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Air Pollution and Changes in Forest Nitrogen Status:

Fog and Rain Deposition and Nitrogen Losses From Forested Watersheds in the San Bernardino Mountains

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
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Research Division

AIR POLLUTION AND CHANGES IN FOREST NITROGEN STATUS: FOG AND RAIN DEPOSITION AND NITROGEN LOSSES FROM FORESTED WATERSHEDS IN THE SAN BERNARDINO MOUNTAINS

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information leading to preferred management options for protecting water quality in watersheds receiving high atmospheric N loads.

Nitrogen export from the forest also occurred as gaseous nitric oxide (NO) emissions from soil. Estimated annual NO flux rates from soil were 4.5 kg N ha^{-1} yr^{-1} at Camp Paivika and 0.25 kg ha^{-1} yr^{-1} at Camp Osceola (a site 4 km east of Barton Flats). Annual NO emission rates from Camp Paivika were among the highest reported for temperate forests, and constitute a significant ecosystem N loss. Gaseous N losses at Camp Osceola were more typical of relatively undisturbed forests.

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Abstract

The primary objective of this project was to address knowledge gaps in our understanding of the effects of N deposition on forest ecosystems in California. This study was carried out at key sites located across an air pollution gradient in the San Bernardino Mountains. The research entailed three major components: measuring nitrogen (N) deposition to the forest in fog and throughfall, determining spatial and temporal patterns of nitrate (NO_3^-) export in streamwater, and quantification of trace gas fluxes from soil at a high and a low-to-moderate N deposition site. We estimate that N deposition in fog contributed 21% of the total annual N deposition at Barton Flats (1.0 kg ha^{-1} yr^{-1}) and 43% at Camp Paivika (13.4 kg N ha^{-1} yr^{-1}). Although fog water inputs were low compared to rain and snow, N deposition in fog was significant because of the high ionic concentrations in fog and the frequency of occurrence, especially in the western San Bernardino Mountains. Annual throughfall deposition of N was 19 kg ha^{-1} yr^{-1} at Camp Paivika (CP) and 2.9 at Barton Flats (BF). Total forest stand-level N deposition was estimated to be 31 and 5 kg ha^{-1} yr^{-1} at CP and BF, based on literature values of throughfall underestimation of total atmospheric N deposition. The throughfall data from this study demonstrated that N inputs that are associated with N saturated sites in the San Bernardino Mountains are similar to levels reported to cause N saturation or elevated streamwater nitrate export in more mesic forests.

We report streamwater nitrate (NO_3^-) concentrations from 19 sampling sites across the deposition gradient in the SBM for December 1995 through December 1997. Sampling frequency varied from biweekly during the first winter rain season to predominantly monthly thereafter. Six streams (seven sampling sites) are in Devil Canyon (DC), a high-pollution area on the western end of the range. Twelve of the streams sampled are located in a horseshoe pattern surrounding the San Gorgonio Wilderness (SGW) on the eastern end of the SBM, a region which is characterized by relatively low-to-moderate N deposition. Streamwater NO_3^- concentrations in DC are the highest values reported in North America for undisturbed watersheds. The streams in DC exhibited a wide range of temporal NO_3^- concentration profiles. Concentrations in the primary stream draining western DC peaked at 350 μeq L^{-1} in December 1997 and minimum baseflow NO_3^- concentrations were nearly always greater than 70 μeq L^{-1}. Nitrate concentrations at the source of a spring-fed stream averaged 70 ($\pm$0.9 s.e.) μeq L^{-1} in DC and 10.3 ($\pm$1.3) μeq L^{-1} in the SGW with little seasonal variation. Base flow NO_3^- concentrations in five of the six streams in DC were greater than base flow concentrations in all of the SGW streams. In the SGW, only the five catchments on the southwestern and western end (streams 1-5), where N deposition is greatest, consistently exported levels of NO_3^- well above detection limits. Peak NO_3^- concentrations in DC and in the SGW occurred after large winter storms, and a short-term large spike in NO_3^- export (10-370 μeq L^{-1}) in SGW streams 1-5 was observed after slight thundershower activity in July 1997. Streamwater NO_3^- concentrations in the 19 sampling sites corresponded with levels of N deposition across the N deposition gradient. Greater than expected spatial variation in streamwater NO_3^- concentrations within DC, an area of high N deposition, was attributed to differences in N processing within the upland catchments and riparian zone. Further studies of the factors responsible for the variability in streamwater NO_3^- in DC may provide useful

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conifer forests (Fenn et al., 1996) exposed to high levels of atmospheric N deposition. However, annual estimates of how much N may be lost from these ecosystems as trace gas emissions from soil have not been determined previously.

The purpose of this study was to fill in information gaps in our understanding of N inputs from atmospheric deposition processes, and to characterize ecosystem responses to N inputs in terms of N export in streamwater/groundwater and as gaseous emissions from soil. We report two years of data on streamwater NO_3^- and SO_4^{2-} concentrations from catchments located along N deposition gradients in the San Bernardino Mountains (SBM) in southern California. In addition, we report on trace gas emissions from soil at a high (Camp Paivika) and a low N deposition site (Camp Osceola), and we report on ionic concentrations and landscape-level estimates of N and S deposition in fog and throughfall.

MATERIALS and METHODS

Study sites

Fog and Throughfall Inputs

Fog was collected at Camp Paivika (CP), a western high-deposition site and at Barton Flats (BF) a relatively low-deposition site (Fig. 1). Barton Flats (1976 m elevation) is 42 km ESE of Camp Paivika (1600 m elevation). The active fog collector at CP was located on the roof of a building at the Camp Paivika childrens camp near the town of Crestline. The passive collectors were placed in the forest canopy ca. 0.5 km east of the childrens camp where previous studies have been reported (Fenn, 1991; Fenn and Bytnerowicz, 1997; Fenn et al., 1996). The active fog collector for BF was located on the roof of the BF monitoring station (Fenn and Bytnerowicz, 1997), and the passive collectors were located in mature pine trees along a 25 m transect adjacent to the monitoring station. Throughfall samples were collected from January 1996 to January 1997 at CP and at BF plot 2. Plot 2 is one of three experimental plots established in 1991 in a previously-funded ARB study (Miller et al., 1996). Major overstory species at CP are ponderosa pine (*Pinus ponderosa* Laws.), incense cedar (*Calocedrus decurrens* [Torr.] Florin.), California black oak (*Quercus kelloggi* Newb.), and to a lesser degree, sugar pine (*P. lambertiana* Dougl.). The understory at CP is dominated by bracken fern (*Pteridium aquilinum* var. *pubescens* Underw.). The dominant overstory species at BF are ponderosa pine and the closely-related Jeffrey pine (*Pinus jeffreyi* Grev. & Balf.), white fir (*Abies concolor* Gord. & Glend.) and California black oak.

Trace Gas Fluxes

Trace gas measurements from soil were done at CP and at Camp Osceola (CAO). Camp Osceola is located ca. 4 km east of BF and is a low N-deposition site. The trace gas flux chambers were located in open or clear areas, under pine trees, and under California black oak canopies. Two chambers were placed in the open, two under pine, and two under oak in two replicate plots at CP and two plots at CAO. Flux measurements were made monthly.

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The actuation system for the automatic collectors was designed as follows: A relative humidity (RH) sensor relays RH data to a Campbell data logger, which at a specified RH, is programmed to actuate a minifan in a horizontally-positioned PVC cylinder containing a wetness sensor. When moisture from the air passing over the sensor accumulates on the wetness sensor, a relay signal is transmitted to the power supply sending electricity to the collector fan, which opens the baffles and begins the fog collection.

Fog samples were collected from the passive and active samplers on a weekly basis when fog occurred. Fog events did not occur every week, especially during the dry summer months. The collector strings on the active sampler were cleaned with distilled water and the collection bottle replaced weekly. Fog samples collected by the active samplers (one per site) were analyzed for NO_3^- and SO_4^{2-} with ion chromatography (Dionex series 4000i, Sunnyvale, CA) and for NH_4^+ colorimetrically with a Technicon TRAACS 800, Autoanalyzer (Tarrytown, NY). Fog samples in the passive collectors were measured for volume in order to determine fog deposition rates per m^2 collector surface. The amount of fog deposited to the forest during the study was calculated as a factor of ionic concentrations in fog and the fog water deposition fluxes to the passive collectors. These calculations assumed that fog deposition fluxes to the canopy was similar to fluxes to the collector strings. The canopy surface area used to calculate ionic deposition in fog was conservatively estimated using a leaf area index (LAI) of 5.2, the lowest LAI published from several studies reporting LAI for ponderosa pine mixed conifer forests in the Western U.S. (Gholz, 1982; Grier and Running, 1977; McLeod and Running, 1988). During winter LAI values were reduced according to the percent of the stand composed of oak, due to winter defoliation as described previously (Fenn and Bytnerowicz, 1993).

Throughfall Inputs

Bulk throughfall (collector left open, thus including some dry deposition directly into the collectors) was collected using the flip-top collectors described previously (Glaubig and Gomez, 1994), except that the collector tops were not installed (the collectors were open at all times). The diameter of the cylinders was 10 cm (cross sectional area =79 cm^2). Throughfall was collected on an event basis. Collectors were placed in four parallel transects at each site with eight collectors per transect, for a total of 32 collectors per site. Along each transect, collectors were placed 8 m apart. At BF the transects were separated by 20 m. At CP one pair of north-south transects (20 m apart) was located on a west facing slope, and the second pair of north-south transects were located on the adjacent east-facing slope (ca. 50 m west of the first pair of transects).

Throughfall volumes were determined by weight. An equal percent volume subsample was collected from each of the eight collectors per transect and composited for chemical analysis (e.g., five percent of the sample volume was collected from each collector and combined to make one sample per transect). Ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}) concentrations were determined in the throughfall samples using liquid ion chromatography (Dionex series 4000i, Sunnyvale, CA). Throughfall deposition (kg ha^{-1} yr^{-1}) at each site (CP and BF) was determined as the average of the four replicate transects.

INTRODUCTION

Human alteration of the nitrogen (N) cycle is an environmental and ecological issue of major concern, both globally and at the catchment scale (Vitousek et al., 1997). A growing number of studies have identified forested areas exposed to chronic atmospheric N deposition which exhibit symptoms of N excess, analogous to over fertilization of arable land (Fenn et al., 1998; Stoddard, 1994). Excessive N loss is a symptom of terrestrial ecosystem dysfunction and results in degradation of water quality and potentially deleterious effects on aquatic systems. Degraded water quality (e.g., elevated NO_3^-) in forested catchments can be of particular concern when these water supplies are relied upon as pristine sources to improve the quality of polluted water sources (Riggan et al., 1985).

Mixed conifer forests and chaparral ecosystems directly exposed to air pollution from greater Los Angeles are N saturated based on data from a number of edaphic and plant indicators (Fenn et al., 1996; Riggan et al., 1985). Preliminary evidence suggests that symptoms of N saturation (N in excess of plant demand or elevated NO_3^- export in streamwater) are evident in sites receiving ca. 25 kg N ha^{-1} yr^{-1} or greater (Fenn et al., 1996; Kiefer and Fenn, 1997; Riggan et al., 1985). However, data quantifying N deposition inputs on the landscape scale in California are limited. Several studies indicate that deposition of N in fog and dry deposition is highly elevated on the western end of the San Bernardino Mountains (Fenn and Bytnerowicz, 1997; Fenn and Bytnerowicz, 1993), but deposition rates in throughfall and in fog have not been well characterized.

Forests in the summer-dry climate of southern California and possibly other semiarid Western ecosystems with chronic N deposition, may be prone to open or non-conservative N cycling (Fenn et al., 1998) because of active nitrification during all stages of N saturation and temporal asynchrony between hydrologic fluxes (highest in winter) and plant N demand (highest in spring/summer). Steep slopes and coarse-textured soils, typical in many watersheds, also contribute to high NO_3^- export fluxes, especially during the wet winter season. Few studies have addressed ecosystem processing of chronic N deposition in semiarid systems, but the available data clearly indicate the limited capacity of ecosystems with a Mediterranean climate to retain N within the terrestrial ecosystem (Fenn et al., 1996; Riggan et al., 1985; Riggan et al., 1994). Streamwater NO_3^- concentrations in smog-impacted summer-dry montane ecosystems in the Los Angeles Air Basin are among the highest in North America for natural catchments (Riggan et al., 1985). Nitrate concentrations in streamwater were as high as 1120 μeq l^{-1} in severely burned chaparral watersheds with high N deposition in the San Gabriel Mountains near Los Angeles (Riggan et al., 1994).

Nitrogen is also lost from N-enriched or N-saturated ecosystems as nitrogenous trace gases emitted from soil (e.g, nitric oxide (NO) or nitrous oxide (N_2O)). These trace gases are predominantly formed during the N-cycling processes of nitrification or denitrification. Emissions of NO are particularly high from chaparral (Anderson et al., 1988) and mixed

controllers (Porter Inc., Hatfield, PA). Fluxes of NO were calculated from the slope of the regression line of NO versus time (4 - 8 min) after correction of the NO concentration for dilution during sampling.

Analysis of Methane (CH_4) and Nitrous Oxide (N_2O)

For analysis of CH_4 and N_2O, samples were taken through a septum on the top of the flux box every 20 min for 1 hour using 60-ml disposable plastic syringes with rubber plunger tips and fitted with three-way stopcocks. Samples were analyzed for N_2O using a gas chromatograph (Hewlett Packard, model 5890, Palo Alto, CA) with electron capture detector and 10-port valve allowing backflushing of the column following each sample run. The detector temperature was 330°C, oven temperature 50°C, and the column used was a 2-m porapak Q, and argon plus 5% methane was the carrier gas at a flow rate of 30 ml min^{-1}. CH_4 in these samples was measured by gas chromatography with a flame ionization detector using a 2 m stainless-steel column containing 5μm molecular sieve. Detector temperature was 250°C with a column temperature of 70°C. Helium was used as the carrier gas at a flow rate of 30 ml min^{-1}.

KCl-Extractable Soil NH_4^+ and $NO_2^- + NO_3^-$

Measurements were made monthly for extractable mineral N. Samples were taken with a 5 cm PVC plastic coring device to a depth of 10 cm in the mineral soil. The surface organic horizons (O layers) and litter were separated from the mineral soil (A horizon). The organic material and the mineral soil were each extracted with 2 M KCl, using a modification of a previously-described technique (Keeney and Nelson, 1982). For analysis, a 5-g sample was weighed into a 50-ml screw cap centrifuge tube. The tube was sealed after adding 50-ml of 2 M KCl and mixed with a wrist action shaker for 1 hour. The tube was then centrifuged and the supernatant used for analysis. Ammonium and NO_3^- were determined colorimetrically using a Technicon Traacs autoanalyzer, Model 2000 (Technicon Corporation, Tarrytown, NY). Samples for analysis of percent moisture were collected as described above, stored in whirl-pak bags, weighed, and dried to constant weight at 105°C. Percent soil moisture is reported as percent of dry weight.

