ES&T RESEARCH

Deposition and Processing of Airborne Nitrogen Pollutants in Mediterranean-Type Ecosystems of Southern California

Philip J. Riggan,* Robert N. Lockwood, and Ernest N. Lopez†

Pacific Southwest Forest and Range Experiment Station, Forest Service, U.S. Department of Agriculture, Riverside, California 92507

■ Atmospheric nitrogen deposition, associated with chronic urban air pollution, has produced stream water nitrate concentrations as high as 7.0 mg of N L^{-1} in chaparral watersheds in the San Gabriel Mountains of Los Angeles County, CA. Stream water [NO_3^-] and discharge were greatest at high flow and may contribute significantly to existing groundwater NO_3^- pollution. Annual NO_3^- discharge ranged from 0.04 to 10.0 kg of N ha^{-1} over 4 years. Canopy throughfall and precipitation inputs of 23.3 and 8.2 kg of N ha^{-1} $year^{-1}$ were high relative to other undisturbed ecosystems nationwide. Dry deposition was apparently a major source of the throughfall nitrogen. NO_3^- concentrations from nearby, relatively unpolluted watersheds were lower by 1–3 orders of magnitude. NO_3^- yield was elevated on watersheds where chaparral was converted to grassland in 1960 and may be greatly accelerated after wildfire because of high postfire NH_4^+ concentrations and rapid nitrification in terrestrial and aquatic ecosystems.

Introduction

Emissions of nitrogen oxides in the South Coast Air Basin of southern California are among the most extreme in the nation. Within the urbanized basin, 330 kg of N ha^{-1} are released into the atmosphere annually (*1*). Temperature inversions from late spring through autumn contain emissions in the lower atmosphere with some afternoon dispersal into adjacent mountains and deserts by onshore winds. Peak 4-h concentrations of inorganic particulate and gaseous NO_3^- are commonly greater than 40 $\mu g\ m^{-3}$ during autumn smog episodes in the northeast basin (*2*); average annual values are 6 times the long-term national urban average (*3*, *4*). Concentrations of the gaseous pollutants NO_2 and peroxyacetyl nitrate typically exceed those of the inorganic forms (2). High rates of NO_3^- deposition or formation on surfaces are suspected under these conditions. Fogs formed by deliquescence on the existing aerosol are chemically reactive; an event-average pH of 2.25 and [NO_3^-] of 170 mg of N L^{-1} have been observed in Pasadena, CA (*5*).

The Mediterranean-type climate and ecosystems of the region uniquely affect the accumulation, movement, and processing of nitrogen compounds derived from these emissions. Severe drought during summer and autumn restricts root activity and nitrogen uptake by the native chaparral and evergreen woodlands (*6*). Soils are often poorly developed, low in organic matter, and highly erodible. Cycles of wetting and drying produce peaks in soil nitrogen mineralization and nitrification (*7–9*) that coincide with the movement of leaching waters, and nitrification can be rapid (*10*). Together, these conditions promote nitrogen mobility in the system. Chaparral watersheds are also subject to recurring wildfire, with large attendant losses of sediment and nutrients (*11*).

The fate of atmospheric pollutants entering these ecosystems is unresolved. High rates of nitrogen deposition and mobility could eutrophy streams and pollute local water supplies. Indeed, NO_3^- groundwater pollution is a serious problem in parts of eastern Los Angeles County: the aquifer [NO_3^-] in the eastern portion of the Main San Gabriel Basin is often between 10 and 20 mg of N L^{-1}, exceeding the Federal standard for drinking water (*12*).

This paper provides evidence to implicate atmospheric deposition in the NO_3^- pollution of stream water in mountain watersheds of Los Angeles County. It also describes the patterns of NO_3^- yield from chaparral and grassland watersheds and discusses the relation of atmospheric deposition to natural sources and sinks of NO_3^- in the system.

Materials and Methods

Deposition was assessed by measuring NO_3^- and NH_4^+ concentrations in bulk precipitation collected in clearings and beneath the canopy of *Ceanothus* chaparral (the latter of which is referred to as throughfall). Estimated deposition rates were compared with NO_3^- production associated with wetting of dry soils and the NO_3^- production and uptake in a perennial stream after successive applications of NO_3^- and NH_4^+. Stream water was also sampled regionally to determine if high stream water NO_3^- levels are restricted to areas of chronic air pollution or are a trait of chaparral watersheds.

Site Description. The experimental watersheds (Figure 1) are located at the San Dimas Experimental Forest, Angeles National Forest, at elevations from 580 to 1080 m. Streams were gauged and sampled in Bell Canyon watersheds 0801 (32 ha), 0802 (41 ha), 0803 (25 ha), and 0804 (16 ha) and in Volfe Canyon (300 ha). The average hill slope gradient is 69% on the Experimental Forest. Soils are primarily loamy, mixed, thermic, shallow, Typic Xerorthents less than 1 m deep (*13*) that developed from a fractured igneous–metamorphic rock complex.

†Present address: 10678 Ranchito St., El Monte, CA 91731.

Figure 1. Infrared aerial photograph of the Bell Canyon watersheds, San Dimas Experimental Forest, CA. The large debris basin visible is located at the base of watershed 0804; watershed 0803 is the adjacent second-order watershed to the north. North and northeast aspects are dominated by 23-year-old stands of *Ceanothus* chaparral. Southerly aspects are dominated by mixed stands of *Ceanothus*, chamise, and black sage. Watersheds 0802 and 0801 contain the grasslands at the top and right center of the photo.

