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# Temporal and Spatial Trends in Streamwater Nitrate Concentrations in the San Bernardino Mountains, Southern California

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## ABSTRACT

**We report streamwater nitrate ($NO_3^-$) concentrations for December 1995 to September 1998 from 19 sampling sites across a N deposition gradient in the San Bernardino Mountains. Streamwater $NO_3^-$ concentrations in Devil Canyon (DC), a high-pollution area, and in previously reported data from the San Gabriel Mountains 40 km northeast of Los Angeles, are the highest values reported in North America for undisturbed forest or shrub land watersheds. Concentrations in the primary stream draining western DC peaked at 350 μmol $L^{-1}$ in December 1997 and minimum base flow $NO_3^-$ concentrations were nearly always ≥80 μmol $L^{-1}$. In the San Gorgonio Wilderness (SGW), average $NO_3^-$ concentrations in four streams along the southern transect (moderate N deposition), ranged from 10 to 37 μmol $L^{-1}$, while average $NO_3^-$ concentrations were ≤0.7 μmol $L^{-1}$ in seven streams along the northern transect (low N deposition). Peak $NO_3^-$ concentrations in DC and in the SGW occurred after large winter storms, and a large spike in $NO_3^-$ concentrations (10–370 μmol $L^{-1}$) in SGW Streams 1 to 5 was observed after thundershower activity in July 1997. Streamwater export of $NO_3$–N from Devil Canyon ranged from 3.6 to 11.6 kg $ha^{-1}$ $yr^{-1}$ during water years 1995 to 1998. This study further indicates that N emissions from fossil fuels and agriculture impact not only air quality, but also water quality from watersheds that are recipients of atmospheric N deposition.**

Human alteration of the nitrogen (N) cycle is an environmental 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 that exhibit symptoms of N excess, analogous to over fertilization of arable land (Dise et al., 1998; 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 terrestrial and 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 (e.g., from agricultural runoff; 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 hydrologic, edaphic, and plant indicators (Anderson et al., 1988; Fenn et al., 1996; Riggan et al., 1985). Preliminary evidence suggests that symptoms of N saturation (N in excess of plant demand or elevated hydrologic $NO_3^-$ export) are evident in mixed conifer or chaparral sites receiving atmospheric deposition of 20 to 25 kg N $ha^{-1}$ $yr^{-1}$ or greater (Fenn et al., 1996; Kiefer and Fenn, 1997; Riggan et al., 1985). 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 nonconservative 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 and Poth, 1999; Fenn et al., 1996; Riggan et al., 1985, 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, 1994). Dry-deposited N accumulates in watersheds and nitrate accumulates in soil during the extended dry *smog* season (Fenn et al., 1996; Padgett et al., 1999). Fire suppression favors N accumulation in aging biomass, litter, and surface soils. When fires do occur under these primed conditions, extremely large pulses of N are released into the atmosphere and into the riparian system in subsequent storms. Postfire nitrification, leaching, and erosion also release large amounts of $NO_3^-$ into streams (Dunn et al., 1979; Riggan et al., 1994). Nitrate concentrations in streamwater were as high as 1120 μmol $L^{-1}$ in severely burned chaparral watersheds with high N deposition in the San Gabriel Mountains near Los Angeles (Riggan et al., 1994). Significant losses of N as trace gas emissions (e.g., NO, $N_2O$) also occur in montane areas of southern California with high levels of N deposition (Anderson et al., 1988; Fenn et al., 1996).

In this study we present 3 yr of data on streamwater $NO_3^-$ concentrations from catchments located along N deposition gradients in the San Bernardino Mountains (SBM) in southern California. The primary objective was to evaluate stream water quality in the SBM in terms of $NO_3^-$ concentrations, and to determine if streamwater $NO_3^-$ concentrations co-vary with N deposition across pollution gradients in the SBM. A secondary objective was to determine the level of $NO_3^-$ export from Devil Canyon, an N-saturated watershed in the western SBM.

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**Abbreviations:** DC, Devil Canyon; SGW, San Gorgonio Wilderness; SBM, San Bernardino Mountains; USGS, U.S. Geological Survey; WY, water year.

**Table 1. Characteristics of the catchments and streams sampled in this study.**

| Stream no.; name; elevation, m | Catchment area, ha; % slope; streambed slope | Vegetation cover, %† Conifer | Hardwood | Chaparral | Stream characteristics‡ | Alder in stream; watershed fire history§ |
|---|---|---|---|---|---|---|
| | | | Devil Canyon | | | |
| Stream 1, 933 | n/a; underground spring | 5 | 12 | 77 | A spring sampled at the source, perennial | No alder; underground flow; 91% burned in 1954, 30–50% in 1918, 1924, 1942 and 1980 |
| Stream 2; lower West Fork; 767 | 667<br>49<br>14 | 12 | 22 | 65 | Main drainage, perennial, large boulders in channel | Alder is common in riparian zone; 74% burned in 1954, 52% in 1980; minor burn in 1912 |
| Stream 3; 1144 | 28<br>66<br>49 | 27 | 39 | 34 | Relatively short stream, intermittent; accumulation of acorns/leaf litter in stream channel | No alder; 84% burned in 1954, 14% in 1980 |
| Stream 4; 1193 | 31<br>50<br>41 | 36 | 56 | 8 | Moderate length, perennial | Alder is common in riparian zone; 91% burned in 1954 |
| Stream 5; upper West Fork; 1191 | 137<br>47<br>11 | 67 | 21 | 12 | Main drainage, perennial, large boulders in channel | Alder is common in riparian zone; 17% burned in 1954 |
| Stream 6; 954 | 6<br>51<br>102 | 0 | 1 | 99 | 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; 100% burned in 1954, 71% burned in 1980 |
| Stream 7; 803 | 52<br>50<br>32 | 13 | 4 | 81 | Longest tributary, perennial, narrow stream channel | No alder; 99% burned in 1954, 32% in 1980, 35% burned in 1912 |
| | | | San Gorgonio Wilderness | | | |
| Stream 1; Vivian Creek; 1843 | n/a; mostly underground spring | n/a | n/a | n/a | 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; area around spring is unburned. |
| Stream 2; Alger Creek; 1662 | 637<br>58<br>23 | 90 | 0.6 | 9 | Sampled a few m below a seep in Alger Creek, intermittent | Alder in some stretches of Alger Creek; 10% burned in 1909 and in 1926 |
| Stream 3; Monkey Face Creek; 1380 | 287<br>78<br>32 | 70 | 8 | 21 | Moderate length, intermittent | No alder near sample site; total of 16% burned in 1958 and 1965—mostly in 1958 |
| Stream 4; Frustration Creek; 1414 | 40<br>77<br>52 | 38 | 0.5 | 59 | Short length, sampled near the base of a waterfall, perennial | No alder; 24% burned in 1915; 49% burned in 1958 |
| Stream 5; Mountain Home Creek; 1513 | 820<br>50<br>24 | 76 | 9 | 15 | Very steep canyon, long stream with relatively high flows, large boulders in channel, perennial | No alder visible upstream, a few below the sampling site; unburned |
| Stream 6; Kilpecker Creek, West Fork; 1744 | 74<br>48<br>39 | 74 | 0 | 26 | Short stream, sampled a few m below a waterfall, intermittent | No alder; 4% burned in 1930 |
| Stream 7; Forsee Creek, East Fork; 1838 | 726<br>50<br>24 | 93 | 0.4 | 7 | Long stream, gentle slope, wide channel, perennial | Dense alder stand covering the wide stream channel; unburned |
| Stream 8; Barton Creek, East Fork; 2096 | 399<br>46<br>27 | 97 | 0 | 2 | Moderate length, perennial, constant flow rate | No alder; unburned |
| Stream 9; Frog Creek; 2226 | 38<br>49<br>32 | 100 | 0 | 0 | Short length, low flows, perennial | No alder; unburned |
| Stream 10; Lost Creek; 1923 | 84<br>36<br>22 | 97 | 0 | 3 | Long stream, intermittent | No alder; unburned |
| Stream 11; Ciénaga Seca Creek; 2081 | 2595<br>35<br>6 | 89 | 0 | 9 | Long stream, perennial | No alder; 18% burned in 1952 |
| Stream 12; Fish Creek; 2187 | 989<br>43<br>8 | 98 | 0 | 2 | Long stream, perennial | No alder; 23% burned in 1951 |

† Vegetation cover is given according to Calveg vegetation life form classes (USDA Forest Service, 1981). The dominant classes in our study areas were: Conifer, Hardwood, and Chaparral, with a minor soft chaparral (sage) component in some areas. The conifer designation generally represents a mixed conifer type (including a hardwood component), with conifer species coverage ranging from 40–70% in the study watersheds. Vegetation cover data was obtained from a digital GIS database for the four southern California National Forests (USDA, Forest Service, Region 5, Remote Sensing Laboratory, Sacramento, CA).