Streamwater Nitrogen Fluxes

Grab samples of streamwater were collected in triplicate in 60 ml polyethylene bottles prewashed in distilled/deionized water. Sample bottles were rinsed three times with streamwater prior to sample collection. Samples were then transported to the Forest Fire Laboratory and stored in a freezer until time of analysis. Samples were collected at varying intervals; usually once or twice per month during the winter wet season and monthly or bimonthly during summer. All streamwater samples were analyzed for NO_3^- and SO_4^{2-}. Samples collected from December 1995 to June 1996 were also analyzed for NH_4^+. However, because NH_4^+ concentrations were nominal and not a focus of this study, NH_4^+ analysis was discontinued after June 1996. Anion concentrations were determined with ion chromatography (Dionex series 4000i, Sunnyvale, CA). NH_4^+ was determined colorimetrically with a

Streamwater Nitrogen Fluxes

Streamwater samples were collected for chemical analysis from seven streamwater sampling sites in Devil Canyon (DC), a western high-pollution area in the San Bernardino Mountains (DC) and from 12 stream sampling sites in an eastern low-to-moderate pollution region surrounding the San Gorgonio Wilderness (Table 1; Figs. 1-3). Devil Canyon is immediately downslope of the N-saturated mixed conifer forest at Camp Paivika (Fenn et al., 1996). The elevation at Camp Paivika is 1600 m. At the bottom of the canyon at the site of the USGS streamflow gauging station (Station No. 11063680) the elevation is 632 m asl. Vegetation in DC is mixed conifer forest near the crest of the watersheds, but grades to hard chaparral and coastal sage scrub at the lower elevations, with riparian woodland bordering the stream channels. In some of the streams in DC and the SGW white alder (*Alnus rhombifolia* Nutt.) trees inhabit the stream channels. Vegetation in the San Gorgonio Wilderness (SGW) below tree line consists of various pine/fir mixes, while mixed conifer forests which include oak species are dominant at the lower elevations of the wilderness. Several peaks in the SGW exceed 3000 m in elevation with the highest being San Gorgonio Mountain at 3497 m.

Precipitation data for DC during this study is from a rain gauge located near the hydroelectric plant at the base of the watershed. Average precipitation (1970-1991) near the base of DC is 584 mm (Corneille, 1992), and increases to ca. 860 mm at higher elevations in the canyon (Troxell et al., 1954). Precipitation data for the SGW area is from the Barton Flats (BF) Monitoring Station (Fenn and Bytnerowicz, 1997), which is adjacent to Streams 7 and 8 (Figs. 1 and 3). Average precipitation at Barton Flats for the 1991-1997 hydrologic years was 565 mm.

Field Sampling and Laboratory Analyses

Fog Inputs

Fog samples were collected for approximately one year from passive and active collectors at Camp Paivika (high N deposition) and at Barton Flats (low N deposition). The passive collectors were used to estimate fog water deposition rates to the forest canopy. The active collectors were used to collect fog samples for chemical analysis. The passive samplers consist of a series of 120 nylon lines (31 cm long, 0.2 mm diameter) arranged in parallel. Fog collected on the lines drained into the funnel base and was collected by a polypropylene bottle connected to the funnel (Fig. 4). A passive collector was placed in each of the canopies of seven mature trees at CP and at BF. The active fog collectors (one at each site) are designed to exclude rain and snow (Daube et al., 1987). We modified the collectors to exclude dry deposition and to automatically activate and collect fog samples during fog events. Dry deposition was excluded by adding louvers to the front and back openings (Fig. 4). The louvers or baffles remained closed until the collector fan was activated. Air flow by the fan automatically opened the louvers and allowed fog to be drawn over the collector strings. When the fog dissipated, the fan was automatically turned off and the baffles closed until the next fog event.

as wet, dry or fog deposition at CP and BF is presented in Table 2. Fog deposition of N and S at CP was a much greater percentage of total deposition than at BF.

Trace Gas Fluxes

The integrated annual soil flux of NO was greater at CP than at Camp Osceola (CAO). There is a strong seasonal pattern of NO production at both sites. This is reflected in the relationship between NO flux and soil temperature and moisture data for both sites (Figs. 9a & 10a). The integrated annual flux of N from CP was 4.5 kg N ha^{-1} yr^{-1} and 0.25 kg N ha^{-1} yr^{-1} at CAO. Carbon dioxide fluxes were not significantly different between CP and CAO. There were no detectable fluxes of N_2O, and soil methane uptake was below detectable limits at both sites.

KCl Soil Extractable NH_4^+ and $NO_3^- + NO_2^-$ From Soil

Seasonal trends for extractable NH_4^+ and $NO_3^- + NO_2^-$ in mineral soil (A horizon) and surface organic materials (O horizons) are shown in Figs. 9b and 10b. There are seasonal patterns evident for both CP and CAO in the O horizon. Concentrations are much higher at CP than CAO. At CP, NO_3^- in the A horizon is always higher than NH_4^+. This is not the case at CAO where NH_4^+ is the dominant form of N in the A horizon.

Streamwater Nitrogen Fluxes

Spatial Trends

Nitrate concentrations during baseflow were consistently higher in five of the six streams at DC compared to the SGW streams (Fig. 11). Average NO_3^- concentration in the spring-fed stream (Stream 1) in DC (70 μeq L^{-1}) was seven-fold greater than in the spring-fed stream (Stream 1) in the SGW (10.0 μeq L^{-1}). Spikes in NO_3^- concentrations in the SGW streams during or shortly after winter storms were of brief duration, although of considerable magnitude. Peak winter NO_3^- concentrations in the SGW were 182 and 128 μeq L^{-1} in 1996 and 1997 (Stream 4), compared to 295 and 350 μeq L^{-1} in the West Fork in DC (Stream 5; Fig. 11).

Spatial trends in streamwater NO_3^- concentrations were also apparent within the SGW region (Figs. 11 and 12). Only the five catchments on the southwestern and western end of the SGW (streams 1-5), where N deposition is greatest, consistently exported levels of NO_3^- above detection limits. Nitrate concentrations in Streams 3 and 4 were elevated for several weeks before and after peak NO_3^- concentrations, indicating the much greater severity of N saturation of these two streams. Peak NO_3^- concentrations in Streams 1 and 2 were intermediate, but baseline NO_3^- levels in Stream 2 was often greater than in Streams 3 and 4. Nitrate concentrations in streams on the northern side of the SGW (Streams 6-12) were frequently at or below detection limits during baseflow conditions and peak values during high flow were relatively low, ranging from 0.0 to 9.9 μeq L^{-1}.

The streams in DC exhibited a wide range of NO_3^- concentration profiles (Fig. 11). Concentrations in the primary stream draining western DC (West Fork, the upper sampling site

Trace Gas Fluxes

Fluxes of NO, N_2O, CH_4, and CO_2 were measured using a closed box flux technique (Anderson and Levine, 1987). For this study new flux cylinders were prepared from 25 cm diameter PVC tubing. Prior to making flux measurements at each site, six cylinders covering an area of 0.073 m^2 were driven 2.5 cm into the soil. In order to measure fluxes of either CO_2 or NO, a Teflon-lined, expanded-cell polycarbonate box fitted with a fan and with a total volume of 10.0 L (including the frame volume) was placed over the frame. The base of the flux box was sealed to the frame via a Teflon-covered foam lining. Two openings (0.64 cm) in the top of the flux box prevent pressure changes from developing during sampling. For N_2O and CH_4 measurements, a flux box with a total volume of 5.0 L was used to increase sensitivity appropriately (Anderson and Poth, 1998).

Analysis of Carbon Dioxide (CO_2)

The flux box cover system described above served as the source of CO_2 emitted from soil and the forest floor. Immediately upon setting the flux chamber on its frame, CO_2 was analyzed in sample air over a 3-min period using a LiCor 6262 infrared gas analyzer and data system.

Analysis of Nitric Oxide (NO)

Immediately following the 3-min sampling period for CO_2, the sample stream was switched to a system for analysis of NO, which is detected over an 8-min period with a Luminox, nitrogen dioxide (NO_2) detector (Model LMA-3, Scintrex-Unisearch, Toronto, Canada) as described by Anderson and Poth (1989). Sample air from the flux box, pumped at approximately 2.8 L min^{-1} by a Teflon bellows and a battery-operated pump, was dried by passage through nafion tubing (Type 815, Dupont perfluorinated polymer, Perma Pure, Inc., Toms River, NJ) packed with silica gel. NO in the dried sample gas was converted to NO_2 by passage through a tube (7.6 cm) containing 10% chromium trioxide on firebrick (30/60 mesh, Chromosorb P, Altech) before being pumped to a tee inlet on the LMA-3 NO_2 detector, which then samples the gas stream at the rate of 1.5 L min^{-1}. A three-way valve, which switches flow of sample air from the converter tube to a blank tube, allows measurement of either background NO_2 in sample air (following passage through the blank tube) or NO + NO_2 (following passage through the converter tube). The chromium trioxide/firebrick was replaced whenever a decrease in converter efficiency is observed during calibration. Calibrations and measurements of flow rates through the pumping system and the LMA-3 were performed at the beginning and at the end of each day of data collection. During calibration, the LMA-3 was zeroed with room air which was passed first through a column containing pellets of alumina coated with $KMnO_4$ (Purafil, Southeastern Engineering Co., Midlothian, VA). This column reduces the background NO in room air to approximately 2 to 4 ppbv (parts per billion by volume) and obviates the need for transporting cylinders of zero air to field sites. For calibration, NO (approximately 9 ppmv, Scott Environmental Technology, Plumsteadville, PA) was mixed with room air (after passage through $KMnO_4$ coated alumina) providing known concentrations of NO ranging from 20 to 50 ppbv. Gas flows were controlled with mass flow

Annual precipitation was greater in the first year of the study, with 525 and 374 mm total precipitation at Barton Flats in 1996 and 1997, compared to 821 and 620 mm at DC. Distribution of precipitation throughout the year differed between the two years. In 1996, precipitation peaked in February, but continued into April. In 1997, rainfall peaked in January, and very little precipitation occurred again until September, except for a few infrequent light summer thundershowers in the SGW (Fig. 11).

On September 4, 1997 a sudden storm originating from humid air transported from the Gulf of California, resulted in ca. 6.5 cm of precipitation within one hour at Forest Falls (near streams 1 and 2). Severe flash flooding occurred in Forest Falls as a result of the deluge. However, by the time stream sampling occurred on September 12 in the SGW, stream flows were normalized and NO_3^- concentrations were at baseline levels (Fig. 11). No precipitation was reported in DC in early September 1997 and no effects on NO_3^- concentrations were apparent.

Ammonium concentrations were also measured in streamwater during the first six months of the study. Concentrations were very low in all of the streams of this study, with peak values $\leq$ 1.8 μeq L^{-1} in winter and nondetectable concentrations during spring and summer (Fig. 13). Because of the inconsequential levels of NH_4^+ in streamwater, further monitoring of NH_4^+ was discontinued after June 1996.

Although the focus of this study was on N deposition and processing, sulfate (SO_4^{2-}) concentrations in streamwater were also measured concurrently with nitrate. Peak SO_4^{2-} concentrations were often 3-6 times higher than peak NO_3^- concentrations (Fig. 14). Sulfate concentrations in some streams in DC and in the SGW fluctuated widely. Concentrations in Streams 1-4 in the SGW exhibited a grossly parallel oscillating trend, while SO_4^{2-} concentrations in the other streams in the SGW were relatively low and constant (Fig. 14). In DC SO_4^{2-} concentrations were unusually high in Stream 7, and in Stream 6 high concentrations occurred only in Dec. 1996 (Fig. 14). The second highest SO_4^{2-} concentrations in DC were in Stream 1 (a spring sampled at its source). Sulfate concentrations, like NO_3^- concentrations, were relatively constant in Stream 1 throughout the study.

DISCUSSION

Fog Inputs

The greater fog water exposure at CP was apparent from the observation that at CP fog often resulted in saturation of the forest canopy with moisture and resulted in heavy fog drip from the canopy onto the forest floor. Fog drip was not frequently observed at BF. Dense fog is a common occurrence at CP during the fall and spring. In addition, fog frequency was approximately twice as high at CP compared to BF. Fogwater deposition fluxes were also nearly twice as high at CP. Thus, the combination of greater fog occurrence, higher fogwater deposition fluxes, and much greater ionic concentrations in fog at CP resulted in much greater deposition of N and S in fog at CP compared to BF. Fog deposition was also a greater

Technicon TRAACS 800, Autoanalyzer (Tarrytown, NY). Laboratory QA/QC protocols are followed for all analyses. These protocols include the use of sample replicates and random duplicate analyses.

RESULTS

Fog Inputs

Ionic concentrations of fogwater (Fig. 5), fog occurrence (Fig. 6), and fog density were all higher at CP compared to BF. During a ten month period in 1997, fog was collected from the passive collectors on 19 dates at CP but on only 9 dates at BF. The average volume of fog collected by the passive collectors was 50 mls at CP compared to 28 mls at BF (Fig. 6). Average fog deposition fluxes during the study were 54 ml m^{-2} h^{-1} at CP and 32 ml m^{-2} h^{-1} at BF. At CP, peak concentrations of NH_4^+, NO_3^- and SO_4^{2-} were 1423, 1234, and 326 μeq L^{-1}. At BF, corresponding values for peak concentrations of NH_4^+, NO_3^- and SO_4^{2-} were 254, 324 and 156 μeq L^{-1} (Fig. 5). Thus, fog frequency, fogwater deposition fluxes, and ionic concentrations in fog were generally much greater at CP than at BF. Annual stand-level deposition of NH_4-N, NO_3-N and SO_4-S in fog were 6.0, 7.4 and 2.3 kg ha^{-1} respectively at CP. Analogous values for BF were 0.3, 0.7 and 0.3 kg ha^{-1}. We estimated that N deposition in fog contributed 21% of the total annual N deposition at Barton Flats (1.0 kg ha^{-1} yr^{-1}) and 43% at Camp Paivika (13.4 kg N ha^{-1} yr^{-1}).