Grasses were established in watersheds 0801 and 0802 by seeding and application of herbicides after a wildfire that burned the Experimental Forest in 1960. The annual grassland in watershed 0802 consists of *Bromus* and *Festuca* spp.; 0801 was converted to a mixed annual–perennial grassland with some *Agropyron intermedium*. A subshrub, *Eriogonum fasciculatum* (California buckwheat), has since been established over large areas of 0801.

The chaparral communities in watersheds 0803 and 0804 and in Volfe Canyon are predominantly *Ceanothus crassifolius* and *Adenostoma fasciculatum* (chamise) with some *C. oliganthus*, *E. fasciculatum*, and *Salvia mellifera*. Volfe Canyon also contains a *Quercus agrifolia* riparian woodland.

Sampling and Analytical Methods. Discharge was measured with 90°- or 120°-V-notch weirs and 3-ft flumes, depending on velocity and the specific installation. Stream water was sampled weekly before Oct 1980 and at 6-h intervals thereafter. NO_3^- and NH_4^+ in waters or soils were analyzed with a Technicon AutoAnalyzer II (*14*). Annual NO_3^- yield was estimated for hydrologic years beginning Oct 1 by numerically integrating the product of stream discharge and $[NO_3^-]$. Concentrations were estimated for intermediate times with a linear interpretation on discharge, with the restriction that estimates not exceed measured values. This procedure resulted in conservative estimates of NO_3^- yield.

Samples of bulk precipitation were collected, by storm, in 200-cm^2 funnels, four to six beneath and two adjacent to a mature stand of *C. crassifolius*. Throughfall volumes, including stemflow, were estimated as the difference between precipitation, P (mm), and poststorm evaporation in the canopy, $E = 0.062(P) + 2.1$ (*15*). The $[NO_3^-]$ in stemflow was assumed to equal that in throughfall. The timing of throughfall NO_3^- transport was also studied at the end of the 1980 summer drought by collecting, at 10-min intervals, the washings from individual branches of *C. crassifolius*.

Soil and Stream Treatments. In a field experiment conducted during Sept 1980, an initially dry surface soil (0–10 cm) was sprayed with stream water of low $[NO_3^-]$, raising the moisture content from 2 to 12% for 10 days with a decline to 5% during the subsequent 8-day period. The net nitrification response was assessed on duplicate

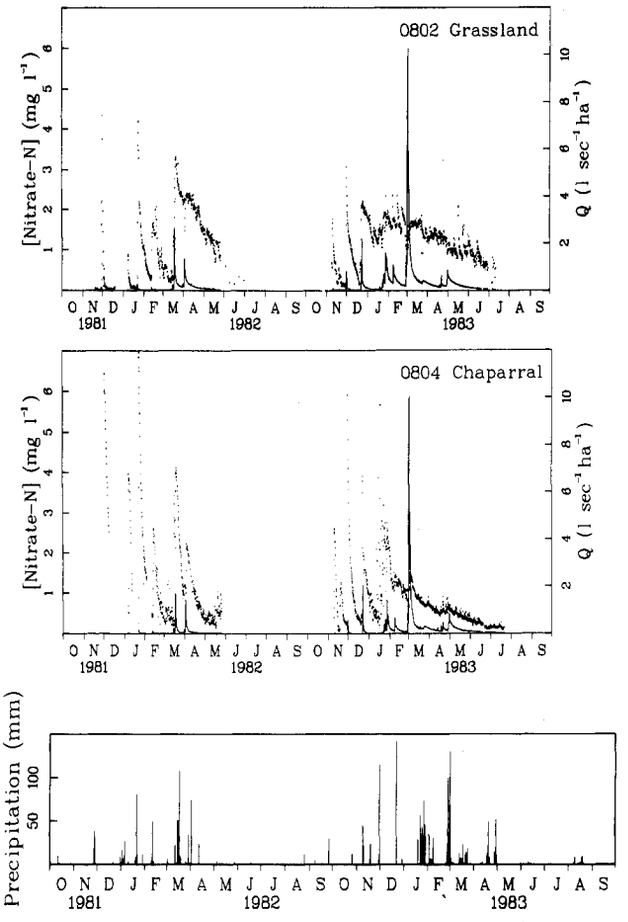

Figure 2. Stream water NO_3^- concentration (mg of N L^{-1}) (symbols) and discharge rate, Q (L s^{-1} ha^{-1}) (solid lines), for representative chaparral (no. 0804) and grassland (no. 0802) watersheds during the 1981–1982 and 1982–1983 hydrologic years. Precipitation for individual storms is shown for comparison. NO_3^- concentration responded markedly to changes in stream discharge with the highest peaks occurring during early seasonal storms. Concentrations fell rapidly following early storms but remained elevated for an extended period after large storms that saturated the soil profile.