‡ Stream length refers to the length of tributary streams above the streamwater sampling point.

§ Fire history data is from a database provided by the USDA, Forest Service, Region 5, Remote Sensing Laboratory, Sacramento, CA.

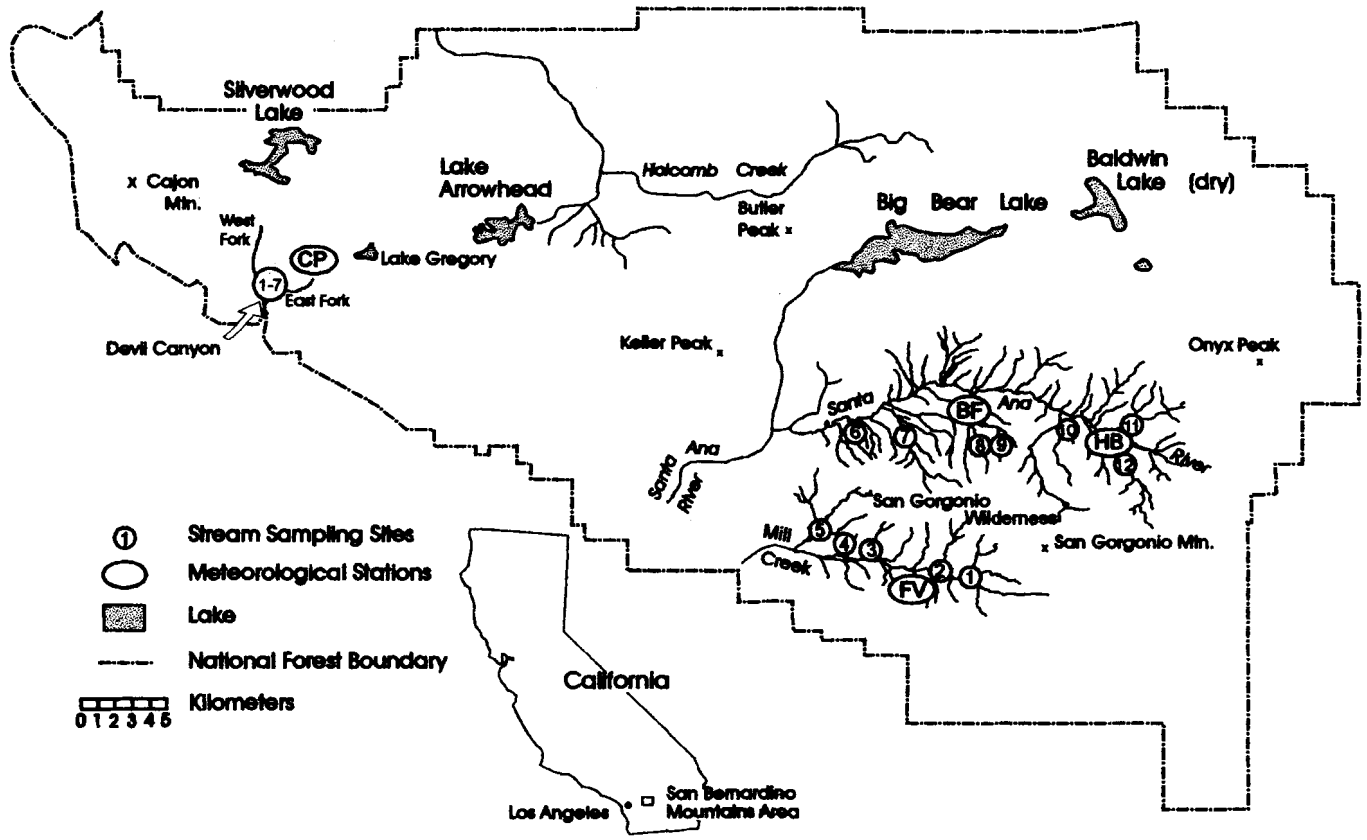


**Fig. 1. Map of the San Bernardino Mountains showing the location of the streamwater sampling sites and watersheds. Nitrogen deposition in the San Bernardino Mountains decreases from west to east. CP = Camp Paivika, FV = Fallsvale, BF = Barton Flats, HB = Heart Bar. Six streams were monitored at seven sites in DC. The 12 stream sampling sites around the San Gorgonio Wilderness are indicated by the 12 encircled numbers.**

## METHODS

### Study Sites

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, and from 12 streamwater sampling sites in an eastern low to moderate pollution region surrounding the San Gorgonio Wilderness, a Class I wilderness area as defined under the Clean Air Act (Table 1, Fig. 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 1580 m. At the bottom of the canyon at the site of the USGS stream gauge station (Station no. 11063680) the elevation is 632 m (Fig. 2). Vegetation in DC is mixed conifer forest near the crest of the watersheds, but grades to chaparral at lower elevations, with riparian woodland bordering the stream channels. Along some of the streams in DC and the SGW white alder (*Alnus rhombifolia* Nutt.) trees inhabit portions of the stream channels. Vegetation in the San Gorgonio Wilderness (SGW) below tree line consists of various pine–fir (*Pinus* spp.–*Abies* spp.) mixes, while mixed conifer forests that include oak species (*Quercus* spp.) 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 (Fig. 3). Further descriptions and details about the San Bernardino Mountains and air pollution impacts on these montane ecosystems are reviewed in a recent book (Miller and McBride, 1999).

The San Bernardino Mountains are composed of a complex assemblage of crystalline and sedimentary rocks ranging from ancient Precambrian basement terranes to modern Quaternary deposits. The regional chronology and landscape evolution primarily reflect the fault history of a tectonic plate boundary. The majority of the western and central San Bernardino Mountains, including our study sites at Devil Canyon and San Gorgonio, are made up of plutonic igneous rocks of Mesozoic age (late Triassic–Cretaceous). These granitoid rocks, mostly quartz monzonite and granodiorite, are similar to and have affinities with those of the Mojave Desert to the north (Dibblee, 1982; Matti and Morton, 1993).

Estimated total N deposition decreases from 25 to 35 kg $ha^{-1}$ $yr^{-1}$ at Camp Paivika (the crest of DC) to 3 to 6 kg $ha^{-1}$ $yr^{-1}$ at Barton Flats (Table 2) in the eastern San Bernardino Mountains near the base of the northern side of the San Gorgonio Wilderness and near SGW Stream 8 (M.E. Fenn, 1999, unpublished data; Fig. 1–3). Previous studies of throughfall and dry deposition across the SBM reported a fivefold decrease in N deposition from Camp Paivika to Barton Flats (Fenn and Bytnerowicz, 1993, 1997). Annual N deposition is not known for the SGW, but recent deposition measurements along an elevational gradient (1192–2775 m) in the western SGW demonstrated that moderately high N deposition occurs in the western portion of the wilderness (Bytnerowicz et al., 1999). Although total annual N deposition is not known for the catchments or for the stream sampling sites, spatial trends in pollution exposures are known based on published ozone concentrations and dry deposition data in the San Bernardino Mountains (Fenn and Bytnerowicz, 1993; Miller et al., 1986). Nitrogen deposition decreases from west to east

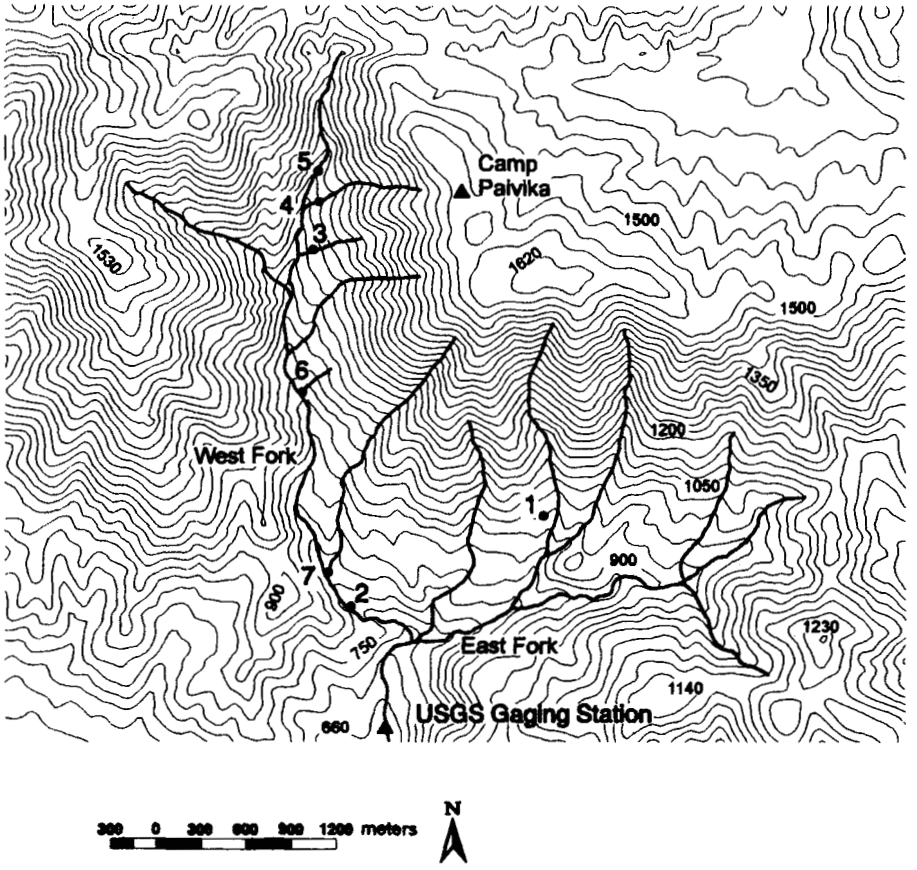


**Fig. 2. Contour map of the catchments showing the location of streams and sampling sites in Devil Canyon. Contour intervals are 30 m.**