Throughfall Inputs

Annual throughfall precipitation inputs were 1507 mm at CP and 433 mm at BF (Fig. 7). Total deposition of NO_3^- and NH_4^+ were 5 and 14 times greater at CP, and SO_4^{2-} deposition was 7 times greater at CP compared to BF. Total N (NO_3-N + NH_4-N) and SO_4-S deposition equaled 19.0 and 2.9 kg ha^{-1} yr^{-1} at CP, and 2.9 and 0.4 at BF (Fig. 7). Average ionic concentrations of NO_3^-, NH_4^+ and SO_4^{2-} were 4360, 3039 and 1024 μeq L^{-1} at CP compared to 986, 253 and 140 μeq L^{-1} at BF (Fig. 8). Ionic concentrations NO_3^-, NH_4^+ and SO_4^{2-} at CP were 4, 12 and 7 times greater at CP than at BF.

Variability in ionic deposition and concentrations in throughfall varied widely between transects. Throughfall water inputs also varied, but to a much lesser degree than ionic inputs. At CP, total N deposition (NO_3^- + NH_4^+) ranged from 12.1 to 31.7 kg ha^{-1} yr^{-1} in the four transects. Deposition was similar in transects 2-4, and deposition of the three ions in transect 1 was 2.0 to 2.7 times greater than the average deposition in transects 2-4. A similar pattern was evident from the ion concentration data. Throughfall precipitation inputs were 20% greater in transect 1 compared to transects 2-4 at CP.

At BF total N deposition ranged from 0.9 to 4.2 kg ha^{-1} yr^{-1} in the four transects. Deposition was similar in transects 2-4, and average deposition of the three ions in transects 2-4 were 2.1 to 3.8 times greater than in transect 1. Throughfall precipitation inputs were 6.5% greater in transect 1 compared to transects 2-4 at BF. The portion of total N and S deposition

(e.g, HNO_3) compared to ozone. The decrease in N deposition between CP and BF (from 19.0 to 2.9 kg ha^{-1} yr^{-1}) is dramatic considering that these sites are only 42 km apart (26 miles).

A major unknown in terms of estimating total N deposition from throughfall is the portion of total N deposition which is retained by the forest canopy, either via adsorption or uptake by plant tissue or plant-associated microbes. Canopy retention of S is usually minimal. On the other hand, typically 25-40% of the N deposited to forests is retained and not accounted for in throughfall measurements (See discussion in Fenn and Bytnerowicz, 1997).

Assuming that 40% of atmospheric N deposition is retained by the canopy, total deposition of N in the four transects at CP ranged from 31 to 53 kg ha^{-1} yr^{-1}. Analogous values for total N deposition at BF would be 2 to 7 kg ha^{-1} yr^{-1}. Total N deposition at BF was previously estimated to be 6-10 kg ha^{-1} yr^{-1} based on branch rinse data and leaf area index values for the stand (Fenn and Bytnerowicz, 1997; Miller et al., 1996). These estimates are in reasonable agreement considering the number of assumptions underlying the calculation of N deposition from branch rinsing. Furthermore, these studies are for different years. As discussed above, atmospheric deposition may vary considerably from year to year depending on meteorological conditions.

Comparisons of throughfall inputs among the four transects demonstrates that throughfall deposition varies widely across the landscape. Spatial variability in deposition is expected to be much greater in western mixed conifer forests because of the heterogenous nature of the stands. In the San Bernardino Mountains, stands are typically only two-thirds covered by canopy. This leads to high spatial variability in N inputs because open areas have little capacity to intercept atmospheric pollutants and precipitation. The large number of open spaces also creates extensive areas of the forest where edge effects strongly affect deposition. Deposition inputs to areas completely covered by vegetation will have higher inputs than areas which are largely open, although deposition may be highest at the edge boundary between open areas and canopy-covered areas. Availability of nutrients in throughfall to individual trees in the vicinity will be a function of subsequent processing and hydrologic transport of nutrients within the forest floor and underlying soil and parent material. Considering only average deposition rates for the forest at CP may be useful at the watershed scale or in calculating stand-level budgets. However, average deposition values may grossly misrepresent the range of deposition inputs that occur at smaller scales, such as the scale of small groups of trees.

In California, where fossil fuel consumption is the by far the primary source of nitrogenous air pollutants, oxidized forms of N predominate (Bytnerowicz and Fenn, 1996; Bytnerowicz et al., 1987). Camp Paivika does not follow this trend, however. Results from this and other studies demonstrate that inputs of NH_4^+ are similar to NO_3^- inputs at Camp Paivika. The unusually high NH_4^+ inputs are due to emissions of NH_3 from the large dairy industry concentrated in the Norco-Chino area ca. 30 km to the west of CP. A similar situation occurs in the western and southern Sierra Nevada where atmospheric deposition of reduced forms of N from agricultural sources in the Central Valley is also a significant fraction of the total N

referred to as Stream 5) peaked at 295 μeq L^{-1} in Feb. 1996 and 350 μeq L^{-1} in Dec. 1997. Minimum baseflow NO_3^- concentrations were rarely less than 70 μeq L^{-1}. In contrast, NO_3^- concentrations in stream 3, which is a tributary of the West Fork, exhibited moderate peak concentrations during periods of high precipitation and runoff (52 and 19 μeq L^{-1}) in winter 1996 and 1997, but streamwater NO_3^- concentrations returned to baseline levels ($\leq$1 μeq L^{-1}) during low flow. The other five stream sampling sites in DC exhibited a range of intermediate NO_3^- concentration patterns (Fig. 11). Except for Stream 1, which is a spring sampled ca. 15 m from the outlet, all of the streams in DC showed a seasonal pattern of peak NO_3^- concentrations during winter when precipitation is greatest followed by declining values during late winter and early spring. Nitrate concentrations were usually at their lowest and were most stable during the summer dry season (Fig.11).

Streamwater was sampled at two points along the West Fork in DC. The uppermost point is referred to as Stream 5 and the sampling point four km downstream is referred to as Stream 2 (Fig. 2). Nitrate concentrations at both sites peaked in Feb. 1996 and in Dec. 1997. The lowest NO_3^- concentrations were in September before the wet season began. Nitrate concentrations in the upper West Fork sampling site (Stream 5) were on average over three times greater than in streamwater from the lower sampling site (Stream 2; Figs. 11 and 12).

Temporal Trends

Although streamwater NO_3^- concentrations in DC peaked during high flows in winter, NO_3^- concentrations were also elevated during base flow during the summer in most of the streams. About half of the streams in the SGW also showed seasonal NO_3^- export patterns. But in contrast to the trends at DC, NO_3^- concentrations in most of the SGW streams decreased to near background levels in the weeks following major storms. In summer, NO_3^- concentrations nearly always declined below 10 μeq L^{-1} in the SGW streams, although NO_3^- concentrations in streams 1-4 rarely dropped below 1 μeq L^{-1}. Nitrate concentrations in Streams 6-12 in the SGW were frequently below detection limits. However, the largest peak in NO_3^- concentrations in Streams 1-5 in the SGW (from 10-370 μeq L^{-1}) occurred on July 22, 1997. Slight thundershower activity (9.9 mm on July 21-22) was preceded by a 5-month dry period when only 14.9 mm of intermittent precipitation occurred. No rain occurred in DC in July 1997, so no analogous increase in streamwater NO_3^- occurred on that date. Following winter storms, NO_3^- concentrations in Streams 1-5 in the SGW ranged from 16-182 μeq L^{-1} in Feb. 1996, 2-66 μeq L^{-1} in February 1997, and 3-128 μeq L^{-1} in Dec. 1997.

Stream 1 at DC is a small spring sampled at the source, and Stream 1 in the SGW is also a spring-dominated stream, although subsurface flow and surface runoff may contribute to the SGW Stream 1 during periods of storm runoff. In the DC spring, NO_3^- concentrations averaged 70 ($\pm$0.9 s.e.) μeq L^{-1} with little seasonal variation. Nitrate concentrations averaged 10 ($\pm$1.3 s.e.) μeq L^{-1} in Stream 1 in the SGW. The limited seasonal variation in NO_3^- concentrations in the spring-fed streams is striking in contrast to the seasonal variation in the other streams exporting high NO_3^- in DC and SGW (Figs. 11 and 12).

The temporal trends in NH_4^+ and NO_3^- show that nitrification can be limited by low temperatures and low soil moisture. Soil moisture may affect soil and litter NH_4^+ and NO_3^- in several ways. Rain will increase soil moisture and may immediately increase soil NH_4^+ and NO_3^- as dry deposition to trees and shrubs is moved into the soil via throughfall. Rain will also remove water limitations on the formation of NH_4^+ by the mineralization of organic matter, and will also stimulate nitrification. As the rainy season progresses NH_4^+ and NO_3^- are leached from the litter and into the soil. This is clearly evident at CAO where early in 1997 as litter NH_4^+ and NO_3^- are decreasing, soil concentrations are increasing. During the summer dry season nitrification produces NO_3^- which accumulates as NH_4^+ decreases. At CP high N deposition and associated high nitrification rates attenuate seasonal patterns to a great extent.

The inferred increased population of soil nitrifying bacteria and concomitant observations of increased rates of nitrification at sites affected by N deposition is consistent with the N 'saturation' hypothesis. Nitrification is the key process in making N mobile. Our data indicate that nitrification is being stimulated by N deposition. This stimulation of nitrification then provides a mechanism that converts N to nitrate, a highly mobile form and allows it to be moved by hydrologic processes into streamwater and groundwater. Nitrification is a key process that may link air and water quality in many California forests. The much higher levels of nitrate compared to ammonium at CP, but not at CAO supports the concept of using the ratio of nitrate to ammonium in soil as an effective indicator of forest N status (Aber, 1992).

Streamwater Nitrogen Fluxes

Streamwater NO_3^- concentrations at DC, and in chaparral watersheds in the San Gabriel Mountains northeast of Los Angeles (Riggan et al., 1985) are the highest reported in North America for undisturbed watersheds. The streams at DC which exhibit high baseline NO_3^- levels during summer can be classified as stage 2 of the watershed N saturation model (Stoddard, 1994). The only undisturbed forested sites in North America in which relatively similar streamwater NO_3^- values have been reported are the Fernow Experimental Forest in West Virginia (Gilliam et al., 1996; Peterjohn et al., 1996) and the Great Smoky Mountains National Park in Tennessee (Cook et al., 1994). Nitrate concentrations in the upper West Fork in DC (Stream 5) in the two years of this study, were ca. three times greater than the 10-yr average concentrations reported for Fernow and in the Smokies. Monthly averages for 1984-1994 ranged from 44-64 μeq L^{-1} in Fernow (Peterjohn et al., 1996), compared to average NO_3^- concentrations of 61 and 146 μeq L^{-1} in the lower and upper West Fork in DC (Streams 2 and 5). At Fernow and at DC, NO_3^- concentrations were high even during summer baseflow conditions (Gilliam et al., 1996; Peterjohn et al., 1996).

Spatial Trends in N Deposition and Streamwater Nitrate

Parallel spatial trends in N deposition and streamwater NO_3^- concentrations in the SBM support the hypothesis that elevated N deposition is a major contributor to NO_3^- export in streamwater. Spatial trends in streamwater NO_3^- were apparent on two different scales---between DC and the SGW, and also among the streams within the SGW. According to previous studies of N deposition in the SBM (Fenn and Bytnerowicz 1993; 1997; and in this

percentage of total N deposition at CP (43%) compared to BF (21%). Nitrogen deposition (NH_4^+ plus NO_3^-) in fog at CP was 13.4 kg ha^{-1} yr^{-1} compared to 1.0 kg ha^{-1} yr^{-1} at BF. Fog deposition of N has high potential for canopy N retention because of the extremely elevated N concentrations in fog and the long residence time of the nutrient solutions saturating the foliage and branches.

At CP, deposition and concentrations of NH_4^+ in fog and throughfall were of similar magnitude to NO_3^-. Usually dry deposition and wet deposition of NO_3^- are several times greater than for NH_4^+ in southern California because of high NO_x emissions from fossil fuel combustion. The high density of large dairy farms in the Chino/Norco area west of the San Bernardino Mountains results in the high NH_x deposition in the western San Bernardino Mountains. Nearly 300,000 cows are located within a 50 km^2 area (20 square miles), reportedly resulting in the greatest concentration of dairy cows in the world.

Throughfall Inputs

An important reason for more accurately quantifying N deposition in these forests is to increase the ability to predict at what levels of N deposition ecological and environmental impacts become significant. Throughfall collection is a useful method for determining N inputs to forests, especially if data are needed for a number of sites. Throughfall measurement is especially useful in areas with significant dry deposition, because of the difficulty in quantifying dry deposition. In a broad survey of 65 watersheds in Europe it was reported that below a deposition threshold 10 kg N ha^{-1} yr^{-1}, no significant NO_3^- leaching occurred, while at intermediate levels of 10-25 kg ha^{-1} yr^{-1} leaching occurred at some sites. Above a deposition level of 25 kg ha^{-1} yr^{-1} N leaching occurred at all sites (Dise and Wright, 1995). Ecosystems in the San Bernardino and San Gabriel Mountains in southern California support this general finding, notwithstanding the widely different climatic, biological and physical characteristics of watersheds in California compared to northern Europe. A high-elevation mixed conifer forest in the San Gabriel Mountains where throughfall deposition of N was 11 kg ha^{-1} yr^{-1} was N-limited based on responses of Jeffrey pine trees to N fertilization (Kiefer and Fenn, 1997). On the other hand, the forest at CP is clearly N saturated as evidenced by a number of botanic and edaphic N status indicators (Fenn et al., 1996). In addition, average NO_3^- concentrations in five streams in Devil Canyon, located immediately west of CP, ranged from 18 to 146 μeq L^{-1}. Streamwater NO_3^- concentrations were also elevated in chaparral watersheds in the San Gabriel Mountains where throughfall N deposition was reported to be 23 kg ha^{-1} yr^{-1} (Riggan et al., 1985).

As expected, ion concentrations and deposition in bulk throughfall were several-fold greater at CP than at BF. Throughfall deposition is expected to vary from year to year depending on weather conditions. Several years of throughfall data are needed to fully characterize long-term throughfall deposition. This study supports earlier findings that the decline in N deposition and concentrations across the west-east gradient in the San Bernardino Mountains is much steeper than the decline in ozone concentrations (Fenn and Bytnerowicz, 1993). The steeper decline in N pollutants is presumably due to the greater deposition velocity of the major N pollutants

runoff events such as snowmelt or rainstorms, and lowest values in summer. However, the large increase in streamwater NO_3^- following summer precipitation in the SGW streams differs from these temporal trends. Summer peaks in streamwater NO_3^- concentrations may be characteristic of watersheds in Mediterranean summer-dry climates when dry periods are interrupted by occasional summer precipitation events (Fenn and Bytnerowicz, 1997).

