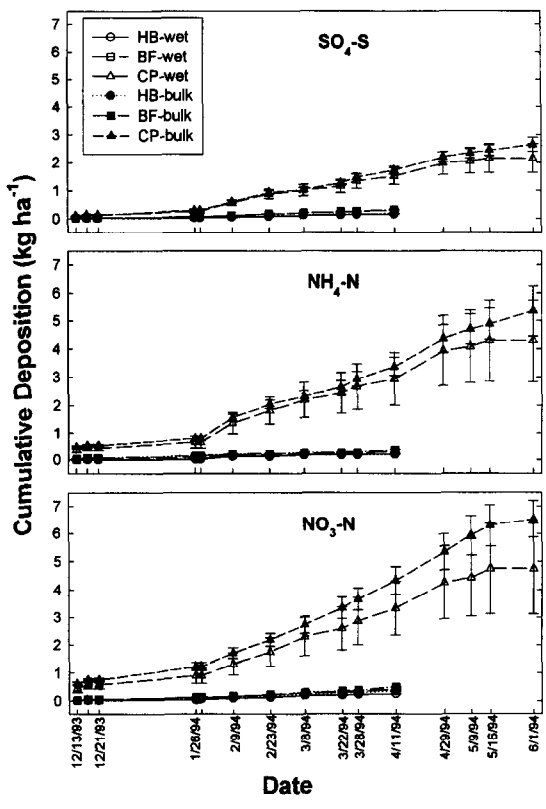

Fig. 6. Cumulative wet and bulk deposition at Heart Bar (HB), Barton Flats (BF), and Camp Paivika (CP) during the winter and early spring of 1993/1994. Error bars represent standard errors of the plot mean.

bulk collectors at CP from 13 December 1993 to 1 June 1994 (15 collection dates) were 11.9 and 2.7 kg ha^{-1}, respectively (Fig. 6).

Fog and dry deposition to nylon line collectors also clearly demonstrated the greater magnitude of N deposition compared to S deposition. The molar ratio of NO_3:NH_4:SO_4 in the fog plus dry deposition samples at CP was 98:50:1. By the end of the eighth collection on 6 April 1994 cumulative deposition to the fog and dry deposition collectors (mg m^{-2}) at CP, BF and HB was 17.21, 1.18 and 1.38, respectively, for NO_3–N, and 3.86, 0.21 and 0.14 for NH_4–N. Analogous values for SO_4–S were 0.32, 0.06 and 0.04 mg m^{-2} at CP, BF and HB. Cumulative deposition (mg m^{-2}) to the collectors at CP on the last collection date on 1 June 1994 increased dramatically to 43.73 for NO_3–N, 22.12 for NH_4–N and 1.02 for SO_4–S.

DISCUSSION

Summer throughfall and wet deposition at Barton Flats

Atmospheric deposition of N, S, and presumably of other nutrients at BF, are not expected to cause serious perturbations in nutrient cycling, according to our current understanding of atmospheric deposition effects on forests (Dise and Wright, 1995; Fenn *et al.*, 1996). However, cumulative long term effects cannot be ruled out. Recent studies in the San Bernardino and San Gabriel Mountains suggest that the threshold N deposition level at which N saturation effects are evident in these mixed conifer forests is approximately 25 kg ha^{-1} yr^{-1} (Fenn *et al.*, 1996). A survey of 65 forested plots throughout Europe also indicated that above a N deposition threshold of 25 kg ha^{-1} yr^{-1} significant N saturation occurs, as evidenced by N leaching (Dise and Wright, 1995). The estimated summertime deposition levels at BF for 1993 and 1994 of 1.9–4.0 kg ha^{-1} for N ($NH_4^+ + NO_3^-$) and 0.2–0.4 for S are within expected deposition levels for this area (Fenn and Bytnerowicz, 1993). Calculations of annual N deposition in plot 2 at BF, based on branch rinse data, yielded an estimate of 4–8 kg N ha^{-1} yr^{-1}, with deposition varying based on estimated stand leaf area index values obtained using two different methods (Bytnerowicz *et al.*, 1996). Fenn and Bytnerowicz (1993) calculated (from branch rinse data) annual wet and dry deposition inputs of 6.0 and 0.9 kg ha^{-1} yr^{-1} for N and S at Camp Osceola, located approximately four km east of BF. However, the deposition of N at BF may be as much as 25–40% greater than the throughfall and branch rinse estimates due to canopy retention of N (Lovett and Lindberg, 1993). Although N input estimates for the BF area are well below the levels associated with N saturation in the San Gabriel and San Bernardino Mountains (Riggan *et al.*, 1985; Kiefer, 1995; Fenn *et al.*, 1996; Kiefer and Fenn, 1996), N inputs are not trivial, especially when considered in the long term. Annual N deposition at BF is similar to expected annual vegetation increment of N (N necessary to build woody tissue) in dry environments such as in the SBM (Johnson, 1992).