and from south to north in the San Bernardino Mountains. Nitrogen deposition is expected to be much greater along the southern transect (SGW1–5) of streamwater sampling sites in the SGW compared with the northern sites (SGW6–12). The four most southern sites (SGW1–SGW4) are directly exposed to polluted air masses transported directly through the Mill Creek drainage from the adjacent urban areas, while the northern SGW watersheds (SGW6–SGW12) are less directly exposed to air pollution loading. In the San Bernardino Mountains N deposition decreases much more rapidly than ozone exposure along the west to east gradient (Fenn and Bytnerowicz, 1993). Thus, N deposition likely decreases significantly from west to east along the two SGW transects (Fig. 1).

Data on mean annual precipitation, temperature, and estimated N deposition at five sites within the DC and the SGW regions are given in Table 2. Two of the sites are in the DC region, one at the base of the canyon and Camp Paivika is at the crest of DC. Data from Fallsvale is presented to characterize the southern SGW watersheds, and Barton Flats and Heart Bar are located along the northern SGW transect (Fig. 1). Data for Barton Flats is from a monitoring station maintained by the USDA Forest Service since 1991 (Fenn and Bytnerowicz, 1997), while data for the other four sites are from the San Bernardino County Flood Control District.

The sampled watersheds in the SGW region have burned little in the last 90 yr compared with Devil Canyon. In eight of the watersheds in the SGW region, 10% or less of the watershed area has burned since 1909 (Table 1). Only the watershed of SGW Stream 4 (49% burned) has burned >23% of the area. In contrast, six of the seven watersheds in DC were burned over 71 to 99% in 1954 and 31 to 71% in 1980 (Table 1). Watershed DC5 is the only watershed in Devil Canyon without major burning this century. Only 17% of the area within DC5 has burned, and that occurred in 1954 (GIS database; USDA, Forest Service, Region 5, Remote Sensing Lab., Sacramento, CA).

## Field Sampling and Laboratory Analyses

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 before sample collection. Samples were then transported to the Forest Fire Laboratory and stored in a freezer until time of analysis. The streamwater samples were not filtered before analysis. Samples were collected at varying intervals; once or twice per month during the winter wet season and usually monthly during summer. All streamwater samples were analyzed for $NO_3^-$ and $SO_4^{2-}$ (data not reported here). Samples collected from December 1995 to June 1996 were also analyzed for $NH_4^+$. However, because $NH_4^+$ concentrations were near detection limits and not a focus of this study, $NH_4^+$ analysis was discontinued after June 1996. Anion concentrations were determined with ion chromatography (Dionex[1] series 4000i, Sunnyvale, CA). Ammonium was determined colorimetrically with a Technicon TRAACS 800, Autoanalyzer (Tarrytown, NY). Laboratory QA/QC protocols were followed for all analyses. These protocols include the use of sample replicates and random duplicate analyses.

Nitrate export in streamwater from the entire DC watershed was calculated using stream discharge data from a U.S. Geo-

[1] Mention of trade names or products is for information only and does not imply endorsement by the USDA.

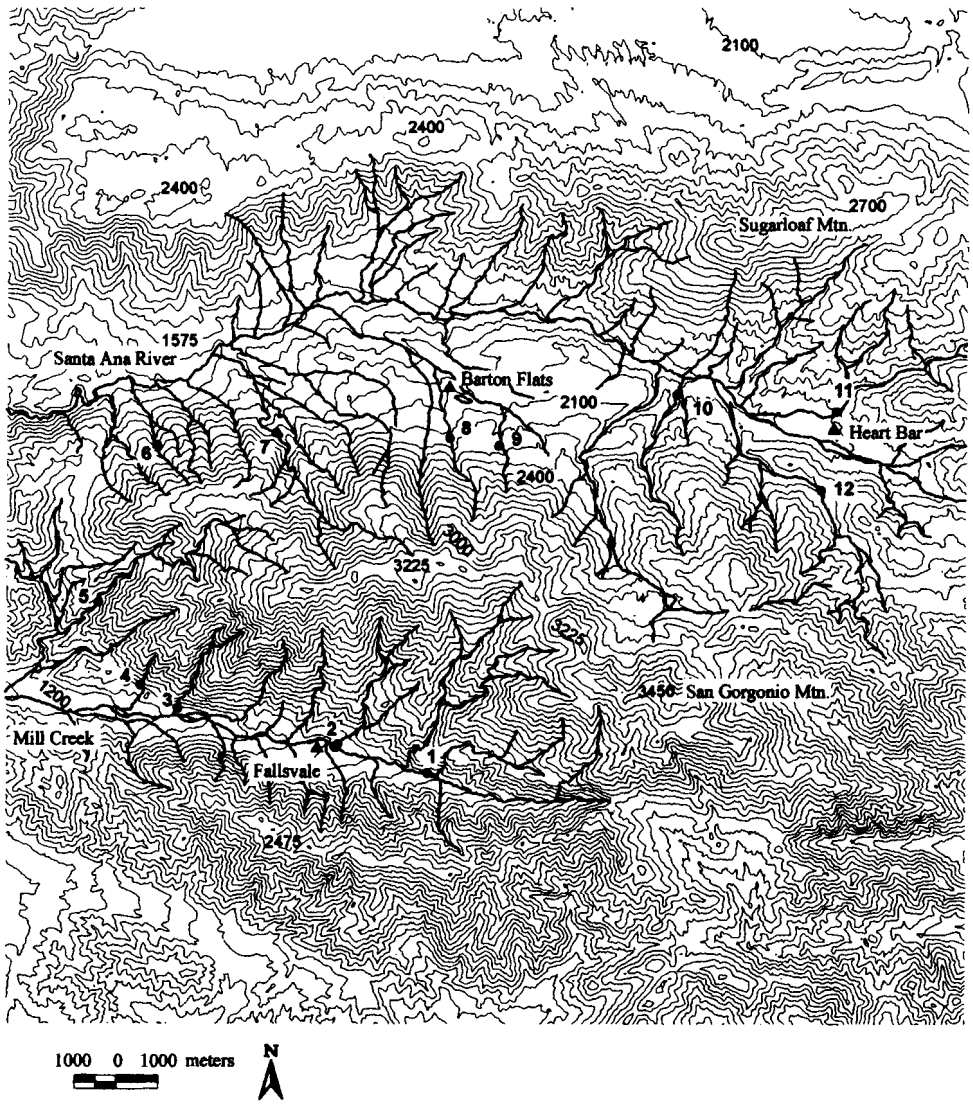


**Fig. 3. Contour map of the catchments showing the location of streams and sampling sites in the San Gorgonio Wilderness. Contour intervals are 75 m. Triangle symbols represent monitoring sites at Fallsvale, Barton Flats, and Heart Bar where precipitation and temperature data were collected.**

logical Survey (USGS) 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 1422 ha (USGS, 1995). Annual $NO_3^-$ export for water years 1996 to 1998 was calculated on monthly time steps as the product of streamflow volume and $NO_3^-$ concentration in DC2. Average $NO_3^-$ concentrations from samples at the USGS gauging station were nearly identical to concentrations from DC2 during a 10-mo period (M.E. Fenn and M.A. Poth, 1998, unpublished data). Nitrogen export was also calculated for WY95 using streamwater $NO_3^-$ concentrations estimated from a regression ($r$ = 0.75) of $NO_3^-$ concentration vs. streamflow rates for December 1995 to September 1998.