Ammonium and Sulfate Trends in Streamwater

No clear trends in streamwater NH_4^+concentrations were observed in this study. Concentrations were extremely low compared to NO_3^- concentrations in all cases. We conclude that NH_4^+ export is inconsequential in terms of watershed N budgets and water quality. This study and previous field studies in the San Bernardino Mountains (Fenn et al., 1996) indicate that NH_4^+ in soil is rapidly oxidized to nitrate, especially in high-deposition areas. Furthermore, NH_4^+ is also effectively adsorbed onto mineral soil and organic matter, which results in low levels of NH_4^+ leaching compared to the highly mobile NO_3^- ion.

Although SO_4^{2-} export in streamwater was not the focus of this study, we measured SO_4^{2-} concentrations in the streamwater samples as additional information on streamwater chemistry. High SO_4^{2-} concentrations in streamwater can be important because of cation export from the watershed and potential acidification of streamwater. Sulfate concentrations in streamwater were generally several-fold higher than NO_3^- concentrations. Sulfur deposition is relatively low compared to N in the San Bernardino Mountains and is not expected to contribute significantly to the SO_4^{2-} levels in streamwater. However, the highest SO_4^{2-} concentrations in the SGW occurred in streams 1-5 where air pollution is greatest and NO_3^- export is highest. The cause of greater SO_4^{2-} in SGW Stream 1-5 is not known, but could be related to geological differences, differences in weathering rates, or greater sun exposure and evapotranspiration rates along the southern edge of the SGW compared to the northern side of the wilderness (Streams 6-12). High evapotranspiration rates reduces streamwater flows and concentrates ions in streamwater. Sulfate levels in Streams 1-5 in the SGW generally decreased following rain events and increased during dry periods (Fig. 14), again suggesting that SO_4^{2-} concentrations increased with lower streamwater flow rates. In DC Streams 5 and 2 (the main West Fork) where NO_3^- levels were greatest, SO_4^{2-} levels were among the lowest in DC, suggesting that atmospheric deposition isn't related to SO_4^{2-} in streamwater. In Stream 1 (a spring) SO_4^{2-} concentrations (like NO_3^- concentrations) varied little throughout the year. Sulfate concentrations in Stream 7 fluctuated widely. Geological and hydrological factors are thought to be the major controls on SO_4^{2-} export in DC and the SGW.

Possible Factors Affecting Nitrate Export

We found greater than expected spatial variation in streamwater NO_3^- concentrations within DC, an area of high N deposition. Since deposition is not expected to vary greatly among the adjacent catchments in DC, differences in streamwater NO_3^- concentrations were attributed to variation in N processing in the upland watershed, the near stream zone, or in the stream channel and hyporheic zone (Duff and Triska, 1990; Mulholland, 1992; Mulholland and Hill, 1997; Nihlgård et al., 1994; Pionke and Lowrance, 1991). Varying flow paths within the

deposition (Bytnerowicz and Fenn, 1996). At BF, on the eastern end of the deposition gradient, NO_3^- deposition in throughfall is 4 times greater than NH_4^+ deposition, a ratio which is more typical for areas influenced primarily by fossil fuel emissions. These findings are also supported by studies of fog deposition at CP and BF.

Trace Gas Fluxes

The annual NO flux from CP (4.5 kg N ha^{-1} yr^{-1}) is the highest reported for a temperate forest in North America. The next highest rate reported in the literature (1.9 kg N ha^{-1} yr^{-1}) is for a deciduous forest in Tennessee (Valente and Thornton, 1993). Our site and the one in Tennessee are in areas with high rates of N deposition. There is evidently a strong influence of chronic N deposition on the ability of mixed conifer forests to produce NO. The NO flux rate at CAO (0.25 kg ha^{-1} yr^{-1}) was typical for a temperate forest ecosystem. Disturbances to N cycling processes can stimulate NO fluxes from ecosystems. This has been demonstrated in chaparral ecosystems in California after wild fire where rates may rise to 6.0 kg N ha^{-1} yr^{-1} (Anderson and Poth, 1989). The seasonal pattern of NO flux indicates that the observed rates are sensitive to temperature, moisture and soil NH_4^+ and NO_3^- status. These links provide indirect evidence that nitrification is important in the production of NO. This is most apparent in the soil chemistry described below. The lack of any difference in the annual flux of CO_2 at CP and CAO is surprising given the differences in the forest floor at these sites. At CP the O horizons (litter layers) are typically over 10 cm in depth, but are usually less than 2 cm at CAO. Hence the production of CO_2 per unit forest floor carbon is drastically different at these two sites.

The lack of a detectable N_2O flux is not surprising since anaerobic soil conditions favor N_2O production formation in soils. Our forest soils are well drained and hence are seldom anaerobic. We cannot draw any conclusions about methane fluxes since our methodology was not sensitive enough to detect methane fluxes.

KCl Extractable NH_4^+ and $NO_3^- + NO_2^-$ From Soil

Soil and O horizon NH_4^+ and NO_3^- concentrations are a function of inputs from deposition, losses due to leaching, production of N trace gases, and in situ transformations. At CP, observed concentrations of NH_4^+ and NO_3^- are high reflecting high atmospheric deposition and overall N enrichment of the site. The oxidation of NH_4^+ to NO_3^- (nitrification) is a prominent process as evidenced by the decrease in NH_4^+ as the concentration of NO_3^- increases. The evidence for nitrification is clear at CAO, where in both horizons when NH_4^+ decreases in concentration there is a corresponding increase in NO_3^-. The rate of nitrification and the chemical kinetics of nitrification will determine the residence time for NH_4^+ within any particular horizon. At CAO the accumulation of soil NH_4^+ indicates that the rate of deposition and of formation from soil mineralization is greater that the nitrification rate. This contrasts with CP where NH_4^+ is apparently quickly nitrified to NO_3^-. This is indirect evidence for a much greater soil population of nitrifying bacteria at CP than CAO since a large population would be required to produce such rapid nitrification (Johnson, 1992).

streamflow (Duff and Triska, 1990). In the alder riparian site, denitrification potentials were nitrate-limited, but not C limited, indicating the high denitrification capacity of the stream-side sediments. Similar cycling processes of N released from alder roots may be occurring in the alder riparian zones in our study.

Nitrate concentrations were consistently higher in the upper West Fork (Stream site 5) than in the lower West Fork (Stream site 2) in DC. The chemistry of Stream 2 is affected by several small tributaries in which NO_3^- concentrations vary over a wide range. The difference in NO_3^- concentrations is presumably because of a dilution effect as tributaries feeding into the West Fork between the two sampling sites are lower in NO_3^- than the stream at the upper West Fork sampling site. Nitrogen immobilization along the stream channel probably also reduces NO_3^- concentrations along its course. However, dilution effect by tributaries feeding the West Fork was probably the most important mechanism, since NO_3^- concentration differences also occurred during winter storms when in-stream N immobilization is expected to be limited by low temperatures.

Fate of Excess Nitrogen in Semiarid Watersheds

Major N inputs to the catchments include atmospheric deposition and possibly biological N_2 fixation. Outputs include streamwater discharge, percolation to groundwater, denitrification, soil erosion, and N released in fire. No harvest activities occur in the DC or SGW areas and fires are suppressed in DC, thus limiting these outputs. Atmospheric inputs of N at Camp Paivika are estimated to be 30-35 kg ha^{-1} yr^{-1} (This study; Fenn and Bytnerowicz, 1997). Nitrogen inputs from N-fixing species such as alder and ceanothus in DC are not known. The United States Geological Survey (USGS) maintains a stream gauging station (Station No. 11063680) at a point 1 km downstream from the confluence of the East and West Forks in DC. The drainage area for this larger watershed is 1,422 ha (USGS, 1995). Using USGS monthly mean discharge data (for the period 1920-1995) and monthly average NO_3^- concentration data from this study, we calculated annual export of NO_3^--N from Devil Canyon. Average surface and subsurface runoff in Devil Canyon equals 25% of the precipitation (Troxell et al., 1954; Crippen, 1965). Based on this information, the long-term (1920-1995) USGS data on stream discharge from DC, and streamwater NO_3^- concentrations at the gauging station, we calculated an average runoff of 2 kg N ha^{-1} yr^{-1}. In 1995, a water year of above average runoff and precipitation (1081 mm at DC), calculated annual runoff was 9 kg ha^{-1} (Table 3). In Streams 2-4 along the southern transect of the SGW, stream runoff was estimated to range from 1.2-2.4 in an average year, with values ranging from 6.4-13.1 in 1995 (Table 3). High N export from the SGW streams was likely due to the high elevation and low temperatures (compared to DC) which result in lower evapotranspiration, steep slopes, and high hydrologic fluxes. These factors contribute to low watershed N retention capacity and greater hydrologic N export, especially in years with above-average precipitation (Fenn et al., 1998). Thus, topographic, hydrologic, and biological factors in the southern SGW may result in greater N losses than in DC, notwithstanding the greater N deposition in the DC area.

In years of similar precipitation, the level of N export in streamwater discharge estimated

study), N deposition decreases dramatically between the DC area and the SGW. Nitrogen deposition at DC is conservatively estimated to be at least five times greater than in the SGW (Fenn and Bytnerowicz, 1993). Air pollutant concentrations decrease from west to east and from south to north in the SBM (Miller et al., 1986). The only streams in the SGW in which NO_3^- concentrations were always above detection limits, were the five streams draining watersheds on the southwest and western end of the SGW. This corresponds with the sites most directly exposed to incoming air pollution loads from the west/southwest.

Differences in watershed NO_3^- export between DC and the SGW were especially apparent in spring water (Stream 1 at both sites). Nitrate concentrations in the spring in DC (70 μeq L^{-1}) were seven times greater than in the spring-dominated stream in the SGW (10 μeq L^{-1}). Nitrate concentrations in these springs varied little seasonally compared to the other streams. Nitrate concentrations in the springs are probably good indicators of "baseline" groundwater NO_3^- concentrations in these catchments, and as such are also indicators of the long-term N status of the watersheds. Stream 1 in the SGW exhibited slightly greater temporal variability than the spring at DC, possibly because of greater inputs from surface or lateral subsurface flow during storm runoff.

Temporal Trends in Streamwater N and S

Temporal trends in NO_3^- concentration patterns clearly indicate the more severe N saturation of the catchments in DC compared to the SGW catchments. Nitrate concentrations in Streams 1-5 in the SGW briefly peaked to high levels following storms, but concentrations decreased to near background levels during baseflow in late spring and in summer (Stage 1 of watershed N saturation). Elevated NO_3^- concentrations were maintained during base flow in most of the streams in DC (Stage 2 of watershed N saturation; Stoddard, 1994).

Nitrate concentrations in the SGW streams peaked in February 1996 and December 1997, and even greater concentrations occurred following precipitation in July 1997. The first two peaks were due to high winter flows which are effective in flushing stored NO_3^- out of the watershed (Riggan et al., 1985). The runoff associated with a summer thunderstorm in July 1997 produced streamwater NO_3^- concentrations as high as 370 μeq L^{-1}. The high NO_3^- concentrations in Streams 2-5 in the SGW is presumably a result of leaching of NO_3^- which had accumulated in the system during the six previous relatively dry months. Although NO_3^- concentrations were high following the July precipitation, the amount of N exported from the catchments was probably moderate since precipitation volumes were not as great as during winter storms. Sampling frequency during summer was not high enough to determine the duration of the increased NO_3^- export, but it was likely a brief event compared to winter storms, which produce a more prolonged runoff due to snowmelt and greater precipitation volumes when snow is the dominant form of precipitation.

In general, the temporal trends in streamwater NO_3^- fit the Stoddard watershed N saturation model based on data from the eastern U.S. and Europe (Stoddard, 1994). This trend is characterized by peak streamwater NO_3^- concentrations in the off season as a result of large

North America. The NO flux rate at CAO (0.25 kg ha^{-1} yr^{-1}) is much more typical of temperate forests. Increases in the apparent population of soil nitrifying bacteria and the dramatic increase in nitrification rates is strongly associated with NO production. Nitric oxide flux rates from the high N-deposition site were consistently higher, and so the measurement of soil NO flux may be a good diagnostic indicator of N status. There was no detectable flux of N_2O from these sites. High soil water contents favor formation of N_2O. These soils are well drained as is typical of this type of forest and so no N_2O was observed. Methane fluxes were below detection limits.

Streamwater Nitrogen Fluxes

Five of six streams monitored at DC, a high-deposition area in the western San Bernardino Mountains, exported elevated NO_3^- concentrations throughout the entire year (peak values ranging from 40 to 350 μeq L^{-1}). These streams are at stage 2 of the Stoddard watershed N saturation model (Stoddard, 1994) which is characterized by high base-flow NO_3^- concentrations and highly-elevated episodic concentrations during high-flow events. Of the twelve streams sampled in the SGW, only the five with the greatest air pollution exposure exported appreciable levels of NO_3^- (peak values ranging from 16 to 182 μeq L^{-1} in winter and 10 to 370 μeq L^{-1} in summer). Baseflow concentrations in summer in these same streams decreased to low levels (typically 0.3 to 10 μeq L^{-1}). Peaks in NO_3^- concentration in the SGW occurred after winter storms and following a summer thundershower. Streams 1 to 5 in the SGW are classified as Stage 1 of the watershed N saturation model, but may be approaching Stage 2. Nitrate concentration profiles of the other 7 streams in the SGW are typical of Stage 0, with minor peaks in NO_3^- during runoff and little or no NO_3^- leakage during the growing season. Nitrate concentrations in spring-fed streams were relatively constant throughout the year, may reflect groundwater NO_3^- levels, and may be a long-term indicator of watershed N status. The results of this study suggest a strong link between levels of NO_3^- export in streamwater and the severity of chronic N deposition to the terrestrial watersheds. However, even in areas with high N deposition, streamwater NO_3^- concentrations are determined by N processing within the associated terrestrial and aquatic systems. Estimates of N fluxes in storm runoff and groundwater runoff suggest that as much as 13 kg N ha^{-1} yr^{-1} is exported in high rainfall years. Nitrogen export values may even be much greater than our conservative estimates considering the high degree of uncertainty in hydrologic fluxes belowground.

Recommendations

The San Bernardino Mountains are the primary water source for over half a million people in the Inland Empire. Water quality is significantly impacted by N deposition to these montane watersheds. A greater understanding of the factors responsible for the wide variation in streamwater NO_3^- in Devil Canyon, where N deposition is highly elevated, would indicate what land management practices could be used to enhance watershed N retention and thus reduce NO_3^- concentrations in streamwater and groundwater. This should be a high priority research area.

catchments, and catchment characteristics such as size, slope, vegetation, stream length, and stream morphology may also be important factors influencing N processing (Cirmo and McDonnell, 1997; Manga, 1996; Piñol et al., 1997; Piñol et al., 1992; Schnabel et al., 1993). Precipitation amounts strongly affected NO_3^- concentrations in the streams, as evidenced by the high streamwater NO_3^- concentrations during the wet season or after precipitation inputs.