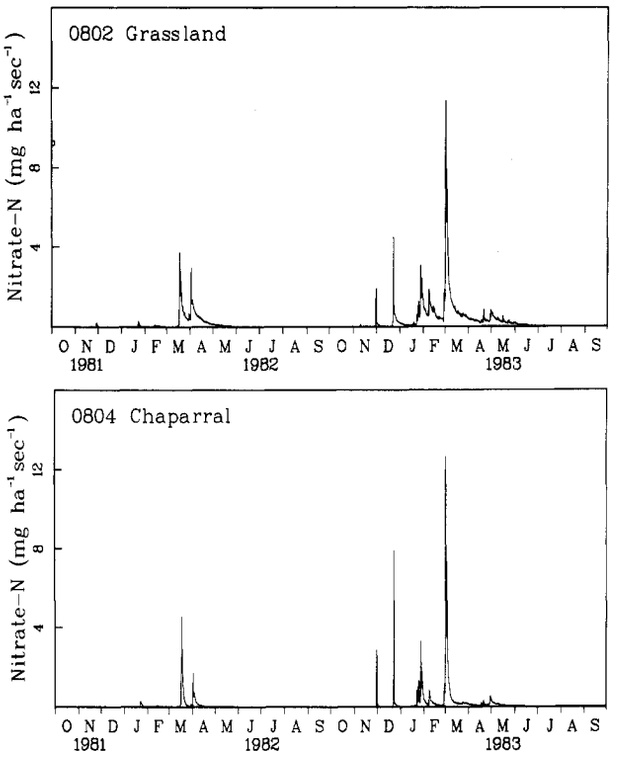

Figure 3. Patterns of instantaneous NO_3^- discharge (mg of N ha^{-1} s^{-1}) during the 1981–1982 and 1982–1983 hydrologic years. Substantial movement of NO_3^- only occurred during large storms despite the high stream water concentrations associated with early seasonal rainfall. The grassland watersheds showed a more sustained NO_3^- discharge relative to the chaparral such as during March 1982.

100-m^2 plots that were otherwise undisturbed or fertilized with 50 kg of N ha^{-1} as $(NH_4)_2SO_4$. On eight occasions, exchangeable NH_4^+ and NO_3^- were determined in four soil samples per plot, comprised of 20 cores each, that were sieved to 2 mm and extracted 3 times with 1 N KCl. Net rates of change in soil $[NO_3^-]$ were determined as the slopes of linear regressions of $[N] = f(\text{time})$. Canopy NO_3^- accumulation also was determined at this time after a rain-free period of 114 days.

The nitrification and NO_3^- uptake responses to added nitrogen were determined in the stream ecosystem of Volfe Canyon during Dec 1980 when discharge rates reflected the base flow of late autumn (1.2–1.3 L s^{-1}). KNO_3 (8.3 g of N) and then $(NH_4)_2SO_4$ (42 g of N) were added to the stream 300 m above the weir on successive days. Water samples were collected 10 m above the addition point and 150 and 300 m downstream. The intermediate location and weir were assumed to have equivalent stream discharge rates since they received flow from virtually the same watershed area.

Regional trends in stream water $[NO_3^-]$ were assessed in mid March 1982 after a 244-mm winter storm (3/11 to 3/18), the first of the year to generate substantial stream flow. Chaparral watersheds were sampled in areas where air pollution was chronic, at San Dimas and the adjacent San Gabriel Mountains from Pasadena to Upland, intermediate, in the Santa Ana Mountains 24 km east and 32 km southeast of Santa Ana, and slight, 35–50 km east and northeast of Oceanside near Palomar Mountain in northern San Diego County and the Santa Monica Mountains 28–68 km west of Los Angeles.

Results

Patterns of Nitrogen Yield. Stream water $[NO_3^-]$ responded markedly to changes in discharge rate in both chaparral and grassland watersheds (Figure 2). Low NO_3^- concentrations during the base flow of the summer drought were supplanted by sharp peaks during the first winter storms. Concentrations were greatest during early storms, yet NO_3^- movement was substantial only during major storms that saturated the soil mantle (Figure 3). Concentrations remained elevated for a more extended period after recession of major flows.

No consistent differences in peak instantaneous NO_3^- discharge rates were observed between grassland and chaparral watersheds (Figure 3). However, the NO_3^- concentrations and NO_3^- discharge rates of the grassland streams remained elevated for a longer period of time after major storms (Figures 2 and 3).

During periods of low flow, NO_3^- concentrations fluctuated diurnally with minima occurring at about noon. The diurnal patterns were out of phase with and greater than the dilution effects expected from midday evapotranspiration and reduced stream flow.

Annual watershed NO_3^- yield was 25–250 times greater in years with twice the long-term average precipitation (1979–1980 and 1982–1983) than in a year with half the mean rainfall (Table I). The maximum observed NO_3^- yields were 10.0 kg of N ha^{-1} $year^{-1}$ from chaparral and 19.4 from grass watersheds. Mean volume-weighted NO_3^- concentrations were 1.7 mg of N L^{-1} for grasslands and 1.2 mg of N L^{-1} for chaparral. Water yield from the grasslands

Table I. Stream Water Discharge and Nitrate Yield from Chaparral and Grassland Watersheds, San Dimas Experimental Forest, CA

Water Yield and Precipitation, cm

	grassland[a] watershed		chaparral watershed		
year[b]	0801	0802	0803	0804	precipitation
-1979	7.6[c]	17.3[d]	8.6[d]	6.1[d]	74.4
1979–1980	92.3	82.0	66.5	49.1	137.1
1980–1981	2.0	3.0	3.2	1.9	37.6
1981–1982	17.4	17.5	8.3	7.5	77.0
1982–1983	69.4	67.8	48.3	42.6	141.2

Nitrate Export, kg of N ha^{-1} $year^{-1}$

	grassland watershed		chaparral watershed	
year	0801	0802	0803	0804
-1979	2.3[c]	5.6[d]	0.55[d]	0.47[d]
1979–1980	19.4	18.9	10.0	6.2
1980–1981	0.11	0.22	0.039	0.077
1981–1982	2.7	3.0	0.75	1.3
1982–1983	6.0	9.6	3.7	5.0
4-year total	28.2	31.7	14.5	12.6

[a] Grassland-type conversion from chaparral established in 1960. [b] Hydrologic year defined from Oct 1 through Sept 30. [c] Partial record: 4/5/79–9/30/79. [d] Partial record: 2/20/79–9/30/79.

was likewise heightened during years of average or above-average precipitation (Table I), so their 4-year NO_3^- loss was twice that from the chaparral.