## RESULTS

### Spatial Trends

Spatial trends in streamwater $NO_3^-$ concentrations were apparent between DC and the SGW and within the SGW sites (Fig. 4). Nitrate concentrations during summer baseflow were consistently higher in five of the six streams at DC compared with the SGW streams (Fig. 5 and 6). Average $NO_3^-$ concentration in the spring-fed stream (DC1) in DC (73 μmol $L^{-1}$) was sevenfold greater than in the spring-fed stream (SGW1) in the SGW (10 μmol $L^{-1}$). During the 3 yr of the study peak winter $NO_3^-$ concentrations in the SGW were 182, 50, and 128 μmol $L^{-1}$ (SGW4), compared with 295, 152, and 350 μmol $L^{-1}$ in the West Fork in DC (DC5; Fig. 5 and 6). Streamwater was sampled at two points along the West Fork in DC. Nitrate concentrations in the upper West Fork sampling site (DC5) were on average more than double those from the lower sampling site (DC2; Fig. 4).

Spatial trends in streamwater $NO_3^-$ concentrations were also apparent within the SGW region. Only the four catchments located along the southern transect of the SGW (SGW1–4; SGW5 is slightly north of the main Mill Creek drainage), where N deposition is greatest, exported levels of $NO_3^-$ averaging at least 10 μmol $L^{-1}$ (Fig. 4). Nitrate concentrations in SGW3 and SGW4 were generally higher than the other SGW streams and were elevated for several weeks before and after peak

**Table 2. Meteorological and environmental data from five monitoring sites within the streamwater study areas. Values in parentheses are the years of temperature and precipitation data.**

| Site | Location | Elevation† | Yearly mean temp.† | Mean annual precipitation† | N deposition‡ |
|---|---|---|---|---|---|
| | | m | °C | mm | kg ha$^{-1}$ |
| Devil Canyon | 34°12′11″ 117°20′6″ | 568 | 18.7 (91–98) | 610 (27–97) | 25–35 |
| Camp Paivika | 34°14′25″ 117°19′33″ | 1580 | 12.9 (56–91) | 987 (56–91) | 25–35 |
| Fallsvale | 34°4′55″ 116°54′25″ | 1821 | 11.1 (61–79) | 869 (70–97) | 10–15 |
| Barton Flats | 34°10′8″ 116°53′17″ | 1945 | 10.6 (92–97) | 608 (91–98) | 3–6 |
| Heart Bar | 34°9′27″ 116°47′55″ | 2033 | 9.0 (66–76) | 399 (66–97) | 2–4 |

† Data for Devil Canyon is at the base of the canyon. Camp Paivika is at the crest of Devil Canyon. Temperature and precipitation data for Camp Paivika is from the Crestline S.E. San Bernardino Flood Control District site number 5181 (elev. 1569 m), located 3.4 km east of Camp Paivika. Temperature data for Fallsvale is from Forest Falls (elev. 1611 m), located <1 km from the Fallsvale precipitation sampling site.

‡ Nitrogen deposition estimate for Camp Paivika at the crest of DC is from unpublished throughfall data (M.E. Fenn, 1999). Total N deposition was calculated from throughfall inputs, assuming that 30–40% of dry-deposited N was retained by the canopy and not measured in throughfall (see Fenn and Bytnerowicz, 1997). Estimated range of N deposition in Devil Canyon is assumed to be similar to Camp Paivika. Deposition at Barton Flats is also from unpublished throughfall data and from dry deposition studies (Fenn and Bytnerowicz, 1997). The estimated range of deposition inputs for Fallsvale and Heart Bar are based on dry deposition flux data reported for the air pollution gradient in the San Bernardino Mountains (Fenn and Bytnerowicz, 1993), and spatial trends in pollution throughout the mountain range (Miller et al., 1986).

$NO_3^-$ concentrations, indicating the much greater severity of N saturation of these two watersheds. Peak $NO_3^-$ concentrations in SGW1 and SGW2 were intermediate, but baseline $NO_3^-$ levels in SGW2 were often greater than in SGW3 and SGW4. Nitrate concentrations in streams on the northern side of the SGW (Streams 6–12) were frequently at or below detection limits during baseflow and peak values during high flow were relatively low, ranging from 0.0 to 9.9 μmol L$^{-1}$, but were usually <1.0 μmol L$^{-1}$. Quantitative relationships between N deposition in the catchments and streamwater $NO_3^-$ concentrations could not be tested because data for N deposition in the individual catchments is not available. However, for the SGW streams along the southern transect (Streams 1–4), average $NO_3^-$ concentrations in streamwater were highly correlated ($r = 0.96$) with east-west location, a measure of the distance from the urban pollution source to the west (Fig. 7).

## Temporal Trends

The streams in DC exhibited a wide range of $NO_3^-$ concentration profiles (Fig. 6). Nitrate concentrations were lowest in DC3, a tributary of the West Fork, with moderate peak concentrations of 52 and 19 μmol L$^{-1}$ during periods of high precipitation and runoff in winter

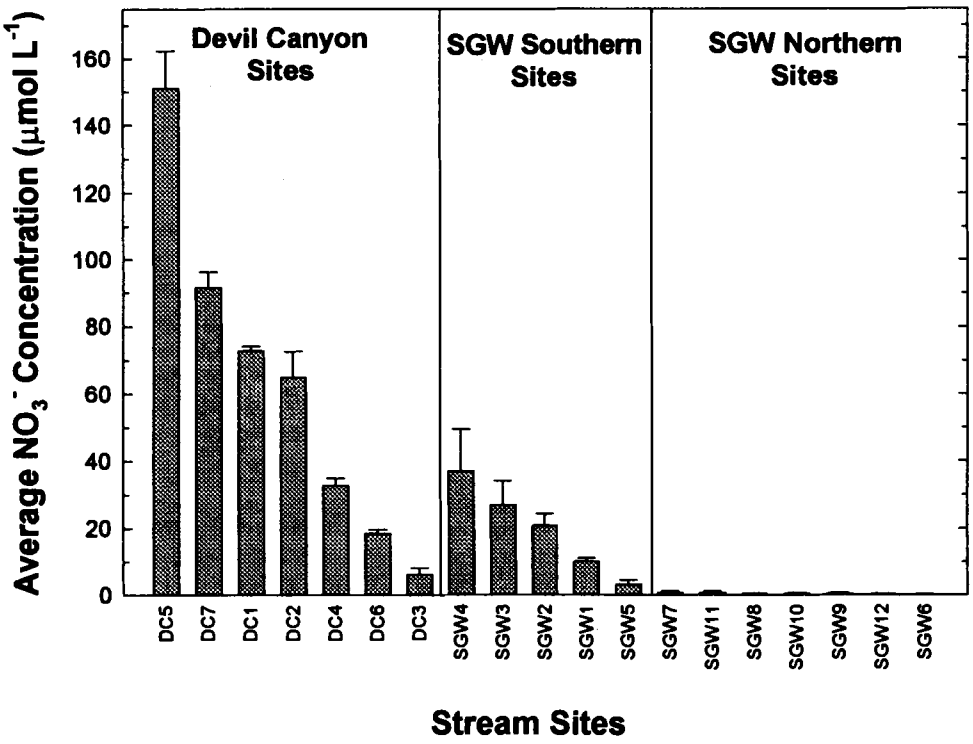


Fig. 4. Average $NO_3^-$ concentrations in streamwater at Devil Canyon and in sites located on the southern and northern transects along the periphery of the San Gorgonio Wilderness. Watershed SGW5 is actually slightly north of the main Mill Creek drainage (see Fig. 3).