Based on the available data, the streams in DC can be grouped into 4 categories: (a) Stream 1 is a spring with constant N concentrations and flow rates. (b) Streams 2 and 5 are upper and lower sampling sites of the West Fork which drains western Devil Canyon, and is characterized by relatively high flow rates. (c) Streams 3 and 6 are tributaries with the shortest stream lengths, and lowest flow rates and NO_3^- concentrations. Stream 3 is intermittent in dry years. The stream channel for Streams 3 and 6 was overlain with an extensive layer of large acorns and leaf litter. This litter layer may supply abundant carbon for N immobilization, or tannins from the acorns could suppress nitrification (Howard and Howard, 1991), thus reducing streamwater NO_3^- concentrations. (d) Streams 4 and 7 are moderate to long streams, perennial (at least during this study) with moderate to high N concentrations. However, Stream 7 is unusual in that chloride concentrations (data not shown) are nearly identical to stream 1 (the spring) during baseflow conditions, and NO_3^- levels are often very high in stream 7--higher than in any of the other tributaries.

Fixation of N_2 by white alder, a species which is widespread along the stream channel of the West Fork in DC, is another possible source of NO_3^- in streamwater. However, high NO_3^- concentrations in spring water (Stream 1) sampled in an area far removed from any alder trees suggests that alder is not a major source of streamwater NO_3^-. Furthermore, of the four tributary streams in DC, NO_3^- concentrations are highest in Stream 7 which has no alder. Nitrate concentrations in Stream 7 are also higher than in the lower West Fork (Stream 2) which supports dense alder stands. Of the tributaries in DC, Stream 4 is the only one with a significant alder community, yet NO_3^- concentrations are moderate. In the SGW, varying levels of alder occur within the stream channels. Stream 7 is located in a wide stream channel supporting a dense and extensive stand of large alder trees. The stream channel for Stream 4 contains no alder, yet NO_3^- concentrations in Stream 4 averaged 39 μeq L^{-1} (peak value, 370 μeq L^{-1}) compared to 0.9 μeq L^{-1} (peak value, 10 μeq L^{-1}) in Stream 7. Average NO_3^- concentrations in the seven streams along the north side of the SGW ranged from 0.02-0.9 μeq L^{-1}. Of these seven streams, NO_3^- was highest in Stream 7 where alder was most dominant, but the differences were marginal. We conclude that N_2 fixation by alder is not a major source of streamwater nitrate in DC or in the SGW streams.

In a study in northwestern California, NO_3^- concentrations in streamwater were similar along segments of a small stream dominated by either red alder (*Alnus rubra* Bong.) or old-growth coastal redwood (*Sequoia sempervirens* (D. Don) Endl.) forest (Duff and Triska, 1990). Nitrate concentrations in water from the stream-side habitat were higher in the alder site than in the old-growth forest site. High denitrification activity in the stream side areas seems to account for the reduction in NO_3^- as water moves from the streamside area into the

Stream 2; Alger Creek	19 ± 4.0; 2-67	Sampled a few m below a seep in Alger Creek, intermittent	Alder in some stretches of Alger Creek
Stream 3; Monkey Face Creek	30 ± 8.5; 1-151	Moderate length, intermittent	No alder near sample site
Stream 4; Frustration Creek	39 ± 16.2; 0.2-370	Short length, sampled near the base of a waterfall, perennial	No alder
Stream 5; Mountain Home Creek	3 ± 1.5; 0-35	Very steep canyon, long stream with relatively high flows, large boulders in channel, perennial	No alder visible upstream, a few below the sampling site
Stream 6; Kilpecker Creek, West Fork	0.03 ± 0.02; 0-0.4	Short stream, sampled a few m below a waterfall, intermittent	No alder
Stream 7; Forsee Creek, East Fork	0.9 ± 0.4; 0-10	Long stream, gentle slope, wide channel, perennial	Dense alder stand covering the wide stream channel
Stream 8; Barton Creek, East Fork	0.4 ± 0.2; 0-4	Moderate length, perennial, constant flow rate	No alder
Stream 9; Frog Creek	0.3 ± 0.3; 0-8	Short length, low flows, perennial	No alder
Stream 10; Lost Creek	0.02 ± 0.01; 0-0.1	Long stream, intermittent	No alder
Stream 11; Ciénaga Seca Creek	0.2 ± 0.09; 0-0.9	Long stream, perennial	No alder
Stream 12; Fish Creek	0.1 ± 0.07; 0-1.6	Long stream, perennial	No alder

[†]μeq L^{-1}

[‡]Stream length refers to the length of stream above the sampling point.

for DC agrees reasonably well with that reported by Riggan et al. (1985) for chaparral watersheds in the San Gabriel Mountains near Los Angeles. In a year of average rainfall (770 mm) 0.75 and 1.3 kg N ha^{-1} yr^{-1} were exported in streamwater from two adjacent watersheds in the San Dimas Experimental Forest. Streamwater NO_3^- export from the two chaparral watersheds ranged from 3.7 to 10.0 kg ha^{-1} yr^{-1} in two years with ca. 1400 mm precipitation (Riggan et al., 1985). In the Fernow Experimental Forest in West Virginia, streamwater export of NO_3^--N in the untreated WS4 watershed ranged from 3.1 to 8.5 kg ha^{-1} yr^{-1} from 1984 to 1991 (Adams et al., 1993). Mean precipitation for WS4 was 1450 mm.

The amount of N lost from the watershed via denitrification is not expected to be significant in the upland areas (Fenn et al., 1996). Denitrification losses in the riparian zone is potentially much greater (Duff and Triska, 1990). In preliminary measurements we found high levels of dissolved nitrous oxide, presumably from denitrification, in streamwater from the spring in DC (Stream 1). No nitrous oxide was detected in the other streams in DC, likely because of rapid degassing once the water was exposed to the atmosphere (Bowden and Bormann, 1986; Davidson and Swank, 1990). Thus, denitrification appears to be an active process for reducing NO_3^- in subsurface water in DC, but no quantitative estimates of rates are available.

Nitrogen storage in biomass isn't expected to exceed 5 kg ha^{-1} yr^{-1} in these semiarid systems (Johnson, 1992). Normally, periodic fires release large amounts of N from litter and biomass. However, after decades of fire suppression and high N inputs in the western SBM, greater than normal litter accumulation has occurred (Fenn et al., 1998). Much of the N inputs in DC are probably stored in vegetation, litter and soil organic matter as reported for other ecosystems (Fenn et al., 1998). We expect that after fire, streamwater and possibly groundwater NO_3^- concentrations will increase dramatically as reported for chaparral watersheds in the San Gabriel Mountains (Riggan et al., 1994).

SUMMARY and CONCLUSIONS

Fog and Throughfall Inputs

Levels of N deposition which induce symptoms of N saturation in southern California are similar to threshold levels in Europe and eastern North America, suggesting that N saturation is a common phenomenon where chronic elevated N deposition occurs. Throughfall deposition of N varies widely among microsites within the forest landscape because of the heterogenous nature of these semi-open mixed-species stands. This raises the possibility that the effects of N deposition, including N fertilization effects on biotic processes may vary widely from site to site. Hydrologic transport of dissolved N within the soil may remove some of the heterogeneity in N availability by distributing N to downslope vegetation. Fog deposition of N was shown to be an important component of the total yearly deposition budget in the San Bernardino Mountains.

Trace Gas Fluxes

Nitric oxide fluxes from forest soils are strongly elevated at CP, a site with high N deposition. The integrated rate of 4.5 kg N ha^{-1} yr^{-1} is the highest reported for any forest in

Table 3. Estimated annual nitrogen budget[†] (kg ha^{-1}) for Devil Canyon and for Streams 2-5 in the San Gorgonio Wilderness. Values are based on the best available information--although highly uncertain, and serve mainly to illustrate the relative importance of hydrologic and trace gas losses of N in the watershed nitrogen budgets.

	Nitrogen inputs		Nitrogen loss		Nitrogen storage	
Stream	Deposition	Fixation	Hydrologic	NO emissions	Vegetation	Litter/soil
Long-term average annual precipitation						
DC	31	Unknown	2	4-5	4-7	17-21
SGW Streams 2-4	10	Unknown	1.2-2.4	0.4	4-7	0.2-4.4
1995--1.85 x long-term average annual precipitation						
DC	31	Unknown	9	4-5	4-7	17-21
SGW Streams 2-4	10	Unknown	6.4-13.1	0.4	4-7	0.2-4.4

[†]Estimate of N storage in vegetation is from Johnson (1992). Nitrogen storage in litter and soil was estimated by difference. Hydrologic losses in DC were calculated from long-term (1920-1995) USGS streamflow data. Hydrologic losses from the SGW streams was calculated from hydrologic data published by Crippen (1965). Deposition at the SGW sites is estimated based on geographic position along the west-to-east N deposition gradient in the San Bernardino Mountains (Fenn and Bytnerowicz, 1993). Nitrogen deposition may increase in a high precipitation year, and NO emissions and N storage in vegetation are also expected to increase with increasing precipitation. However, in the absence of quantitative information, we have kept values constant for deposition, storage in vegetation, NO emissions and storage in soil---thus the estimated budgets for N input, loss and storage for the high precipitation year do not completely balance (only the estimated increase in hydrologic export of NO_3^- is shown).

Nitrogen accumulated in soil, litter and vegetation in these Mediterranean-climate ecosystems are apparently released from these watersheds in episodic events associated with periodic fires and high precipitation years when peak hydrologic export and peak NO_3^- concentrations co-occur.

Table 1. Characteristics of the streams sampled in this study.

Stream No.; Name	Nitrate conc.[†] mean ±s.e.; range	Stream characteristics[‡]	Alder in stream
Devil Canyon			
Stream 1	70 ± 0.9; 58-77	A spring sampled at the source, perennial	No alder; underground flow
Stream 2; lower West Fork	61 ± 9.9; 13-200	Main drainage, perennial, large boulders in channel	Alder is common in riparian zone
Stream 3	5.3 ± 2.4; 0-52	Relatively short stream, intermittent; accumulation of acorns/leaf litter in stream channel	No alder
Stream 4	33 ± 2.4; 22-77	Moderate length, perennial	Alder is common in riparian zone
Stream 5; upper West Fork	146 ± 14.0; 63-350	Main drainage, perennial, large boulders in channel	Alder is common in riparian zone
Stream 6	18 ± 1.4; 11-153	Short length, perennial, during base flow begins as a seep ca. 100 m above the sampling point, accumulation of acorns/leaf litter in stream channel	No alder
Stream 7	87 ± 5.5; 20-153	Longest tributary, perennial, narrow stream channel,	No alder
San Gorgonio Wilderness			
Stream 1; Vivian Creek	10 ± 1.3; 3-31	Sampled a few m below a spring which feeds into Vivian Creek, perennial	Alder common in portions of Vivian Creek, but not near sampling point

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Table 2. Estimated deposition of nitrogen and sulfur in the wet, dry, and fog components of atmospheric deposition at Camp Paivika and Barton Flats[†]. Values in parentheses are the percent of the total deposition from that fraction.

	Nitrogen in Each Fraction ($kg\ ha^{-1}\ yr^{-1}$)		Sulfur in Each Fraction ($kg\ ha^{-1}\ yr^{-1}$)	
	Barton Flats	Camp Paivika	Barton Flats	Camp Paivika
Wet	0.8 (17)	5.3 (17)	0.15 (17)	0.5 (16)
Dry	3.0 (62)	12.6 (40)	0.45 (50)	0.4 (12)
Fog	1.0 (21)	13.4 (43)	0.30 (33)	2.3 (72)
Total[†]	4.8	31.3	0.9	3.2

[†]Total deposition is based on annual throughfall deposition and assuming that 40% of N and 10% of the S deposition is retained by the canopy and not accounted for in throughfall. This is based on literature values from many studies (see discussion in Fenn and Bytnerowicz, 1997). Fog data is from this study. Wet deposition data for Barton Flats is from the wet/dry bucket collector at the Barton Flats monitoring station (see Fenn and Bytnerowicz 1997). Dry deposition equals total deposition minus wet + fog deposition.

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We assumed that LAI under oak was 1.0 during the six winter months, and we reduced total stand LAI accordingly for the November-April period.

Streamwater Nitrate Export

To estimate the amount of N exported from the DC watershed: USGS data on acre-feet of annual streamwater discharge is converted to liters of water exported. L of water exported x NO_3^- concentration (g N/L) = g or kg NO_3^- exported in streamwater per year. Divide kg NO_3^- exported per year by the watershed area (in hectares) to obtain kg N exported ha^{-1} yr^{-1}.

Streamwater NO_3^- data are from samples collected at the USGS gauging station. Streamflow data is from the USGS annual report for 1995. We calculated streamwater NO_3^- export data using long-term average streamflow data (1920-1995) and for 1995, a year of nearly double the average rainfall. Total runoff (streamflow plus groundwater runoff was assumed to be 27% of annual precipitation at Devil Canyon and 34% of precipitation in the SGW (Crippen, 1965; Troxell et al., 1954). Belowground runoff was determined as the difference between total precipitation inputs minus streamwater export from the watershed.

Additional assumptions: That volume-weighted streamwater NO_3^- concentration used in the calculations are representative of streamwater NO_3^- concentrations during years of average and above-average rainfall. This is a reasonable assumption because we used volume-weighted average concentrations for the two years of this study when streamflow rates varied greatly and covered a wide range of runoff volumes. For calculating groundwater export, we used the average NO_3^- concentration for Stream 1 in DC, which is a spring. Nitrate concentrations (70 $\pm$ 0.9 μeq L^{-1}) were constant in Stream 1 throughout the two years of the study. Because Stream 1 is sampled at the spring source, it is believed to represent a groundwater source.

Trace Gas Calculations

Annual average nitric oxide (NO) flux (kg ha^{-1} yr^{-1}) from soil at CP and CAO was calculated from the monthly flux measurements (ng N m^{-2} s^{-1}). The monthly flux values were averaged to provide an annual average flux rate. This value was multiplied by 0.315 to convert to kg N ha^{-1} yr^{-1}. The primary assumption in this calculation is that the observed flux rate for a particular sampling day in a month occurs over the entire month and that there is no diurnal variation. The assumption that there is no diurnal variation is probably not true, especially in the forest floor and upper mineral soil. Diurnal flux rates do change with temperature. Our measurements are made in the morning when temperatures are slightly above the daily mean. This may result in a slight overestimate. This tendency to overestimate may be compensated for by underestimations of the strong increase in NO flux during and following transient wetting events like light spring or summer rains which wet the upper soil and forest floor.