Except for the few relatively high-volume summer rain events which only occur in some years, throughfall in summer is not likely to provide a major nutrient source via root uptake for overstorey tree species. Shallow roots probably periodically utilize wet-deposited nutrients following summer rain events of sufficient magnitude to infiltrate the upper rooting zone. Air pollutants likely also provide plant nutrients as a variable fraction of the nutrient ions and gaseous pollutants intercepted by the canopy are taken up directly by foliage and assimilated (Lovett and Lindberg, 1993; Lovett, 1994; Fenn and Leininger, 1995; Krywult *et al.*, 1996).

Ionic concentrations in rain at BF were generally within the range of values reported for highly polluted forest sites, except for NO_3^- which was commonly several-fold higher in rain at BF plot 1 than the highest concentration reported for rain in a number of studies in Europe and eastern North America. Ionic concentrations in throughfall at BF were frequently many-fold greater than forests with greater annual deposition inputs (Lindberg *et al.*, 1990; Probst *et al.*, 1990; Stevens *et al.*, 1990; Mitchell *et al.*, 1992; Wesselink *et al.*, 1995). Compared to highly-polluted forests in Germany and The Netherlands (Van Breemen *et al.*, 1987; Lamersdorf and Meyer, 1993; Wesselink *et al.*, 1995), throughfall NO_3^- concentrations were greater at BF, SO_4^{2-} concentrations were lower at BF, and NH_4^+ concentrations were comparable between BF and the European studies. The high summertime throughfall concentrations at BF were most likely due to washoff of dry pollutants, accumulated on the forest canopy during long dry "smoggy" periods, by intermittent low-volume rain events. Throughfall intensity has been found to be inversely correlated with ionic concentration of throughfall (Lovett and Schaefer, 1992; Hansen *et al.*, 1994). In this study, the lowest rainfall was in 1994, and corresponded with the highest throughfall concentrations of the three years and the greatest net-throughfall:rain-deposition ratio. Net throughfall is a measure of dry deposition minus deposition which is retained by the canopy (Lovett, 1994; Van Ek and Draaijers, 1994).

Summer throughfall concentrations in the western SBM are expected to be much greater than at BF, since annual N deposition inputs in the western SBM are about five times greater than in the BF area (Fenn and Bytnerowicz, 1993). Throughfall deposition of N was 6.2 and 10.8 kg ha^{-1} yr^{-1} over a four-year period in two stands near Giant Forest in Sequoia National Park in the southern Sierra Nevada Mountains of California (Chorover *et al.*, 1994). These deposition values are similar to estimated deposition inputs at BF. Ionic concentrations in throughfall in the Giant Forest stands were also relatively high during the summer compared to literature values.

However, throughfall NO_3^- and NH_4^+ concentrations were not as high as at BF, probably because of greater summer rain amounts in the Sierra Nevada sites.