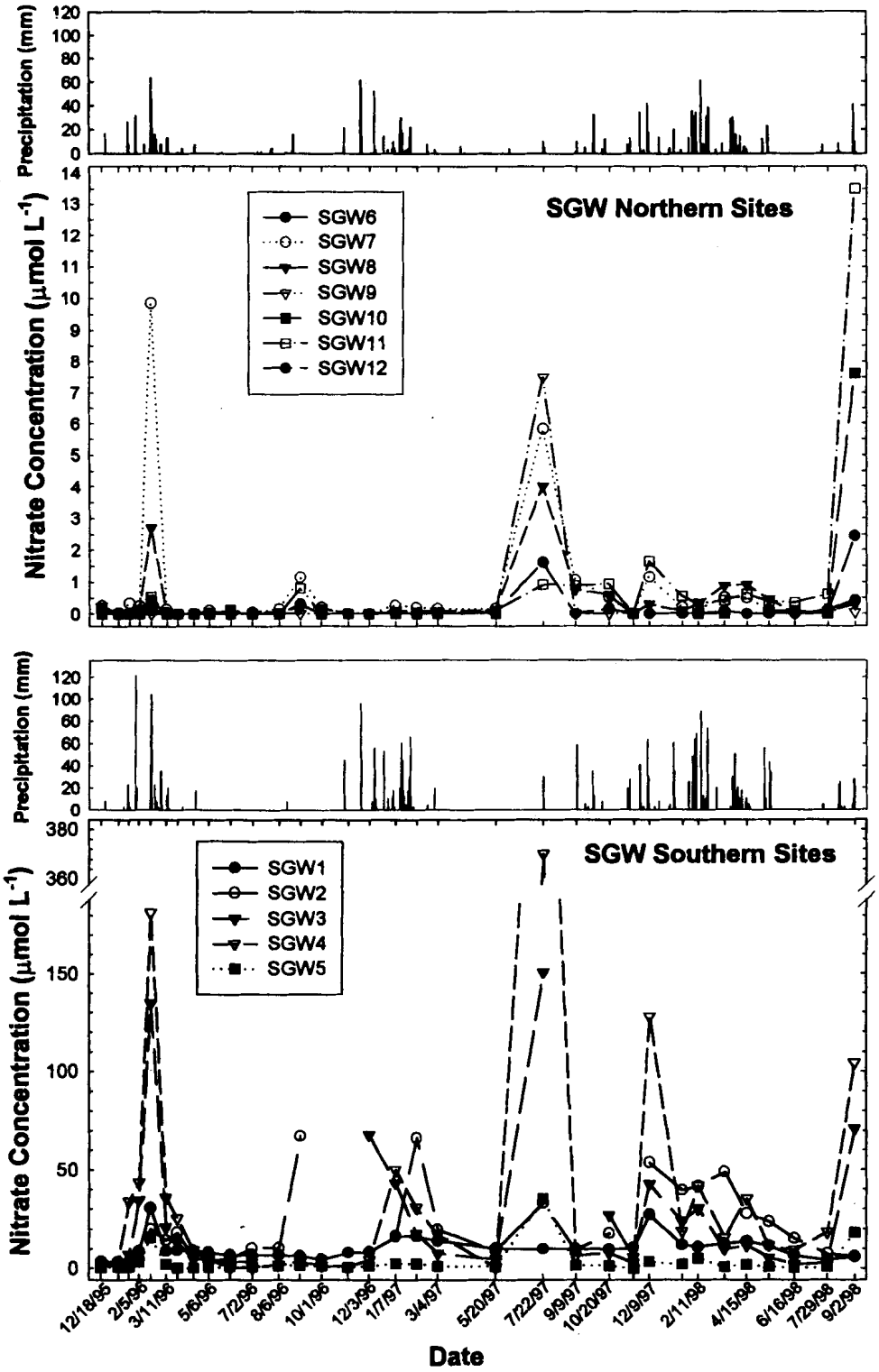


**Fig. 5. Nitrate concentrations in streamwater in the San Gorgonio Wilderness (low to moderate deposition) region. Nitrate in streamwater from SGW6 was only detected on four sampling dates. The upper histogram indicates daily precipitation totals at Barton Flats, near SGW Stream 8. The lower histogram indicates daily precipitation totals at Fallsvale between SGW Streams 1 and 2. Note the different *y* axis scales ($NO_3^-$ concentration) for the southern and northern transects.**

1996 and 1997, and 18 μmol $L^{-1}$ in spring 1998. Streamwater $NO_3^-$ concentrations in DC3 returned to baseline levels (≤1 μmol $L^{-1}$) during low flow. However, in the summer of 1998 when stream flows were high as a result of the El Niño high precipitation patterns, $NO_3^-$ concentrations in DC3 ranged from 4 to 14 μmol $L^{-1}$. In contrast, minimum base flow $NO_3^-$ concentrations were rarely <80 μmol $L^{-1}$ in DC5. The other five stream sampling sites in DC exhibited a range of intermediate $NO_3^-$ concentration patterns (Fig. 6). Except for DC1,

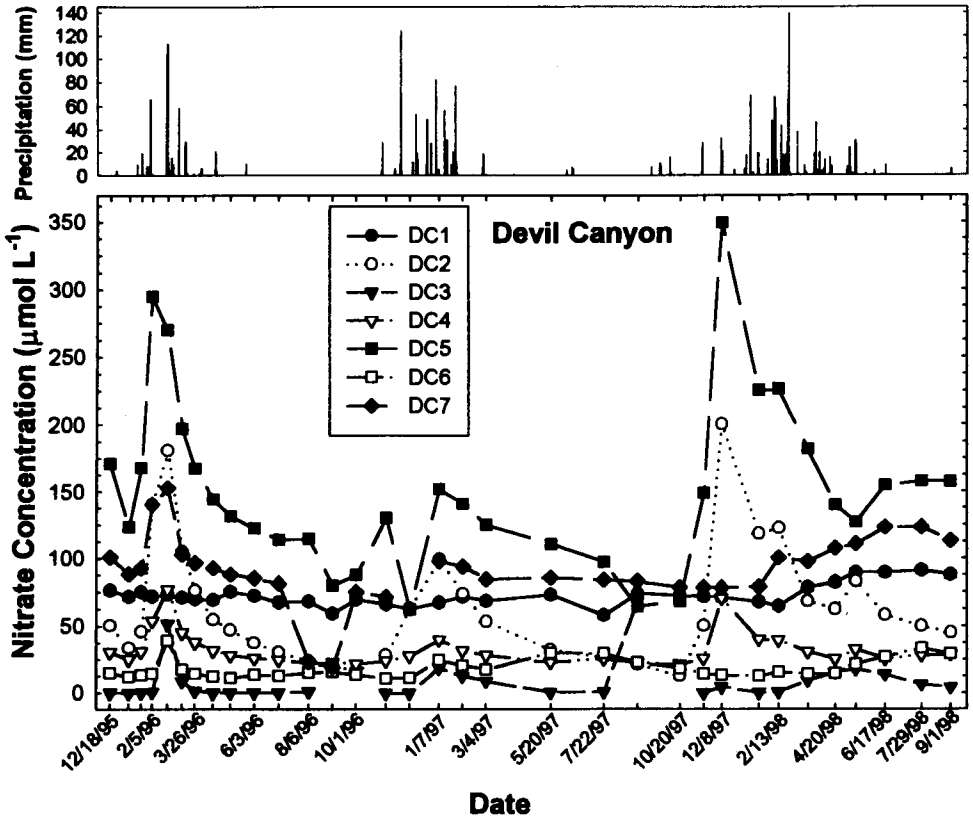


**Fig. 6. Nitrate concentrations in streamwater in Devil Canyon (high deposition area). Precipitation data is from the base of Devil Canyon.**

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 and runoff are greatest, followed by declining values during late winter and spring. Nitrate concentrations were usually at their lowest and were most stable during the summer dry season (Fig. 6). Although streamwater $NO_3^-$ concentrations in DC peaked during high flows in winter, $NO_3^-$ concentrations were also elevated during base flow in the summer in most of the streams.

In contrast to the trends at DC, $NO_3^-$ concentrations in many of the SGW streams decreased to near detection limits in the weeks following major storms. In summer, $NO_3^-$ concentrations nearly always declined below 10 μmol $L^{-1}$ in the SGW streams, although $NO_3^-$ concentrations in Streams 1 to 4 rarely dropped below 1 μmol $L^{-1}$ (Fig. 5). Nitrate concentrations in Streams 6 to 12 in the SGW were frequently below detection limits. However, the largest peak in $NO_3^-$ concentrations (from 10 to 370 μmol $L^{-1}$) in Streams 1 to 5 in the southern SGW occurred on 22 July 1997. Thundershower activity (30.5 mm recorded at Fallsvale on 22 July) was preceded by a 5-mo rain-free period. Nitrate concentrations (0.9–7.5 μmol $L^{-1}$) also increased following the thunderstorm in the northern SGW sites on 22 July 1997. At Barton Flats, thunderstorm activity (9.9 mm on 22 July 1997) was preceded by nearly 5 mo when only 24.7 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. Streamwater $NO_3^-$ concentrations were at their highest (2.4–13.5 μmol $L^{-1}$) in SGW Streams 10 to 12 on 2 Sept. 1998 following an El Niño winter and unusually high summer rainfall in mid to late August 1998 (Fig. 5). Nitrate concentrations were also high in SGW1 to SGW5 in September 1998, ranging from 6 to 105 μmol $L^{-1}$. Following winter storms, $NO_3^-$ concentrations in Streams 1 to 5 in the SGW ranged from 16 to 182 μmol $L^{-1}$ in February 1996, 2 to 66 μmol $L^{-1}$ in February 1997, and 3 to 128 μmol $L^{-1}$ in December 1997.