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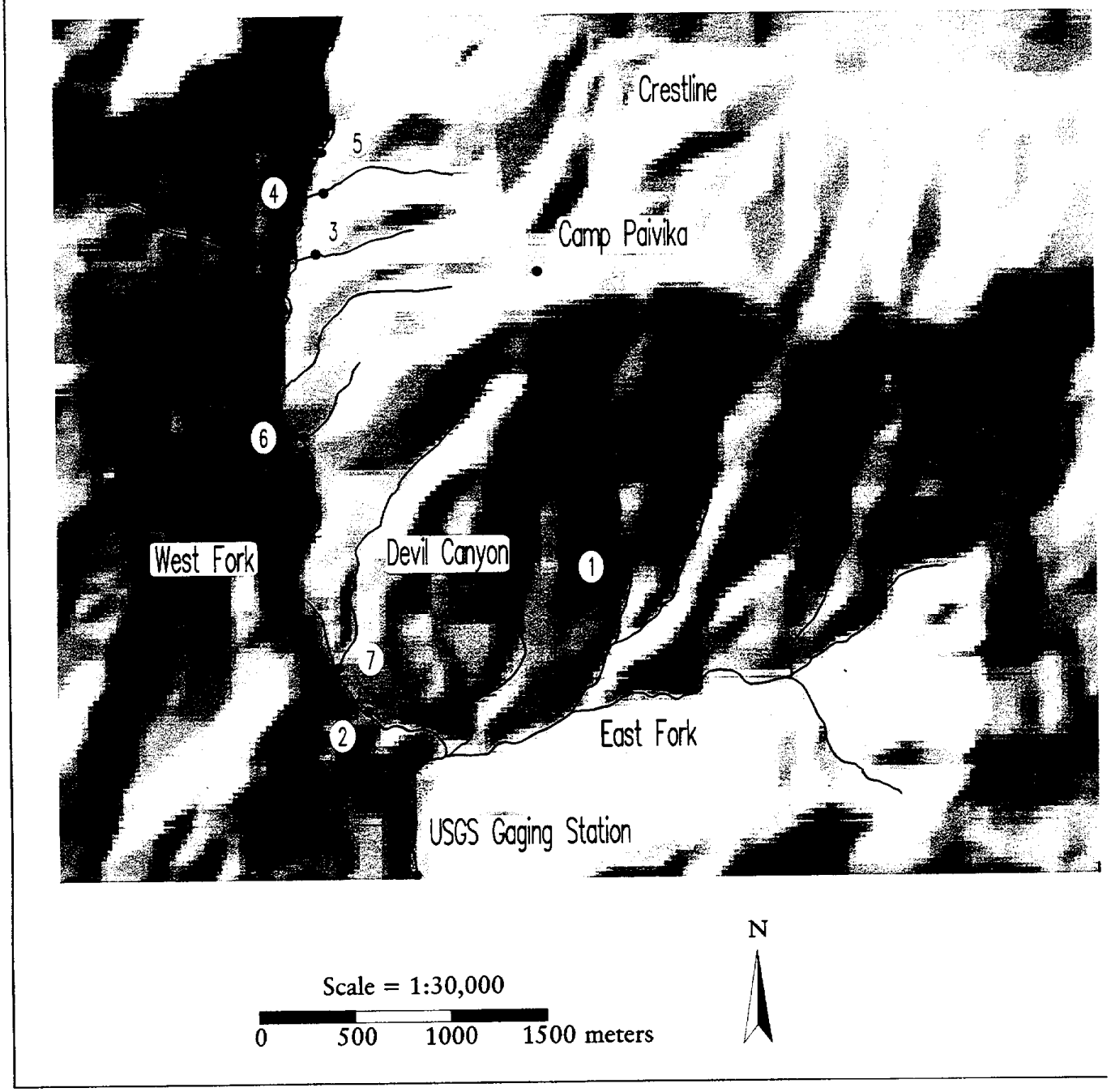


Fig. 2. Three-dimensional map of the catchments showing the location of streams and sampling sites in Devil Canyon.

APPENDIX: Sample Calculations for Throughfall Inputs, Fog Deposition, Streamwater Nitrate Export, and Trace Gas Fluxes

Throughfall Calculations

To calculate the amount of N deposited in throughfall (kg N ha^{-1} yr^{-1}): Throughfall is defined as the precipitation collected near ground level in a forest after it has passed through the overstory forest canopy. Throughfall samples collected in open areas (not covered by tree canopies) are the same as precipitation samples, providing that wind has not blown precipitation from nearby trees into the throughfall sampler. In this study throughfall collectors at each site (CP and BF) were placed along 4 transects (8 collectors per transect) in order to estimate throughfall deposition heterogeneity, and to be able to obtain an estimate of throughfall deposition for the entire forest stand.

Throughfall inputs were calculated by determining the average amount of N or S collected in the samplers of each transect (e.g., mg N/collector). The amount of N in a collector was calculated as the product of N ion concentration x throughfall volume. This was then expressed as N deposition per land area covered by the collector (mg N/m^2), which was then converted to kg N ha^{-1}. This was done for all four transects/site. Deposition to the stand for each throughfall collection date was determined by averaging deposition to the four replicate transects on that date. Annual throughfall deposition was obtained by summing the deposition for all the collection dates. Throughfall was thus expressed in the standard units: kg ha^{-1} yr^{-1}.

Fog Calculations

To calculate the amount of N deposited in fog (kg N ha^{-1} yr^{-1}): The passive line collectors were used to determine the rate of fog water deposition per unit surface area. We assumed that deposition rates to the forest canopy was similar to deposition fluxes to the nylon line collectors. Fog collected by the active (electrically-powered) collector was used for chemical analysis. The calculations were as follows:

mls fogwater/m^2 of passive collector surface X µg ion/ml fog = mg ion/m^2 collector or leaf area

mg ion/m^2 leaf area X m^2 foliage/m^2 land area (this is the LAI)* = mg ion/m^2 land area

We then converted mg ion/m^2 land area to kg ion/ hectare land area. This was done for each fog collection. The yearly total was obtained by summing the deposition for all the events.

*LAI is leaf area index. The value used for Camp Paivika (5.2) is a conservative value from the literature on LAI in ponderosa pine stands in western North America (See Fenn and Bytnerowicz, 1993). Since during winter the oak trees are defoliated we reduced LAI based on the percent of canopy cover due to oak. The stands are 43% oak at CP and 11% oak at CAO.

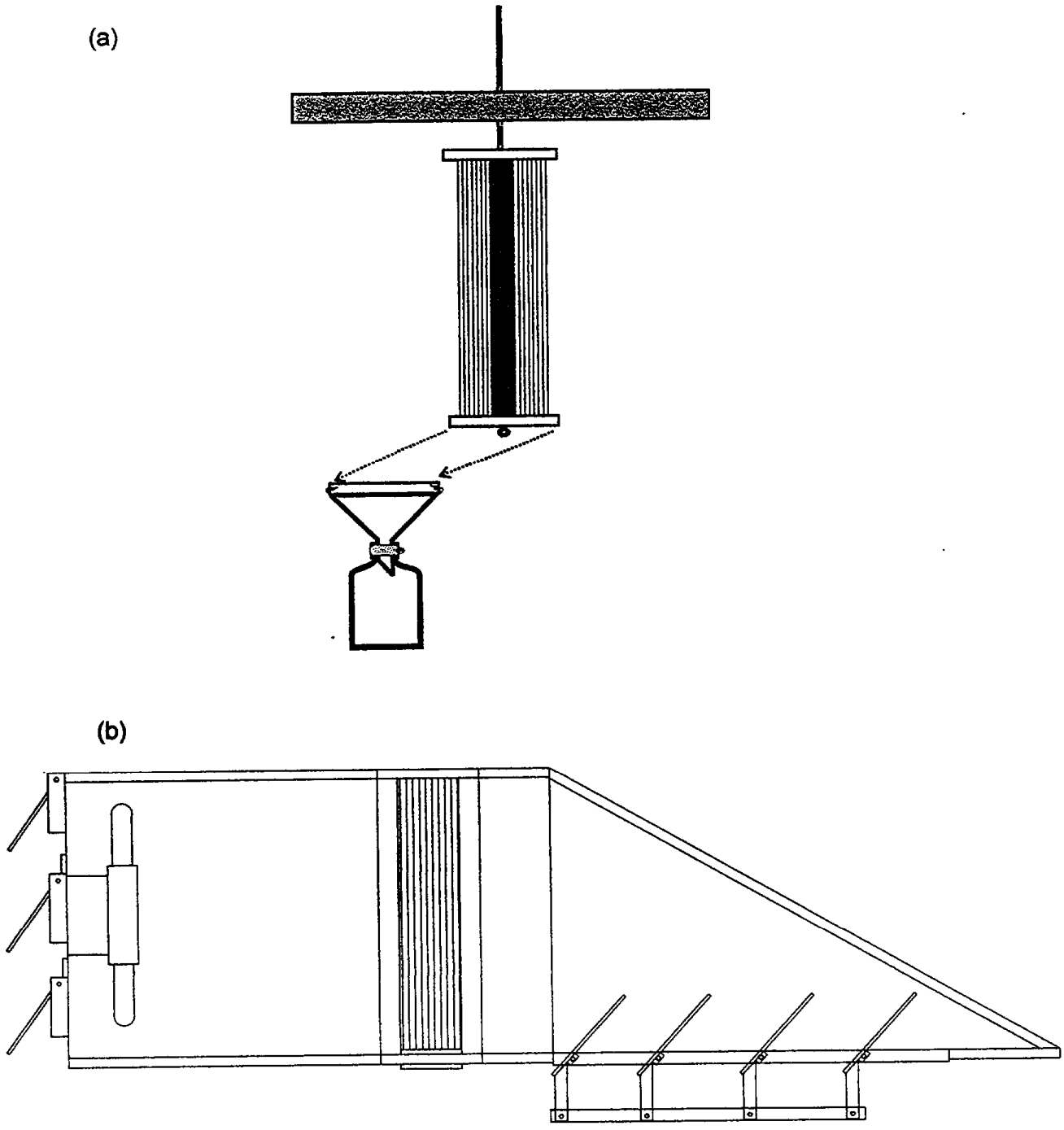


Fig. 4. Schematic diagram of the passive (a) and active (b) fog collectors used in this study.

Fig. 1. Map of the San Bernardino Mountains showing the location of the streamwater sampling sites and watersheds. Nitrogen deposition in the San Bernardino Mountains decreases from west to east. CP=Camp Paivika, BF=Barton Flats. Six streams were monitored at seven sites in DC (represented by the encircled '1-7'). The twelve stream sampling sites around the San Gorgonio Wilderness are indicated by the 12 encircled numbers.

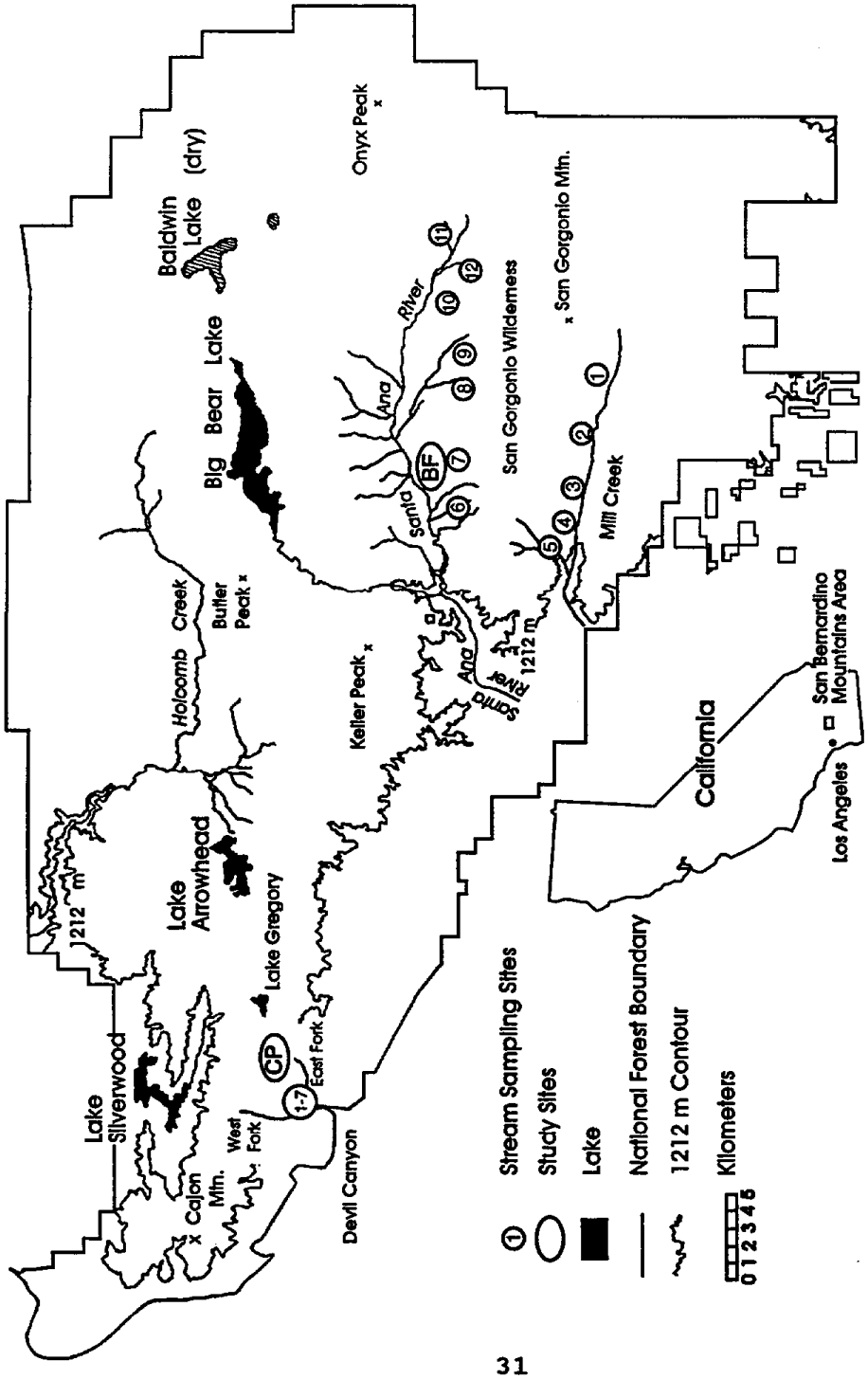
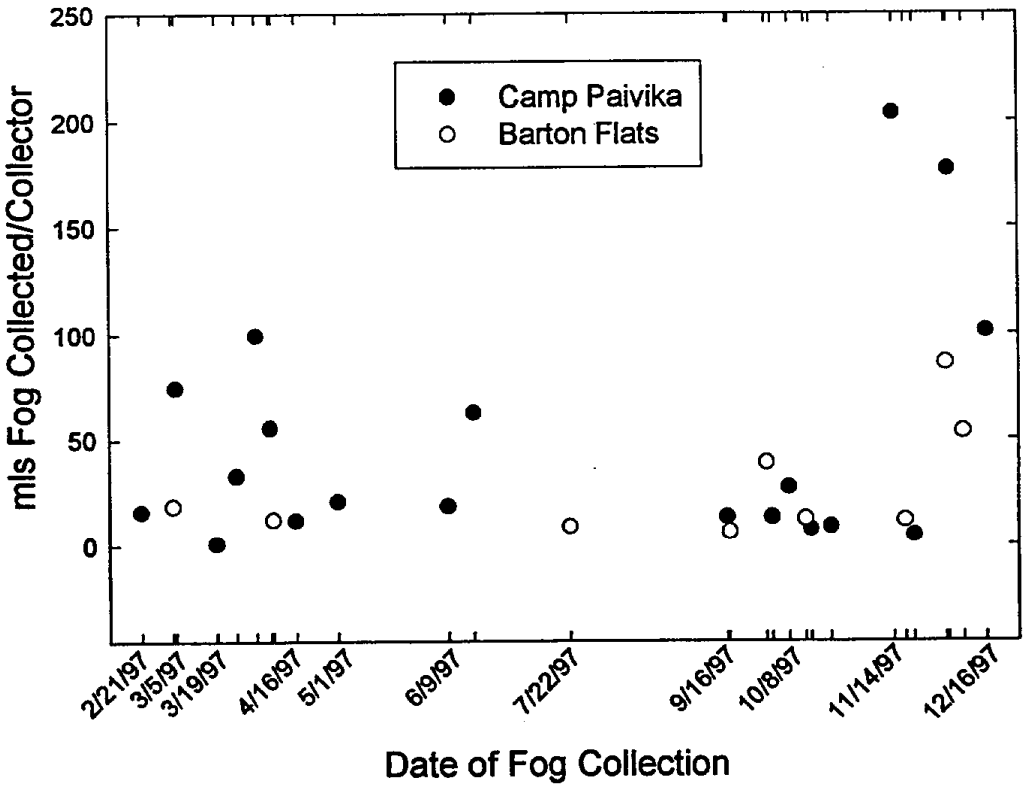