NO_3^--rich stream water was not limited to the San Dimas watersheds; concentrations ranging from 0.74 to 8.14 mg of N L^{-1} were measured in the San Gabriel Mountains after heavy rainfall (Table II). The watersheds with the highest NO_3^- concentrations were adjacent to the urbanized Los Angeles basin. Interior watersheds of the San Gabriel River and those with source areas at higher elevations showed concentrations averaging one-third of those in the front range. The highest [NO_3^-] observed was in Rubio Canyon, an area within the region of chronic air pollution that was severely burned during 1979.

In the Santa Monica Mountains and in northern San Diego County, stream water concentrations were as many as 3 orders of magnitude lower than in the San Gabriel Mountains (Table II). Concentrations from 0.1 to 0.4 mg of N L^{-1} in the areas of relatively unpolluted air could be traced to other anthropogenic nitrogen sources such as orchards or rural developments. The Santa Ana Mountain watersheds showed low to intermediate levels.

Nitrogen Deposition. Precipitation NO_3^- concentrations at San Dimas ranged from less than 0.04 to 21 mg of N L^{-1} in a reciprocal relation with storm volume. The highest values were observed during small summer storms; precipitation from winter frontal systems carried smaller amounts of inorganic nitrogen in much greater volumes of water.

The chaparral canopy added no appreciable amounts of NO_3^- to falling rain during the period of winter storms, but substantial amounts were washed from shrub surfaces during the summer and autumn when small storms were interspersed with periods of chronic air pollution (Figure 4). NO_3^- that accumulated in the canopy from June through October accounted for more than half the annual input to the system (Table III). Early seasonal rains washed two-thirds of this accumulation from the canopy during the first 10 min of canopy drip. Excluding the first storm of 1981–1982, canopy throughfall and stemflow transferred an average of 16.1 kg of NO_3^-–N ha^{-1} $year^{-1}$ to

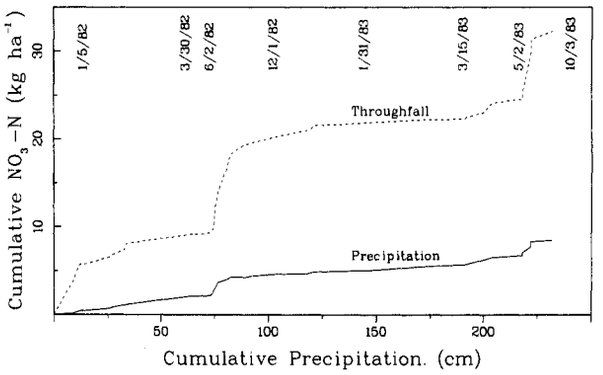

Figure 4. Cumulative NO_3^- transfers (kg of N ha^{-1}) in chaparral throughfall and bulk precipitation during the 1981–1982 and 1982–1983 hydrologic years. Nitrogen input per unit of water was elevated during summer and early autumn of both years. The greater throughfall inputs during these periods apparently resulted from high rates of dry deposition. The first storm of 1981–1982 (17 mm) was excluded.

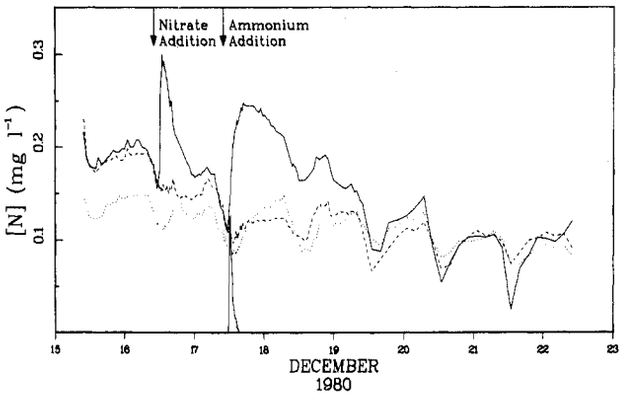

Figure 5. Stream water NO_3^- and NH_4^+ concentrations (mg of N L^{-1}) in Volfe Canyon following nitrogen additions during a period of base flow. NO_3^- and NH_4^+ were added on successive days at a point 300 m above the stream-gauging station. Concentrations were monitored 10 m above the addition point (dashed line), 150 m downstream (solid line), and at the weir (dotted line). A rapid immobilization of NO_3^- and a substantial nitrification response to the applied NH_4^+ were observed. NH_4^+ was detected only as a single pulse at 150 m downstream during midday of 12/17/80 (lower solid line).

the soil surface of which bulk precipitation accounted for 4.3 kg of N ha^{-1}. Washing of NO_3^- from dry deposition on canopy surfaces together with internal foliage leaching, therefore, was the source of 73% of the NO_3^- added to the soil surface.

Transfers of NH_4^+ in canopy throughfall and precipitation were 0.45 and 0.90 as large as the corresponding NO_3^- inputs during 1982–1983. The average combined canopy transfer of inorganic nitrogen was 23.3 kg of N ha^{-1} $year^{-1}$, of which 8.2 kg of N ha^{-1} $year^{-1}$ came from bulk precipitation.

Nitrogen Transformations. Water applied to initially dry soil stimulated NO_3^- production over the subsequent 18-day period at an average rate of 0.44 kg of N ha^{-1} day^{-1} (SE = 0.08). When 50 kg of N ha^{-1} as $(NH_4)_2SO_4$ was applied in addition to the water, soil NO_3^- accumulated at an average rate of 1.3 kg of N ha^{-1} day^{-1} (SE = 0.23). About half of the added NH_4^+ was nitrified.

Nitrification and NO_3^- immobilization were active in the stream of Volfe Canyon (Figure 5). Of the added NO_3^-, sufficient to increase by 50% the expected peak concentration 150 m downstream, biological uptake removed 54% within 150 m of stream reach and 85% after 300 m.