The sampling site at DC1 is a small spring sampled near the source, and SGW1 is also a spring-dominated

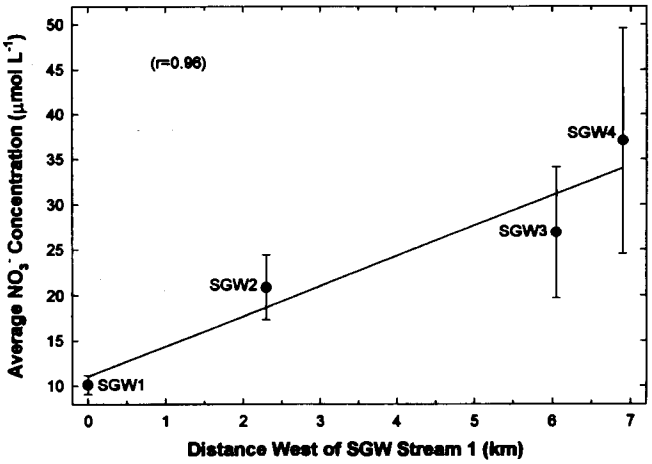


**Fig. 7. Relationship between west-to-east location of stream sampling sites (SGW1–SGW4) along the southern SGW transect and 3-yr average $NO_3^-$ concentrations in streamwater. Bars represent standard errors of the mean ($n$ = 28–33 samples for each data point).**

stream, although both subsurface flow and surface runoff contribute to SGW1 during periods of storm runoff. In DC1 $NO_3^-$ concentrations averaged 73 (±1.4 SE) μmol $L^{-1}$ with little seasonal variation. Nitrate concentrations averaged 10 (±1.0 SE) μmol $L^{-1}$ in SGW1. The lack of 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 (Fig. 5 and 6).

## Nitrate Export from Devil Canyon

Export of $NO_3$–N from the entire DC watershed ranged from 3.6 to 11.6 kg $ha^{-1}$ $yr^{-1}$ for water years (WY) 1995 to 1998 (Fig. 8). Nitrogen export in streamwater corresponded closely with the amount of runoff ($r$ = 0.97) and precipitation ($r$ = 0.88). Precipitation was slightly greater in WY98 (1136 mm), which was an El Niño year, compared with WY95 (1081 mm). However, streamwater runoff and N export were greatest in WY95 (576 mm, 11.6 kg $ha^{-1}$ $yr^{-1}$) compared with WY98 (488 mm, 8.2 kg $ha^{-1}$ $yr^{-1}$; Fig. 8). In WY96, when runoff (191 mm) was close to the long-term average of 150 mm and precipitation (571 mm) was also near average (610 mm), streamwater export of $NO_3$–N equaled 3.6 kg $ha^{-1}$ $yr^{-1}$. Annual runoff ranged from 191 to 576 mm and corresponding precipitation values were from 571 to 1136 mm during the 4 water years.

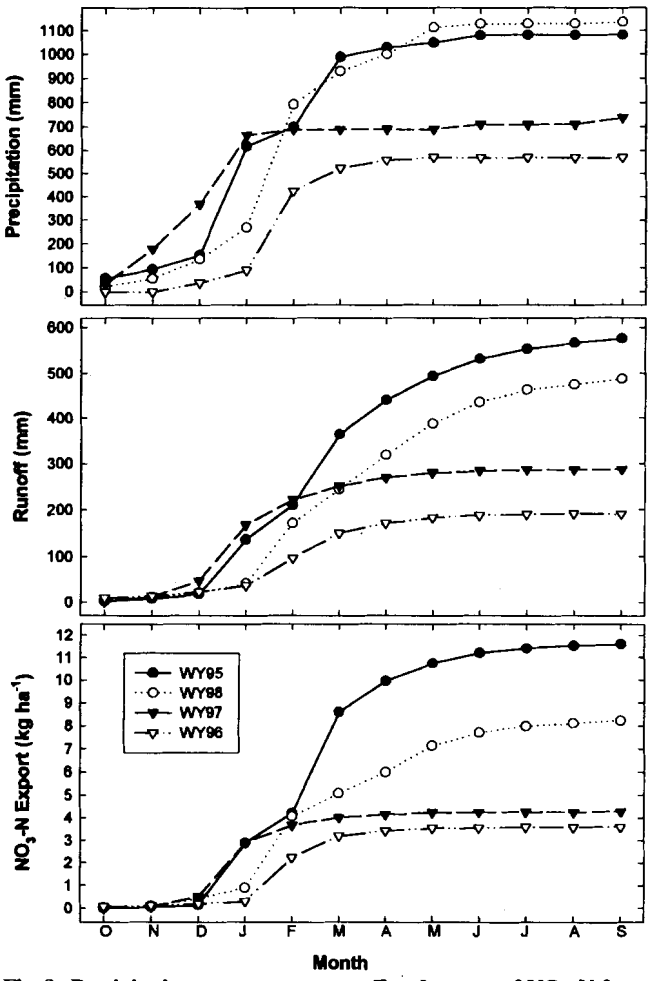


**Fig. 8. Precipitation, streamwater runoff and export of $NO_3$–N from Devil Canyon in water years 1995 to 1998. Nitrate concentrations used to calculate annual N export for WY95 (Oct. 1994–Sept. 1995) and for October and November 1995 (WY96) were estimated from a regression equation relating monthly streamwater $NO_3^-$ concentrations to streamwater fluxes for the period of December 1995 through September 1998 ($[NO_3^-]$ = (streamwater flux × 0.0368) + 33.59; $r$ = 0.75). Note that the figure legend shows the line symbols in order of decreasing runoff and $NO_3^-$ export.**

## DISCUSSION

Streamwater $NO_3^-$ concentrations at DC, and in chaparral watersheds with high smog exposure in the San Gabriel Mountains northeast of Los Angeles (Riggan et al., 1985) are the highest reported in North America for forested watersheds. Chaparral watersheds upwind of Los Angeles, and thus with relatively low air pollution exposure, were characterized by low streamwater $NO_3^-$ (Riggan et al., 1985). Thus, previous studies and the present study support the hypothesis that levels of streamwater and groundwater (as reflected by water from springs) $NO_3^-$ are strongly linked to the magnitude of N deposition to these watersheds. Elevated $NO_3^-$ concentrations in Streams 1 to 5 in the SGW demonstrate that streamwater $NO_3^-$ may be an indicator of atmospheric deposition inputs of N in Class I wilderness areas. We propose that streamwater $NO_3^-$ monitoring in Class I areas can be used in a program for assessment of significant deterioration of air quality (Peterson et al., 1992).

The highest peak (370 μmol $L^{-1}$, SGW4) and highest average (151 μmol $L^{-1}$, DC5) $NO_3^-$ concentrations in streamwater in the present study were 52 and 21% of the drinking water standard (10 mg $NO_3$–N $L^{-1}$; 714 μmol $L^{-1}$). The city of Riverside receives 99.7% of its water from wells in San Bernardino and Riverside where groundwater is recharged from the San Bernardino Mountains. The average $NO_3^-$ concentration over the past several years in Riverside's drinking water was 321 μmol $L^{-1}$ (Annual Water Quality Report, Riverside Public Utilities, 1997). Although, average $NO_3^-$ concentrations in local municipal water supplies are within federal standards, N deposition in the San Bernardino Mountains is probably an important source of $NO_3^-$ in city water supplies. Atmospheric N deposition is also an important streamwater $NO_3^-$ source in chaparral and grassland watersheds in the San Gabriel Mountains on the northeastern edge of the Los Angeles Air Basin. Chronic N deposition and $NO_3^-$ export from these watersheds contribute to the groundwater $NO_3^-$ problems in the eastern San Gabriel Basin, where levels often exceed the federal drinking water standard (10 mg $NO_3$–N $L^{-1}$; Riggan et al., 1985, 1994).

The Fernow Experimental Forest in West Virginia (Adams et al., 1997; Gilliam et al., 1996; Peterjohn et al., 1996), the Great Smoky Mountains National Park in Tennessee (Cook et al., 1994), and watersheds in southwestern Pennsylvania (Dow and DeWalle, 1997) are the only undisturbed forested sites in North America known to have streamwater $NO_3^-$ concentrations within the range of values found at DC. Average $NO_3^-$ concentrations in the upper West Fork (DC5) in the 3 yr of this study were 2.6 to 3.7 times greater than the average concentrations reported for two watersheds in Fernow

(10-yr avg. for control Watershed 4 and 5-yr pretreatment average for Watershed 3) and about 2.6 times greater than in the Smokies. Monthly averages for 1984 to 1994 ranged from 44 to 64 μmol $L^{-1}$ in the Fernow watersheds (Peterjohn et al., 1996), compared with average $NO_3^-$ concentrations of 65 and 151 μmol $L^{-1}$ in the lower and upper West Fork in DC (Streams 2 and 5). At Fernow, the Great Smoky Mountains National Park, and at DC, high $NO_3^-$ concentrations persisted even during summer base flow conditions (Cook et al., 1994; Gilliam et al., 1996; Peterjohn et al., 1996). At the Smokies site, elevated $NO_3^-$ export (avg. base flow streamwater $NO_3^-$ = 57 μmol $L^{-1}$) was attributed to high leaching of N from old-growth forests, which typically have reduced N demand or retention capacity, and from high rates of N deposition. However, at Fernow, high $NO_3^-$ discharge also occurred from a young aggrading forest (Peterjohn et al., 1996).