Fig. 6. Volume of fog collected in the passive collectors by date at Camp Paivika and at Barton Flats.



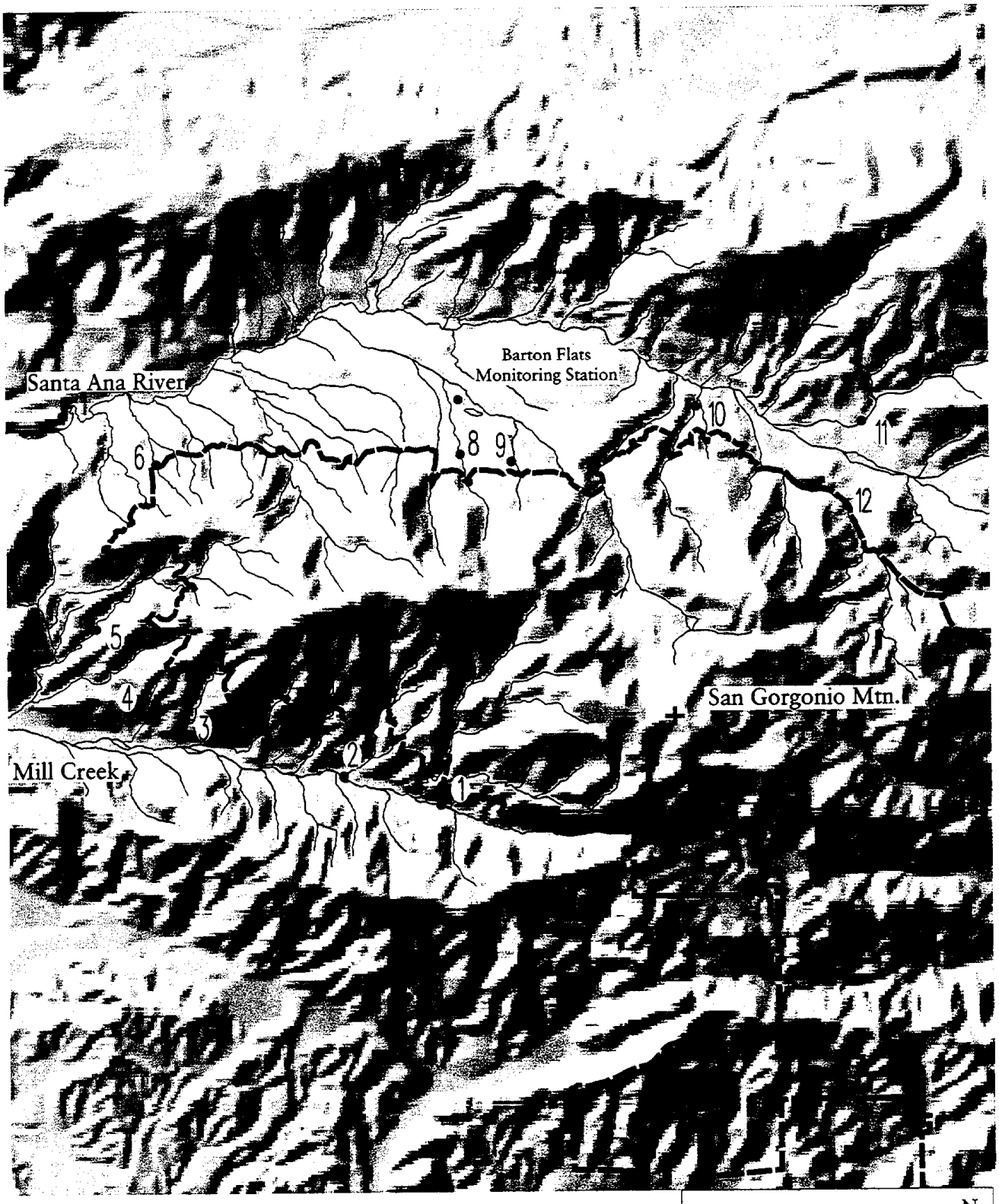


Fig. 3. Three-dimensional map of the catchments showing the location of streams and sampling sites in the San Gorgonio Wilderness.

Fig. 8. Volume-weighted mean ion concentrations in throughfall at Camp Paivika and Barton Flats. Error bars are standard errors of the plot mean.

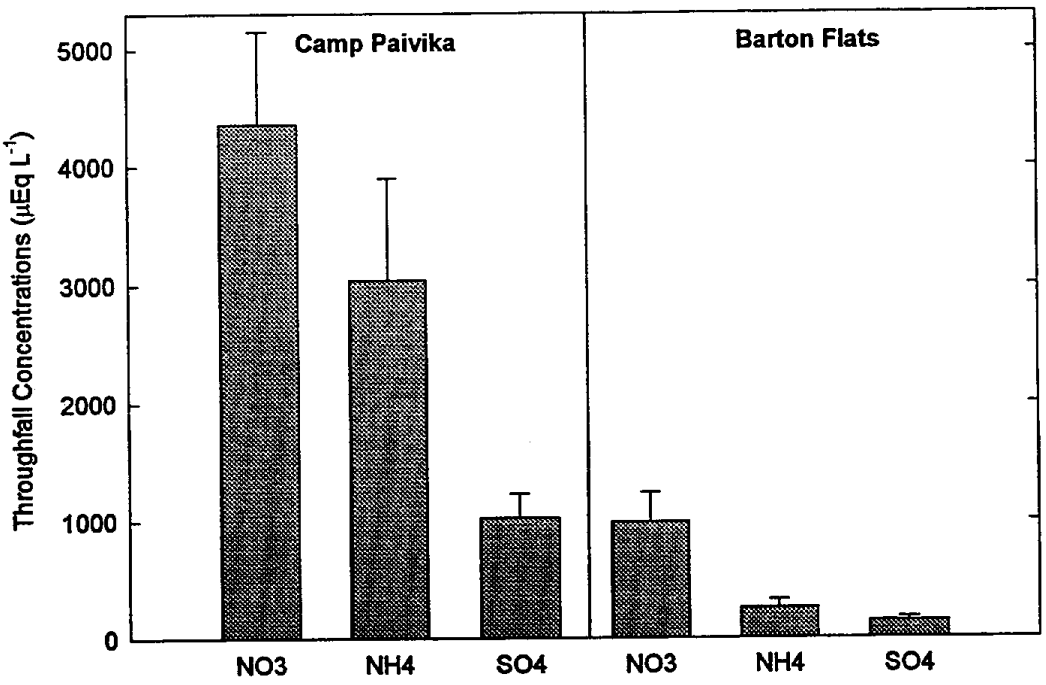


Fig. 5. Ionic concentrations in fogwater at Camp Paivika and Barton Flats.

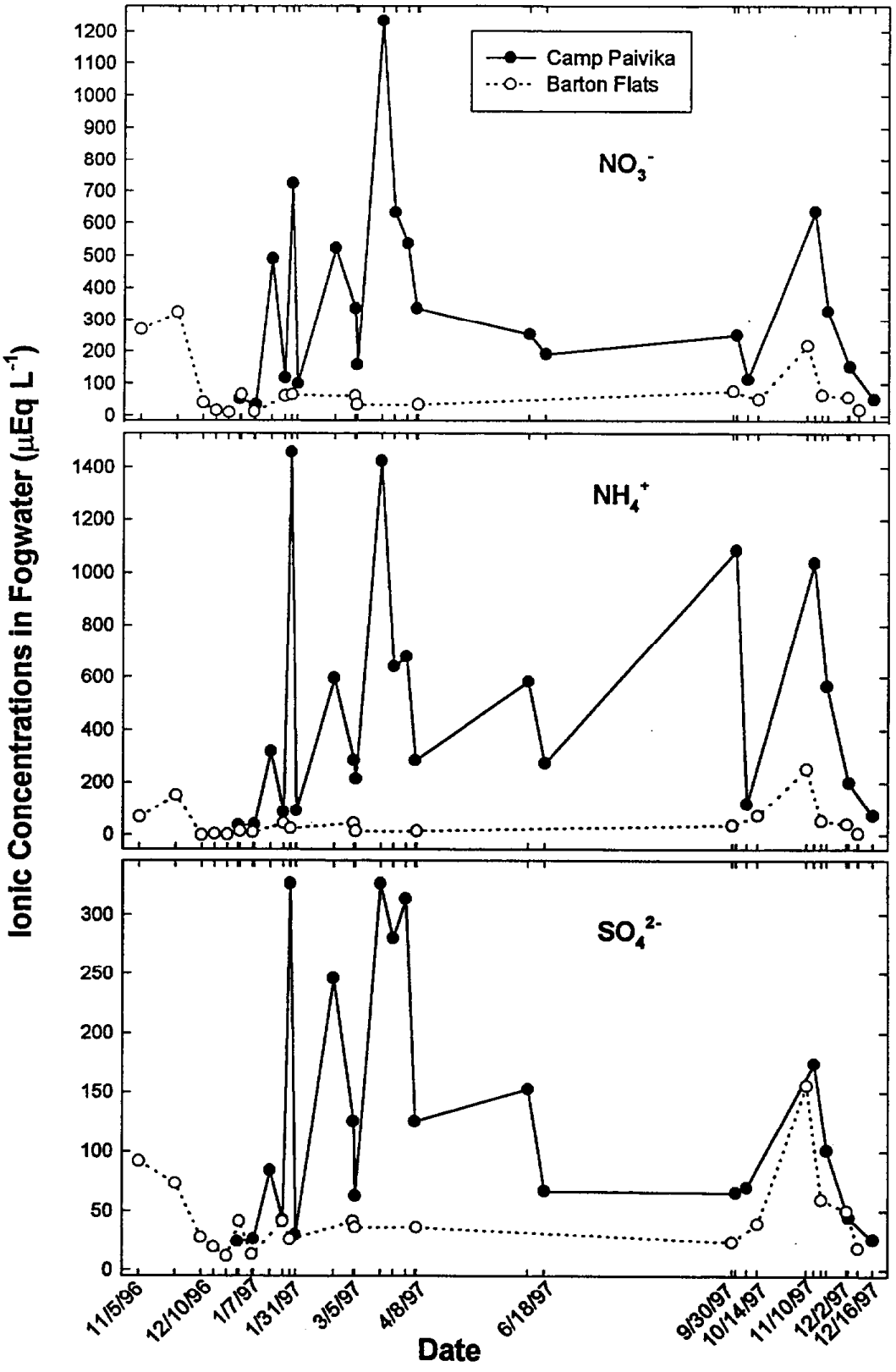


Fig. 10. Soil nitric oxide flux, temperature, and moisture at Camp Osceola (a). Levels of extractable NH_4^+ and NO_3^- in soil and litter at Camp Osceola (b).