The high plant surface areas of the dominant overstorey trees (especially fir and pine) above the throughfall collectors at BF was undoubtedly a major factor causing the high throughfall concentrations. Higher foliage surface area results in higher canopy interception and retention of water from rain and of dry-deposited gases and particles. Oak trees had the lowest leaf surface area above the collectors and fir the highest (Fenn, unpublished data). The lower ionic concentrations and higher volumes of oak throughfall reflect the reduced contact between precipitation and the oak canopy compared to the fir canopy. Throughfall deposition inputs (mg/collector; data not shown) also followed the pattern of ionic concentrations, with highest deposition under fir and pine, intermediate under oak, and lowest deposition in rainfall. Studies in The Netherlands have also reported higher leaf areas and net throughfall deposition in Douglas-fir (*Pseudotsuga menziesii* Mirb. Franco), intermediate values for Scotch pine (*Pinus sylvestris* L.) and Corsican pine (*P. nigra* var. *maritima* Ait. Melville), and lowest leaf areas and deposition with oak (*Quercus robur L.*; Houdijk and Roelofs, 1991; Van Ek and Draaijers, 1994).

Annual N deposition in throughfall to forests in south-central Ontario Canada was over twice as high as at BF, yet maximum NO_3^- and NH_4^+ concentrations in throughfall over a three year period were $< 90\ \mu Eq\ \ell^{-1}$ (Neary and Gizyn, 1994) compared to several thousand $\mu Eq\ \ell^{-1}$ of NO_3^- and NH_4^+ at BF in 1994 when summer precipitation was lowest. In the Canadian forests annual precipitation was greater than 100 cm each year, and was evenly distributed between the dormant season and the growing season (Neary and Gizyn, 1994), thus transporting solutes to the forest floor in larger volumes and as more dilute solutions, compared to summertime throughfall fluxes at BF.

Winter deposition across the air-pollution gradient in the San Bernardino Mountains

The results of this study suggest that winter and early spring deposition of N and S in the SBM is greater than previously thought. A recent study reported that NO_3^- and SO_4^{2-} concentrations in rime ice and snow at Strawberry Peak in the western SBM were higher than at montane sites in central and northern California (Berg *et al.*, 1991). However, only ion concentration data were presented, and no attempts were made to determine landscape level nutrient loadings in rime ice and snow. Bulk deposition of N and S in canopy-free areas in winter and early spring (5.5 months) was 11.9 and 2.7 $kg\ ha^{-1}$ at CP. Presumably, deposition to the forest canopy during the winter and early spring would be considerably higher due to the high surface area of conifer foliage for scavenging of dry gases, particles, fog and precipitation. Somewhat surprisingly, wet deposition of NH_4^+ (4.29 $kg\ ha^{-1}$) was similar to wet deposition of NO_3^- (4.74 $kg\ ha^{-1}$) at CP, possibly due to precipitation scavenging of NH_4NO_3. Ammonia emissions from the dairy farms concentrated in the Chino area approximately 30 km to the west may be a significant source of the high inputs of NH_4^+.

The increase in total deposition of NO_3^- in the bulk collection compared to the wet-only collection was greater than for NH_4^+. This suggests that dry deposition of NO_3^- in winter and early spring is greater than dry deposition of NH_4^+; an observation that has been well-established for summertime measurements in montane areas of the Los Angeles Air Basin (Bytnerowicz *et al.*, 1987b; Fenn and Bytnerowicz, 1993). Nitric acid vapor is probably a major source of the greater dry deposition of NO_3^- compared to NH_4^+ (Bytnerowicz *et al.*, 1987a; Solomon *et al.*, 1992). It should be noted, however, that the open-cylinder collectors were not designed for efficient collection of dry particles and gases. The primary purpose of the collectors was for site comparison and as a surrogate measure of the relative magnitude of winter and early spring dry and wet deposition inputs at three sites traversing the atmospheric deposition gradient in the SBM. Nevertheless, the data clearly indicate that in high-deposition areas such as CP in the western SBM, winter and early spring inputs of N are an important component of the annual N budget, and that dry deposition contributes significantly to the overall winter and spring deposition loading.