## Spatial Trends in Nitrogen 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 three different scales—between DC and the SGW, along the southern SGW transect, and between the southern and northern transects in the SGW. According to previous studies of N deposition in the SBM (Fenn and Bytnerowicz, 1993, 1997), 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 Barton Flats area on the north side of 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 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. Furthermore, average $NO_3^-$ concentrations in Streams 1 to 4 along the SGW southern transect were highly correlated ($r$ = 0.96; Fig. 7) with position along this west-to-east N deposition gradient. While correlation does not prove causation, the strong correspondence of streamwater $NO_3^-$ concentrations and geographic location of the watersheds along the air pollution gradient supports the hypothesis that chronic N deposition within the terrestrial watersheds is an important factor contributing to high $NO_3^-$ in streamwater in the San Bernardino Mountains. Streamwater $NO_3^-$ concentrations in SGW5 (Fig. 4), which is north of the SGW southern transect (Fig. 3), were intermediate between $NO_3^-$ concentrations in streams of the southern and northern SGW transects. Since N deposition decreases from south to north, this is further evidence of a possible causal relationship between N deposition and streamwater $NO_3^-$ concentrations. The high $NO_3^-$ concentrations in streams SGW1 to SGW4 and moderate N deposition levels in this region agree with other studies showing that in high-elevation ecosystems, threshold levels of N inputs that lead to elevated watershed $NO_3^-$ export are severalfold lower than in lower elevation forests (Baron et al., 1994; Fenn et al., 1998).

Precipitation amount was also greater along the southern SGW transect and likely contributed to greater $NO_3^-$ leaching and export from the southern sites. Greater solar exposure along the southern transect also promotes biological activity, when moisture is not limiting. The environmental conditions along the southern side of the SGW stimulate N mineralization and nitrification, but can also increase biological N demand and retention (Fenn et al., 1998). However, with steep slopes, runoff increases rapidly with greater precipitation and favors export of available soil $NO_3^-$. The net effect of greater solar radiation and higher temperatures on N retention in the catchments along the southern transect of the SGW is not known. In any case, the extreme $NO_3^-$ peaks in the SGW streams during high flow clearly demonstrate the inability of these watersheds to effectively retain N within the ecosystem during runoff events—and thus indicate a state of N saturation in portions of this Class I wilderness area. Ever increasing human populations in the inland areas east of Los Angeles, CA, will likely result in increasing N deposition and $NO_3^-$ export from montane watersheds in the future unless pollution controls offset the increased population trends.

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 (73 μmol $L^{-1}$) were seven times greater than in the spring-dominated stream in the SGW (10 μmol $L^{-1}$). Nitrate concentrations in these springs varied little seasonally compared with 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, probably because of greater inputs from surface or lateral subsurface flow during storm runoff.

Peak $NO_3^-$ concentrations in streams draining chaparral and grassland watersheds in the San Dimas Experimental Forest located closer to the metropolitan Los Angeles pollution source area appear to be even higher than in DC. Riggan et al. (1985) reported peak $NO_3^-$ concentrations of approximately 500 μmol $L^{-1}$ in chaparral watershed 804 in the San Dimas Experimental Forest located ca. 49 km west of DC. These observations are from 1981 to 1983 and further suggest a relationship between levels of atmospheric N deposition and streamwater $NO_3^-$ concentrations in southern California watersheds.

## Temporal Trends in Streamwater Nitrate

Temporal trends in $NO_3^-$ concentration patterns clearly indicate the more severe N saturation of the catchments in DC compared with the SGW catchments. Nitrate concentrations in Streams 1 to 5 in the SGW briefly peaked to high levels following storms, but con-

centrations decreased to near baseline levels during baseflow in late spring and in summer (Stage 1 of watershed N saturation). Elevated $NO_3^-$ concentrations were maintained during spring and summer 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, in September 1998, 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 μmol $L^{-1}$. The high summertime $NO_3^-$ concentrations in Streams 2 to 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 amounts were small compared with most 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 with winter storms, which produce a more prolonged runoff due to greater precipitation volumes and as a result of $NO_3^-$ flushing from melted snow and from soil. Additional $NO_3^-$ peaks undoubtedly occurred in this 3-yr study, but were not detected because of the timing of sample collection. The highest concentrations observed were usually from sampling dates occurring within a few days of a significant precipitation event.

Except for DC1 and SGW1 sampled near the spring source, and the large summertime $NO_3^-$ peak in the SGW, the temporal trends in streamwater $NO_3^-$ fit the Stoddard watershed N saturation model based on data from the eastern USA and Europe (Stoddard, 1994). This trend is characterized by peak streamwater $NO_3^-$ concentrations in the winter wet season as a result of large runoff events such as snowmelt or rainstorms, and lowest values in summer. High spring and summer base flow $NO_3^-$ concentrations in some streams indicate Stage 2 of the Stoddard model. However, the large increase in streamwater $NO_3^-$ following summer precipitation in the SGW streams differs from the standard N saturation model. 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).

## Possible Factors Affecting Nitrate Export

We found greater than expected spatial variation in streamwater $NO_3^-$ concentrations within DC. Since deposition within the highly polluted DC catchments is expected to vary little compared to the wide range of streamwater $NO_3^-$ concentrations, differences in streamwater $NO_3^-$ concentrations were attributed to variation in N cycling and processing in the upland watershed, in 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 catchments, and catchment characteristics such as size, slope, depth to bedrock, soil hydrophobicity, vegetation, stream length, and stream morphology may also be important factors influencing N processing (Cirmo and McDonnell, 1997; DeBano, 1981; Manga, 1996; Piñol et al., 1992, 1997; Schnabel et al., 1993).

Additional factors that could contribute to the trend of higher streamwater $NO_3^-$ concentrations in DC compared with the SGW include differences in soil fertility and depth, topography, vegetation, N uptake by vegetation, litter accumulation and quality, biological $N_2$ fixation, fire and disturbance history, and land use history. The soils throughout the larger part of the watershed are shallow, coarse-grained, and not well developed because of the steep slopes that predominate in the DC catchments. Similarly, the SGW is by definition a high elevation wilderness area. The steep slopes that characterize the upper SGW undoubtedly contribute to the elevated $NO_3^-$ concentrations in runoff after precipitation events. It seems unlikely that greater N uptake by vegetation is a major factor in the lower $NO_3^-$ concentrations in the SGW, since the higher elevation and lower temperatures in the SGW are expected to result in lower vegetative N demand. However, N mineralization and nitrification rates may also be affected by low temperatures. Potential effects of $N_2$ fixation by alder on streamwater $NO_3^-$ is discussed below. Nitrogen fixation rates by ceanothus [*Ceanothus gregii* var. *perplexans* (Trel.) Jeps.] in semiarid watersheds in southern California are reportedly very low—ca. 0.1 kg N $ha^{-1}$ $yr^{-1}$ when the stand cover is one-third ceanothus (Kummerow et al., 1978), suggesting that this is not an important factor in this study. Land use history is not a factor either, since both DC and the SGW are protected areas without human structures.

Devil Canyon, with the exception of DC5, has burned much more frequently and extensively this century than have the SGW watersheds. Forest fires reduce watershed N capital by releasing large amounts of N that is exported from the watershed in smoke, as sediments or soil erosion, and as streamwater and groundwater $NO_3^-$ produced from $NH_4^+$ released from organic material by fire (Dunn et al., 1979; Fenn et al., 1998). Thus, except for DC5, fire history should favor lower $NO_3^-$ concentrations in streamwater at DC. Watershed DC5 is the least burned of the watersheds in DC and the stream with the highest $NO_3^-$ concentrations. However, DC7 was the most burned watershed, yet $NO_3^-$ concentrations were high, averaging 92 μmol $L^{-1}$. Watershed SGW4 was the most burned watershed in the SGW region and also had the highest $NO_3^-$ concentrations. In summary, there was no clear relationship between the extent of burning in the watersheds and streamwater $NO_3^-$ concentrations. It appears that other watershed or environmental factors are overriding or confounding the effects of fire history on streamwater $NO_3^-$ concentrations.

In addition to being the least burned watershed in DC, probably due to successful fire suppression in the mixed conifer zone (Minnich, 1999), DC5 is also the watershed with the largest percent coverage with mixed conifer forest (67%). In areas of the mixed conifer forest where fires have been suppressed, stand densification has increased significantly during this century (Minnich, 1999). Greater stand densification and maturation are factors known to lead to greater $NO_3^-$ export (Cook et al., 1994; Fenn et al., 1998). The mixed conifer forest at Camp Paivika at the crest of Devil Canyon is N saturated, with high tree growth rates, deep litter accumulation in the forest floor, high soil nitrification rates, and high levels of excess soil $NO_3^-$ in the soil solution (Fenn and Poth, 1999; Fenn et al., 1996). In the mixed conifer zone of DC5 and in the Camp Paivika area, soils are primarily loam and clay loam, and of much finer texture and higher fertility than in the lower portions of the watersheds where slopes are much steeper. The large stores of organic C in these soils and in the thick forest floor may be an important source of N reaching the streams. One or both of the above-mentioned factors (fire suppression, extensive watershed coverage with N saturated mixed conifer forest) may explain why streamwater $NO_3^-$ concentrations were consistently much greater in DC5.