Adding $(NH_4)_2SO_4$ produced a single pulse of NH_4^+ at 150 m that accounted for only 1.7% of the nitrogen applied. The rapid nitrification that followed peaked after

Table II. Regional Stream Water Nitrate Concentrations following Major Storms in March 1982

location	$[NO_3^-]$, mg of N L^{-1} 3/18/82	3/25/82
San Gabriel Mts		
Arroyo Seco	1.90	
Millard Canyon[a]	2.48	
Rubio Canyon[a]	8.14	
Eaton Canyon[a]	3.96	
Hastings Canyon[a]	4.10	
Winter Creek	1.78	
Santa Anita Canyon	1.53	
Monrovia Canyon[a]	3.64	
San Gabriel River	2.69	
Van Tassel Canyon[a]	3.52	
Fish Canyon[a]	2.68	
Islip Gulch[a]	2.68	
Polecat Gulch[a]	2.50	
West Fork San Gabriel River[b]	0.74	
Bear Creek[b]	0.76	
Phipps Canyon[b]	0.92	
North Fork San Gabriel River[b]	1.14	
Graveyard Canyon[b]	2.28	
East Fork San Gabriel River[b]	1.13	
Cattle Canyon[b]	1.53	
Little Dalton Canyon[a]	4.74	4.36
Lewis Paul Canyon[a]	4.33	4.83
Bell Canyon[a]	3.32	2.41
Volfe Canyon[a]	3.78	3.53
Monroe Canyon[a]	2.81	2.05
Tanbark Creek[a]	4.61	2.08
Hummingbird Creek[a]	2.12	1.19
West Fork San Dimas Canyon[a]	4.26	2.34
Fern Canyon[b]	1.46	
East Fork San Dimas Canyon[b]	0.74	
San Dimas Canyon	2.02	1.19
Rock Quarry Canyon[a]	1.08	
Palmer Canyon[a]	4.48	2.48
Evey Canyon[a]	3.20	2.02
San Antonio Canyon[b]	1.56	0.94
front range[a]		
mean	3.62	2.73
s	1.43	1.14
interior/high elevation[b]		
mean	1.23	
s	0.49	
all watersheds		
mean	2.70	
s	1.56	

location	$[NO_3^-]$, mg of N L^{-1} 3/18/82	3/25/82
Santa Monica Mts[c]		
Deer Canyon		0.004
La Chusa Canyon		0.004
Trancas Canyon		0.005
Ramirez Canyon		0.19
Solstice Canyon		0.057
Corral Canyon		0.009
Carbon Canyon		0.15
Upper Santa Ynez Canyon		0.035
mean		0.06
s		0.07
Santa Ana Mts[c]		
Coldwater Canyon		0.13
Mayhew Canyon		0.46
Lion Canyon		0.12
Decker Canyon		0.12
mean		0.21
s		0.17
Palomar-Black Mts[c]		
Arroyo Seco Creek		0.002
Pala Canyon		0.20
Agua Tibia Creek		0.002
Cedar Creek		0.046
T.10S., R.1E., sec. 25		0.103
Wigham Creek		0.004
T.10S., R.2E., sec. 34		0.007
Washtub Falls		0.085
T.12S., R.2E., sec. 9		0.041
mean		0.05
s		0.07

[a] Front-range watersheds subject to chronic air pollution from the South Coast Air Basin. [b] Interior or predominantly high-elevation watersheds. [c] Regions with an infrequent incidence of air pollution.

Table III. Nitrate Flux (kg of N ha^{-1} $year^{-1}$) and Concentrations (mg of N L^{-1}) in Canopy Throughfall and Bulk Precipitation

	throughfall			bulk precipitation		
	NO_3^- flux			NO_3^- flux		
	annual	June–Oct	$[NO_3^-]$	annual	June–Oct	$[NO_3^-]$
canopy washing expt 9/80		9.1				
1981–1982	16.8[a]	8.5	2.3[a]	4.1[a]	1.6	0.50[a]
1982–1983	15.4	7.5	1.1	4.4	1.8	0.29
mean	16.1	8.5	1.5	4.3	1.7	0.36
s	1.0	0.7	0.9	0.2	0.6	0.15

[a] Values for 1981–1982 exclude the first autumn storm.

5 h and persisted for 5 days. Within the first 150 m of stream reach, 34% of the added NH_4^+ was nitrified and transported downstream; an additional 1% was nitrified within the next 150 m. The remainder presumably was biologically immobilized in sediments or denitrified.

Discussion

Deposition and Water Chemistry. The contention that atmospheric deposition is a primary source of stream water NO_3^- pollution in the San Gabriel Mountains is supported both by regional trends in stream water chemistry and throughfall and by observed patterns of throughfall nitrogen flux.

Stream water NO_3^- concentrations in watersheds subject to chronic air pollution were 2–3 orders of magnitude greater than in chaparral regions outside the South Coast Air Basin. Within the San Gabriels Mountains, they were greatest where watersheds adjoin the urbanized basin.