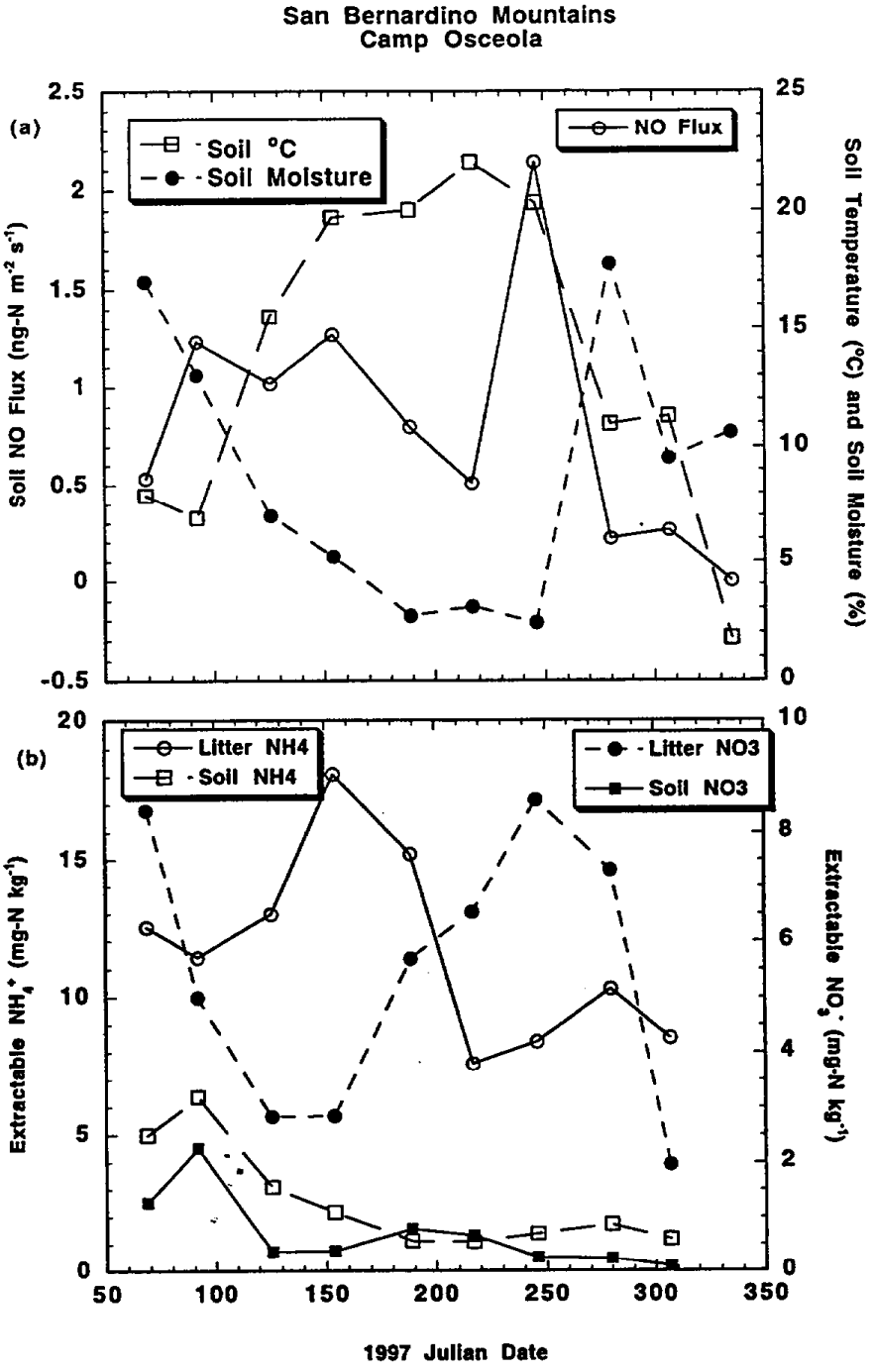
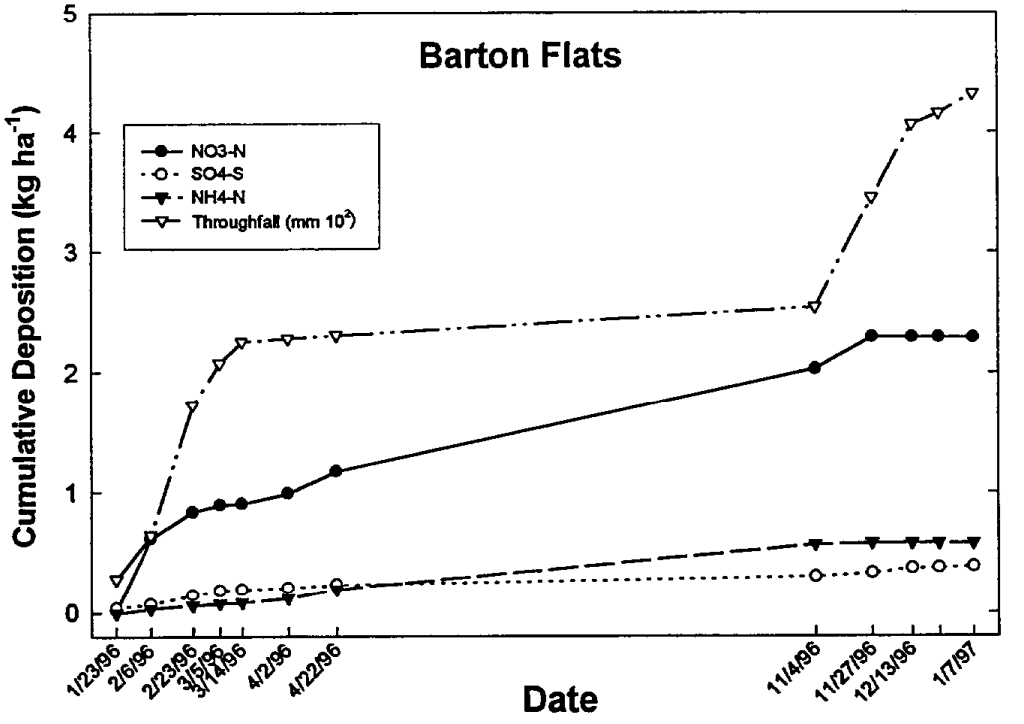


Fig. 7. Cumulative bulk throughfall deposition of NO_3, SO_4^{2-}, and NH_4^+, and throughfall volumes at Camp Paivika and Barton Flats.



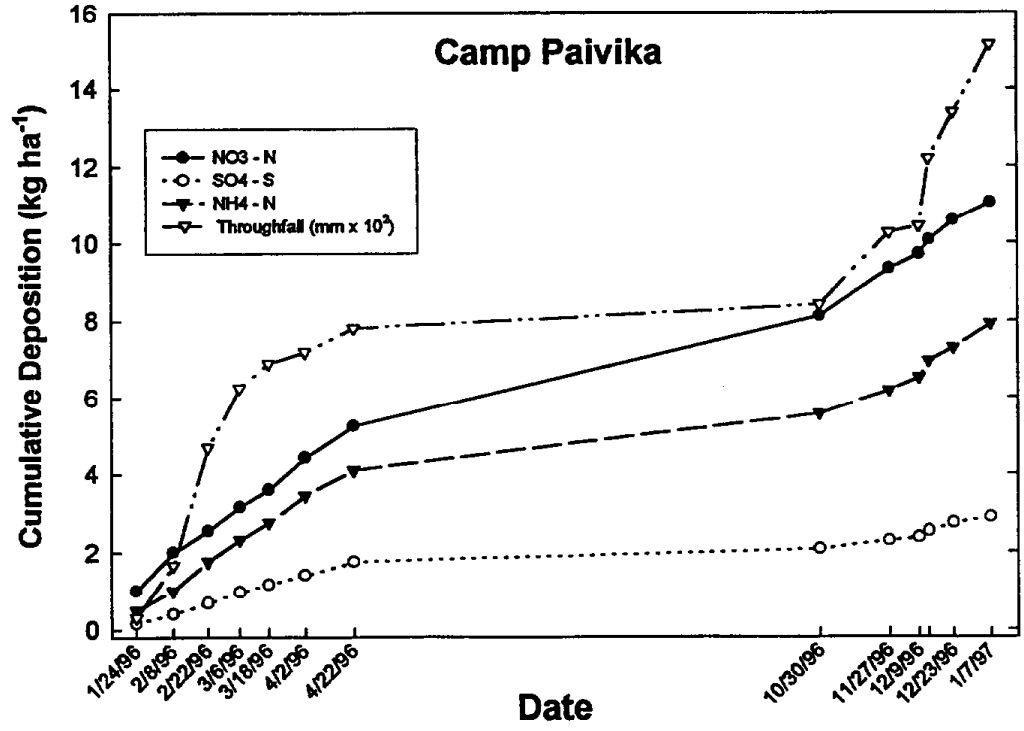


Fig. 12. Average NO_3^- concentrations in streamwater in Devil Canyon and the San Gorgonio Wilderness. Error bars are standard errors of the mean.

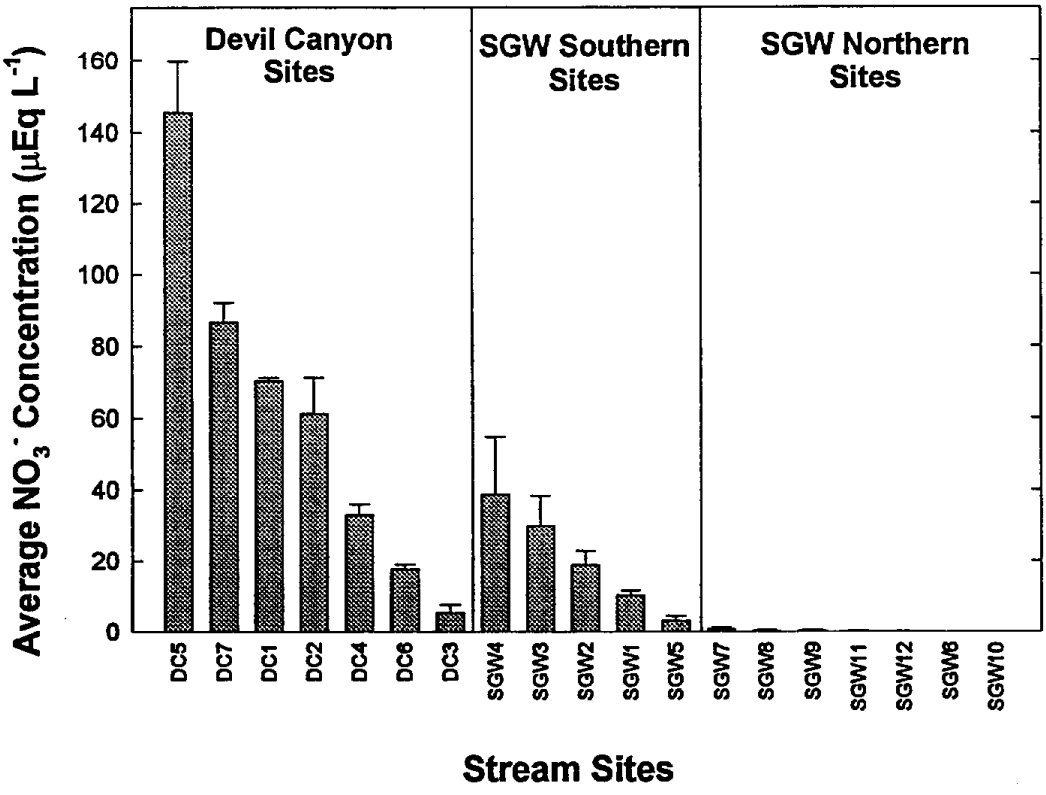


Fig. 9. Soil nitric oxide flux, temperature, and moisture at Camp Paivika (a). Levels of extractable NH_4^+ and NO_3^- in soil and litter at Camp Paivika (b).

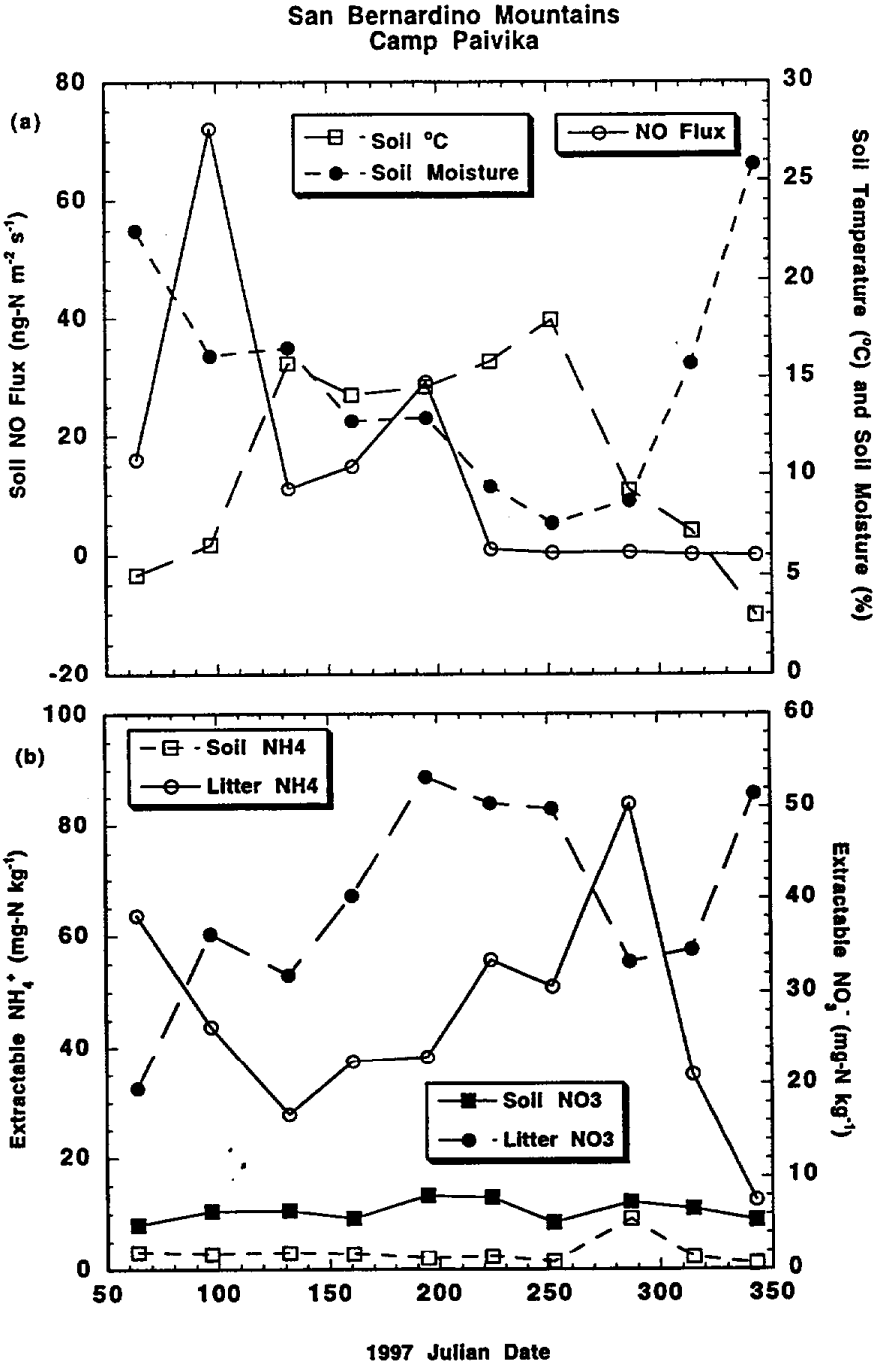


Fig. 14. Sulfate concentrations in streamwater in the Devil Canyon (high deposition) and San Gorgonio Wilderness (low deposition) regions.