Fixation of $N_2$ by white alder, a species that 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 (DC1) sampled in an area far removed from any alder trees suggests that alder is not a major source of streamwater $NO_3^-$. High levels of plant-available N in the riparian zone is also expected to inhibit $N_2$ fixation by suppressing nitrogenase activity and nodule formation (Arnone et al., 1994; HussDanell, 1997). Furthermore, of the four tributary streams in DC, $NO_3^-$ concentrations are highest in DC7, which has no alder. Nitrate concentrations in DC7 are also higher than in the lower West Fork (DC2), which supports dense alder stands. Of the tributaries in DC, DC4 is the only one with a significant alder community, yet $NO_3^-$ concentrations are relatively moderate.

In the SGW, varying levels of alder occur within the stream channels. Watershed SGW7 is located in a wide stream channel supporting a dense and extensive stand of large alder trees. The stream channel for SGW4 contains no alder, yet $NO_3^-$ concentrations in SGW4 averaged 37 $\mu$mol $L^{-1}$ (peak value, 370 $\mu$mol $L^{-1}$) compared with 0.7 $\mu$mol $L^{-1}$ (peak value, 10 $\mu$mol $L^{-1}$) in SGW7. Average $NO_3^-$ concentrations in the seven streams along the north side of the SGW ranged from 0.04 to 0.7 $\mu$mol $L^{-1}$. Of these seven streams, $NO_3^-$ was highest in SGW7 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 streamside 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 streamflow at the alder site. In the alder riparian zone, denitrification potentials were nitrate-limited, but not C limited, indicating the high denitrification capacity of the stream-side sediments (Duff and Triska, 1990). 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 (DC5) than in the lower West Fork (DC2) in DC. The chemistry of DC2 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 is also expected to reduce $NO_3^-$ 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 N immobilization is expected to be limited by low temperatures and rapid transport of water in the stream.

## Fate of Excess Nitrogen in Semiarid Watersheds

Major N inputs to catchments include atmospheric deposition, and in some instances biological $N_2$ fixation. Outputs include streamwater discharge, percolation to groundwater, trace gas production by nitrification and denitrification, ammonia volatilization, soil erosion, and N released in fire. No harvest activities occur in the DC area and fires are suppressed when possible, thus limiting these outputs to occasional uncontrolled fires. Atmospheric inputs of N at Camp Paivika are estimated to be 25 to 35 kg $ha^{-1}$ $yr^{-1}$ (M.E. Fenn, 1999, unpublished data). Nitrogen inputs from N-fixing species such as alder and ceanothus in DC are not known, but alder is restricted to the riparian zone of the larger streams, and as discussed previously, does not appear to be significant in this study. Nitrogen fixation rates by ceanothus are also reportedly quite low in semiarid southern California (Kummerow et al., 1978). Similarly, Johnson (1995) reported that soil solution $NO_3^-$ concentrations were low in a stand of riparian mountain alder (*Alnus tenuifolia* Nutt.) and in a ceanothus (*C. velutinus* Dougl.) stand at a site just east of the Tahoe Basin in the Sierra Nevada Mountains, suggesting that $N_2$ fixation rates by these species were not elevated.

The level of N export in streamwater in DC is similar to that reported by Riggan et al. (1985) for chaparral watersheds in the San Gabriel Mountains near Los Angeles. In years of average (770 mm) or above-average rainfall, 0.8 to 10.0 kg N $ha^{-1}$ $yr^{-1}$ was exported in streamwater from two adjacent watersheds in the San Dimas Experimental Forest. Streamwater $NO_3^-$ export

from the two chaparral watersheds in the San Gabriel Mountains ranged from 3.7 to 10.0 kg $ha^{-1}$ $yr^{-1}$ in 2 yr with ca. 1400 mm precipitation (Riggan et al., 1985). Export of $NO_3$–N from DC was similar, ranging from 3.6 to 11.6 kg $ha^{-1}$ $yr^{-1}$ in water years 1995 to 1998. By comparison, in the Fernow Experimental Forest in West Virginia streamwater export of $NO_3$–N ranged from 3.1 to 8.6 kg $ha^{-1}$ $yr^{-1}$ from 1984 to 1993 (Adams et al., 1997). Average precipitation and runoff were greater at Fernow than at the California sites, but lower $NO_3^-$ concentrations yielded similar total annual N export values. Although $NO_3^-$ export in streamwater in the SGW is not known because of a lack of streamwater flux data, estimates based on hydrological budgets of the greater Mill Creek watershed (Crippen, 1965) indicate that the greater precipitation and runoff in the Mill Creek watershed may result in similar or slightly lower levels of $NO_3^-$ export in the southern SGW compared with DC, particularly in wet years.

Emission of nitrogenous trace gases from soil is normally a minor component of the annual N budget in natural ecosystems, although in a spruce (*Picea* spp.) forest with high N deposition in Germany (Davidson and Kingerlee, 1997) and at Camp Paivika, a high deposition site at the crest of Devil Canyon (M.A. Poth and M.E. Fenn, 1998, unpublished data), nitric oxide emissions from soil were 5.0 and 4.5 kg N $ha^{-1}$ $yr^{-1}$, respectively. These results suggest that NO emissions may be similar to annual inorganic N export in streamwater, at least within the mixed conifer zone at the crest of DC where the trace gas measurements were taken. Nitric oxide fluxes at Camp Paivika are believed to be produced during nitrification (Fenn et al., 1996). The amount of N lost from the watershed via denitrification is not expected to be significant in the upland areas, however. Denitrification losses in the riparian zone are 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 (DC1). No nitrous oxide was detected in the other streams in DC, likely because of rapid degassing once the water is exposed to the atmosphere (Bowden and Bormann, 1986; Davidson and Swank, 1990). Thus, denitrification may be an active process for reducing $NO_3^-$ in subsurface water in DC, but no quantitative estimates of rates are available.

Much of the N inputs in DC are stored in vegetation, litter, and soil organic matter as reported for other ecosystems (Fenn et al., 1998). Nitrogen storage in biomass is not expected to exceed 5 kg $ha^{-1}$ $yr^{-1}$ in these semiarid systems based on previous studies (Johnson, 1992). Normally, the major losses of accumulated N from these fire-adapted ecosystems occur periodically during forest fires, and after fire—due to postfire N mineralization—nitrification, nitrate leaching, and erosion losses. However, after decades of fire suppression and high N inputs in the western SBM, greater than normal litter accumulation has occurred in the mixed conifer zone (Fenn et al., 1998). Long-term fire suppression in areas of chronic N deposition, such as the western San Bernardino Mountains, may favor N saturation by allowing high levels of N to accumulate in biomass, necromass and soil organic matter; and by stimulating nitrification and subsequent $NO_3^-$ leaching (Fenn et al., 1998). Reintroduction of controlled fire could lead to long-term improvement in N retention and water quality in N saturated sites such as Devil Canyon, although over the short-term, fire will release N and result in very high hydrologic $NO_3^-$ export and nitric oxide emissions from soil in N-saturated watersheds (Anderson et al., 1988; Riggan et al., 1994).

## CONCLUSIONS

Five of six streams monitored at Devil Canyon, a high N deposition area in the western San Bernardino Mountains, maintained elevated $NO_3^-$ concentrations throughout the entire year. Peak $NO_3^-$ concentrations in the streams ranged from 40 to 350 μmol $L^{-1}$. Of the 12 streams sampled in the San Gorgonio Wilderness, a low to moderate N deposition area, only the five with the greatest air pollution exposure had elevated $NO_3^-$ levels (peak values ranging from 16 to 182 μmol $L^{-1}$ in winter and 10 to 370 μmol $L^{-1}$ in summer). Peaks in $NO_3^-$ concentration in the SGW occurred after winter storms and following summer thundershowers. Nitrate concentrations in spring-fed streams were constant throughout the year, averaging 73 ± 1.4 μmol $L^{-1}$ in DC1 and 10 ± 1.0 μmol $L^{-1}$ in SGW1, and may reflect groundwater $NO_3^-$ levels and serve as a long-term indicator of watershed N status. Annual streamwater export of $NO_3$–N from Devil Canyon ranged from 3.6 to 11.6 kg $ha^{-1}$ in water years 1995–1998. 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. Future studies addressing the factors responsible for the wide range in N export in DC may provide critical information for developing management options for protecting water quality from watersheds with chronic N inputs.

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