Table IV. Nitrogen Transfers in Chaparral and Forest Ecosystems[a]

ecosystem type	location	form	atmospheric deposition, kg of N ha^{-1} $year^{-1}$ precip.	atmospheric deposition, kg of N ha^{-1} $year^{-1}$ throughfall	watershed yield
(1) *Ceanothus crassifolius* chaparral	San Dimas Experimental Forest, Los Angeles, Co., CA	NO_3^-	4.3	16.1	0.04–10[b]
		NH_4^+	3.9	7.2	
			8.2	23.3	
(2) *Adenostoma fasciculatum* chaparral (*26*)	Santa Barabara Co., CA	NO_3^-		2.7[c]	
(3) *Ceanothus megacarpus* chaparral[d] (*27,28*)	Santa Barbara Co., CA	NO_3^-	1.53		
		NH_4^+	0.52		
			2.05	4.3	
(4) *Quercus turbinella* chaparral[e] (*19*)	Tonto National Forest, AZ	NO_3^-	4.2		0.2–0.5[f]
					0.05[g]
(type conversion to grassland)					5–29[f]
					0.3–4.5[g]
(5) *Quercus ilex* woodland (*29, 30*)	France		14.6	15.1	1.0
(6) *Pseudotsuga menziesii* forest[h] (*31, 32*)	eastern Cascades, WA	total	1.2		
		NH_4^+	0.21		
		NO_3^-	0.27		0.01
(first year following wildfire)					0.11
(second postfire year)					2.65
(7) *Alnus rubra* (*33*)	Alsea, OR	NO_3^-			25–35[i]
P. menziesii		NO_3^-			3–5[j]
(clear cut and slash burn)		NO_3^-			16[k]
(8) *P. menziesii* (*30, 34*)	Andrews Experimental Forest, OR		2.0	5.2	
		inorg N			0.04
(clear cut and slash burned)					2.1[k]
(9) *Eucalyptus globulus* (*35*)	Berkeley, CA	NO_3^-	0.23[l]	0.5	
		NH_4^+	0.8	1.7	
			1.0	2.2	
(10) mixed conifer and meadows[m] (*36*)	Lake Tahoe, CA	inorg N	1–2		
		NO_3^-			0.2–0.3
(11) *P. menziesii*[n] (*37, 38*)	Cedar River, WA	NO_3^-	1.6		
		NH_4^+	1.5		
			3.1	3.6–6.8	
(12) *Quercus-Carya* deciduous forest (*39*)	Coweeta Hydrologic Laboratory, NC	NO_3^-	3.7		0.1
		NH_4^+	2.7		0.06
			6.4		0.16
(13) northern hardwoods (*40*)	Hubbard Bk. Experimental Forest, NH	NO_3^-	4.3	6.0	3.7
		NH_4^+	2.2	3.3	0.26
			6.5	9.3	3.9
(14) *Picea abies* (*41*)	Solling, German Federal Republic		21.8	22.1	4.1
(15) *Quercus-Betula* and *Pinus* woodlands[p] (*42*)	The Netherlands	NO_3^-	7.0	15.5	
		NH_4^+	14.6	48.6	
			21.6	64.1	

[a] Values are for undisturbed stands unless otherwise indicated. [b] Data reported in this study. [c] Throughfall was measured during the first storms of hydrologic years 1971–1972 and 1972–1973. [d] The sum of throughfall and stemflow is reported here. Precipitation input was measured during 1979–1980. [e] The 12-year average for bulk precipitation is reported. [f] Estimates are for annual stream discharge greater than 20 cm. [g] Estimates are for annual stream discharge less than 8 cm. [h] Bulk precipitation was measured 1971–1975. The low watershed yield the first year after fire was due to a delay in soil nitrification response until after the first snow melt in spring 1971. [i] The forest consists of 68% red alder and 32% conifers. The high rate of yield reflects a nitrogen saturated system; a 4-year range of observations is reported here. [j] The forest is 80% Douglas fir. Estimates for 2 years before treatment are shown. [k] The average 2-year postfire response is reported. [l] Bulk precipitation was measured 12/74 through 5/75. [m] Bulk precipitation was measured; estimates are the approximate ranges for the 1973 and 1974 hydrologic years. Watershed yield is for the same period. [n] Throughfall was collected in 22–95-year-old stands. Only trace values of inorganic nitrogen were measured in the soil solution at 1-m depth. [o] Bulk precipitation was measured. Watershed loss is the average from eight undisturbed watersheds for 1972–1974. [p] Values reflect a high deposition rate of NH_3 volatilized from manure.

High NO_3^- concentrations, therefore, were not characteristic of chaparral watersheds.

Nitrogen flux through the chaparral canopy at San Dimas was at record levels and especially elevated after smog episodes. On the basis of annual or periodic rates, the NO_3^- flux was 3–4 times greater than in chamise or *Ceanothus megacarpus* chaparral in the relatively unpolluted coastal environment of Santa Barbara County (Table IV). Inorganic nitrogen in throughfall was 2.5–16 times that reported for forest ecosystems nationally (Table IV). Comparable rates for NO_3^- are found in areas of industrial air pollution in the Solling District of Germany and in The Netherlands. Nitrogen deposition in bulk precipitation at San Dimas showed a similar relation.

The NO_3^- in throughfall apparently was derived largely from dry deposition on canopy surfaces rather than chemical leaching of extracellular spaces within foliage. Such leaching generally is sustained by xylem transport and is proportional to the duration of canopy washing (*16*). In our study, nitrogen loss was protracted during summer and autumn, appreciably occurred only when the *Ceanothus* was desiccated, and was initially rapid during a storm.

Watershed NO_3^- yield during years of high rainfall at San Dimas greatly exceeded that reported for undisturbed forests nationwide (Table IV). Watershed losses are greater only in Pacific Northwest forests dominated by *Alnus rubra*, which supports substantial symbiotic N_2 fixation. NO_3^- yield from chaparral at San Dimas was an order of magnitude greater than that from undisturbed chaparral watersheds in Arizona.

Patterns of Watershed Loss. Mechanics of water movement and the seasonality of biological processes apparently determine the patterns of watershed NO_3^- loss. In addition to washing NO_3^- from the vegetation canopy, early seasonal rains stimulate soil mineralization and nitrification. The net production of NO_3^- observed in the soil wetting experiment (7.9 kg of N ha^{-1}) was equivalent to the throughfall from the first storm after the summer drought (8.5 kg of N ha^{-1}). Early stream flow is generated in a narrow area near the channel and should contain relatively high concentrations of NO_3^- from these sources. Declining flow originates from precipitation later in the storm that has a lower [NO_3^-] and passes through previously washed canopy and soil.