This study confirms that wet and dry deposition of N and S vary greatly across the air pollution gradient in the SBM in the winter and spring as well as during the summer smog season (Fenn and Bytnerowicz, 1993). The fog/dry deposition collectors also confirmed the deposition gradient in the SBM, but the deposition fluxes cannot be quantitatively related to deposition fluxes to the forest canopy and forest floor, nor can the relative importance of the fog and dry deposition components be determined. Currently, year-round throughfall and fog collections are underway at CP and BF with the aim of determining annual N and S throughfall and fog inputs on the western and eastern ends of the deposition gradient.

High winter and springtime N and S inputs may have important effects on nutrient cycling when snowmelt releases concentrated nutrient pulses into the soil. Plant nutrient uptake may be high in the spring due to concomitant high soil water availability, increasing temperatures and nutrient release from snowmelt. A variety of nutritional indicators from CP suggest that this site is N saturated, presumably as a result of at least four decades of N deposition on the order of 25–45 $kg\ ha^{-1}\ yr^{-1}$ (Fenn and Bytnerowicz, 1993, for summer dry deposition; and winter/spring deposition data in this study). Available N at CP seems to be in excess of biotic demand based on: (1) the lack of response in ponderosa pine (*Pinus ponderosa* Laws.) to N fertilization (Kiefer and

Fenn, 1996), (2) high soil NO_3^- concentrations in the soil solution, (3) high fluxes of nitric oxide (NO) from soil, (4) accumulation of NO_3^- in foliage, and (5) high foliar N:P ratios and low soil C:N ratios (Fenn *et al.*, 1996). Temporal changes in soil pH and C:N ratios over the last 20 yr also suggest that the soil at CP has become more acidic and N enriched (Fenn *et al.*, 1996). The available evidence suggests that the primary pathway for short-term plant uptake and utilization of atmospherically deposited N is via throughfall transport of N into the rooting zone of the forest floor and soil, although canopy uptake of N undoubtedly occurs as well (Fenn and Leininger, 1995).

SUMMARY

Summertime throughfall nutrient pulses in the SBM are likely to provide a source of nutrients for limited direct canopy uptake and for root uptake when rain volumes are sufficient to transport nutrients into the rooting zone. However, atmospheric deposition of N, S and other nutrients at BF are below the levels believed to cause short-term perturbations in nutrient cycling processes in temperate forests. Ionic concentrations in throughfall at BF were as high or higher than typically reported for many highly-polluted forests in Europe and eastern North America because of the accumulation of dry deposition on the extensive canopies of large trees, followed by washoff in infrequent low-volume rain events. Throughfall concentrations were highest under white fir, the species with the greatest foliar surface area, and lowest under black oak. Washoff of NO_3^- and NH_4^+ from the canopy led to very high concentrations of these ions. Concentrations of cations and of Cl^- in throughfall were also high relative to rainfall concentrations. The acidity of rainfall ranged from 4.28–4.57 while throughfall acidity ranged from 4.11–4.89. Throughfall was not highly acidic compared to rainfall, due to the high concentrations of basic cations accompanying the more acidic components.

The steep west-to-east deposition gradient previously characterized for the dry summer "smog" season in the SBM appears to be an annual phenomenon, as evidenced by winter and early spring bulk and fog deposition. Total N and S bulk deposition during five and one-half months in the winter/spring period at CP was 11.9 and 2.7 $kg\,ha^{-1}$. Winter and springtime deposition of N may be especially important in the nutrient cycle if snow melt releases and transports N into the soil for microbial and plant uptake during the annual spring growth flush, as has been shown for California montane systems (Williams *et al.*, 1995). Winter and springtime deposition of N appears to be of sufficient magnitude to contribute significantly to N saturation at CP. High winter deposition of N suggests that previous estimates of total annual N deposition at CP (Fenn and Bytnerowicz, 1993) may be too low. Annual deposition of N is roughly estimated to be on the order of 35–45 $kg\,ha^{-1}yr^{-1}$ at CP and 6–10 $kg\,ha^{-1}yr^{-1}$ at BF. Sulfur inputs are estimated to range from 3 to 5 $kg\,ha^{-1}yr^{-1}$ at CP and 1 to 2 $kg\,ha^{-1}yr^{-1}$ at BF. These estimates entail considerable uncertainty, however.

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