Substantial amounts of NO_3^- are removed from hill slope areas only during storms that saturate the system and extend the contributing area into numerous small channels on the steep hillsides. The prolonged elevation of stream NO_3^- concentrations during recessional flow probably reflects sustained unsaturated flow through much greater soil volumes. Peak NO_3^- concentrations are less during later storms because waters traverse both leached and unleached soils, early season NO_3^- accumulations and the microbial response to soil wetting are reduced (*8*, *9*), and vegetation uptake has resumed. The large difference in NO_3^- loss between years of heavy and slight rainfall most likely reflects an associated difference in the stream contributing area.

Biological NO_3^- uptake within the aquatic system probably causes the low [NO_3^-] of summer base flow. Diurnal fluctuations in [NO_3^-] during spring are timed with changes in irradiance and probably derive from growth and nitrogen uptake by the substantial algal community that is present. Reducing environments marked by evolution of H_2S are also present, and these may be sites of active denitrification. Biological uptake is probably unable to affect the larger quantities of NO_3^- transported after major storms or during cooler winter temperatures. Nitrification was shown to be active in the aquatic system, so the observed [NO_3^-] patterns also may reflect seasonally variable rates of organic nitrogen loading and mineralization in the stream.

The Bell Canyon watersheds had similar soils, microclimate, and vegetation before the grasslands were established. The elevated NO_3^- losses from the grassland must be derived from mineralization of residual organic nitrogen, accelerated water movement or soil erosion, greater nitrogen deposition, or reduced nitrogen accretion in vegetation.

Large NO_3^- yields, mineralized from the original chaparral vegetation, accompanied heavy annual precipitation for 11 years after grassland establishment in Arizona (Table IV) (*17*). In the present study, nitrogen in the aboveground chaparral was mineralized during the wildfire of 1960, so this did not contribute to the greater NO_3^- yields. Continued mineralization in decomposing chaparral roots also was unlikely since our measurements were made from 19 to 23 years after initial treatment.

Watershed Nitrogen Accretion. Despite high rates of watershed nitrogen yield, the 4-year balance of deposition and loss produced a net accretion in the chaparral watersheds of 80 kg of N ha^{-1}, 86% of the estimated deposition. The remainder apparently was immobilized in biomass or soil organic material, lost through deep seepage and denitrification, or retained in the lower soil profile.

Table V. Annual Nitrogen Transfers in Chaparral and Grass Vegetation

	kg of N ha^{-1} $year^{-1}$	
	chaparral	grassland
bulk precipitation		
NO_3^-	4.3[a]	same
NH_4^+	3.9	same
	8.2	
Canopy throughfall		
NO_3^-	16.1	unknown
NH_4^+	7.2	
	23.3	
N accretion in standing biomass	10[b]	0[c]
uptake	38[d]	30
leaf litter mineralization	28[e]	30[e]

[a] Average inputs were estimated for 1981–1982 and 1982–1983 hydrologic years; the first storm of the 1981–1982 season (1.7 cm) was not included. NH_4^+ was estimated as a proportion of measured NO_3^- inputs based on precipitation data 6/82–10/83 (see text). [b] The average from 12, 120-m^2 plots in pure 21-year-old *Ceanothus crassifolius* stands in reported. Average annual accretion in vegetation and litter over the entire 21-year period is 32 kg of N ha^{-1} $year^{-1}$. [c] The grassland is annual vegetation with no multiyear accumulation of standing live biomass. [d] The average in 21-year-old *C. crassifolius* is given. [e] Annual turnover of litter was assumed (see text).

Water and NO_3^- losses through deep strata are apparently minimal. During years of heavy rainfall that should maximize deep percolation (e.g., 1979–1980; Table I), 55–75 cm of evapotranspiration would account for unmeasured water losses; rates of 43–50 cm have been estimated for chaparral in years with less rainfall (*18*, *19*), so the higher values are not unreasonable. Water in the lower soil profile may also be available to the deep-rooted chaparral during subsequent years. Denitrification has not been estimated for chaparral watersheds.

The throughfall nitrogen flux was larger than the amount of nitrogen cycled by the mature *Ceanothus* chaparral. It was 2.3 times the annual rate of nitrogen accretion in standing biomass and 60% of nitrogen uptake (Table V). An unknown portion of the annual shrub uptake is also derived from N_2 fixation. There is no net accumulation of nitrogen within the annual grasses.

Nitrogen mineralization in leaf litter is probably comparable in the annual grasses and mature *Ceanothus* chaparral. Annual grass production in watershed 0802 during 1982 contained 30 kg of N ha^{-1} (SE = 5); litterfall in mature *Ceanothus* had a similar nitrogen content of 28 kg ha^{-1} (SE = 4) (*20*). Nitrogen mineralization equivalent to that in the peak standing crop has been reported for annual grasslands elsewhere in California (*21*). A steady state is also thought to exist for organic matter in *Ceanothus* litter after 11–14 years of postfire development (22). If nitrogen mineralization proceeds similarly, nitrogen does not accumulate in the litter of either community.

Higher stream discharge rates are observed in the grassland watersheds than in the chaparral at San Dimas (Table I), especially during storms that accumulate from 20 to 40 cm of water in the system. This higher rate apparently results from accelerated landsliding and loss of soil water storage (*23*, *24*) within the hydrologically active inner canyons, or from some reduction in transpiration rates by the more shallow-rooted grasses. The more

rapid water flux through the grassland apparently hastens the outflow of nitrogen from the watershed. At comparable flow rates, the stream water [NO_3^-] was also higher in the grassland than in the chaparral, probably because no nitrogen annually accumulates in grass biomass.

Water Management. The 4-year volume-weighted mean stream water [NO_3^-] observed in the chaparral, 1.2 mg of N L^{-1}, was small in relation to the peak concentrations of 10–20 mg of N L^{-1} observed in the downstream aquifer of the San Gabriel Valley. However, it may be a significant fraction of current nitrogen additions to the aquifer depending on water management and the amount of evaporation, immobilization, and denitrification in the channel. Sustained peaks of 2–4 mg of N L^{-1} during high flows would more than double the rate of addition when this water is the primary source for groundwater recharge in percolation basins.

Fire Effects. Wildfires in chaparral subject to chronic air pollution may cause inordinate stream water NO_3^- loading. A large proportion of the nitrogen derived from deposition and natural sources accumulates in organic compounds and is liberated as NH_4^+ by burning. Some volatilization occurs depending on the intensity and depth of soil heating and the amount of fuel consumed. The remaining NH_4^+ can be rapidly nitrified in the postfire soils (*25, 26*). Hillside erosion, accelerated after severe wildfires because of changes in soil structure and water repellency (*11*), carries NH_4^+-laden soil and ash to stream channels and basins where nitrification is also active. The NO_3^- loading, coupled with high stream discharge and channel scouring, could saturate the aquatic system and seriously pollute downstream waters.

Burning in coniferous forests often increases watershed NO_3^- yield by more than 2 orders of magnitude (Table IV). In the present study, a prominent [NO_3^-] also was observed in stream water from a chaparral watershed that had burned 2 years previously. Wildfires can occur frequently in the chaparral: the San Dimas watersheds were burned in 1896, 1919, and 1960. Hence, postfire NO_3^- yield may well be a major contributor to regional groundwater pollution. Periodic prescribed burning is being instituted for fire and watershed management in many areas of the chaparral. If NO_3^- yield is substantial after severe wildfires, this more moderate treatment may allow water quality to be managed by reducing the extent of concurrent burning within a major watershed, reducing the severity of fire-induced soil structural changes and erosion, and moderating fire-associated mineralization and NH_4^+ concentrations within soils and sediment.

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Sorbent Concentration Effects in Liquid/Solid Partitioning

Thomas C. Voice*

Department of Civil and Environmental Engineering, Michigan State University, East Lansing, Michigan 48824

Walter J. Weber, Jr.

Department of Civil Engineering, The University of Michigan, Ann Arbor, Michigan 48109

■ Partition coefficients developed in laboratory sorption studies have been observed to vary inversely with the concentration of sorbent solids utilized in the experimental system. A model was developed that relates this phenomenon to the complexation, or binding, of the solute by nonseparable organic matter in the liquid phase, and the subsequent sorption of both free and bound solute. It can be shown that linear partitioning in the resulting bisolute system can produce the nonlinear sorption anomalies that have been observed in isotherm studies. The model was calibrated to previously reported sorption data involving four hydrophobic environmental contaminants—2,4,5,2′,4′,5′-hexachlorobiphenyl, 2,5,2′-trichlorobiphenyl, naphthalene, and chlorobenzene—and three Lake Michigan sediment samples. The strengths and weaknesses of the model along with its environmental implications are discussed.

Introduction

Interphase partitioning phenomena are of paramount significance in environmental systems. They are exploited in the treatment of water and wastes and often determine the extent to which a pollutant is released to and moves through the environment. All such phenomena share a common basis in that they are controlled by fundamental thermodynamic properties defining the relative association energy of a compound with a particular phase. Because of its particular significance and widespread occurrence, considerable attention has focused on liquid–solid phase partitioning or sorption, and a substantial body of literature has developed relative to correlating observed sorption phenomena with theoretical considerations (*1–3*). A notable apparent contradiction of experimental evidence with sorption theory has been cited in several reports that have described a "solids effect" in laboratory isotherm measurements (*4, 5*). These works document a dependence of partition coefficients (ratios of individual phase concentrations) on the mass of the solid phase utilized in the experimental system, whereas simple phase equilibrium relationships predict no such dependence. The effect has been quantified and analyzed by regression analysis, and at least three explanatory models have been recently published on this phenomenon (*6–8*). This paper proposes an alternative model that is capable of representing experimental data reported previously by the authors (*5*) and offers some insight into mechanisms that may be responsible for such observations.

It is commonly assumed that partitioning can be treated as the thermodynamically motivated distribution of a chemical between two readily separable, homogeneous phases. Measurements of this distribution are often expressed as partition coefficients, that is, the ratio of chemical concentrations in the two phases. The "solute complexation model" proposed herein suggests that the liquid phase is in fact more complex, being comprised of at least two nonseparable fractions. Solute molecules can reside in either of these two subphases, but common analytical techniques (solvent extraction/gas chromatography, liquid scintillation spectroscopy) cannot distinguish the two states. Analytical measurements therefore produce "apparent partition coefficients" that express the ratio of total chemical concentration in each of the two apparent bulk phases.

Several assumptions have been made in the development of the model, some of which can be supported by independent evidence. Other assumptions remain untested, possibly untestable. Whenever possible, assumptions and coefficient values are supported by outside evidence, and validation studies are presented in support of hypotheses advanced. It is inevitable, however, that the present work falls short of complete verification, a task that can ultimately be accomplished only through future exhaustive testing and refinement of the model.

Model Assumptions and Formulation

The model, shown schematically in Figure 1, is based on the following assumptions: (1) the liquid phase contains

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