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Fluxes and transformations of nitrogen in a high-elevation catchment, Sierra Nevada

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Abstract. The fluxes and transformations of nitrogen (N) were investigated from 1985 through 1987 at the Emerald Lake watershed (ELW), a 120 ha high-elevation catchment located in the southern Sierra Nevada, California, USA. Up to 90% of annual wet deposition of N was stored in the seasonal snowpack; NO_3^- and NH_4^+ were released from storage in the form of an ionic pulse, where the first fraction of meltwater draining from the snowpack had concentrations of NO_3^- and NH_4^+ as high as 28 μeq L^{-1} compared to bulk concentrations of <5 μeq L^{-1} in the snowpack. The soil reservoir of organic N (81 keq ha^{-1}) was about ten times the N storage in litter and biomass (12 keq ha^{-1}). Assimilation of N by vegetation was balanced by the release of N from soil mineralization, nitrification, and litter decay. Mineralization and nitrification processes produced 1.1 keq ha^{-1} yr^{-1} of inorganic N, about $3\frac{1}{2}$ times the loading of N from wet and dry deposition. Less than 1% of the NH_4^+ in wet and dry deposition was exported from the basin as NH_4^+. Biological assimilation was primarily responsible for retention of NH_4^+ in the basin, releasing one mode of H^+ for every mole of NH_4^+ retained and neutralizing about 25% of the annual acid neutralizing capacity produced by mineral weathering in the basin. Nitrate concentrations in stream waters reached an annual peak during the first part of snowmelt runoff, with maximum concentrations in stream water of 20 μeq L^{-1}, more than 4 times the volume-weighted mean annual concentrations of NO_3^- in wet deposition. This annual peak in stream water NO_3^- was consistent with the release of NO_3^- from the snowpack in the form of an ionic pulse; however soil processes occurring underneath the winter snowpack were another potential source of this NO_3^-. Concentrations of stream water NO_3^- during the summer growing season were always near or below detection limits (0.5 μeq L^{-1}).

Introduction

In alpine basins, multiple stresses, including low temperatures, high winds and short growing seasons limit plant growth and the ability of alpine environments to effectively use N relative to other ecosystems (e.g. Walker et al. 1994). Recent developments add some urgency to increasing our understanding of N-cycling in alpine environments. Concentrations of anthropogenic N in the ambient air in mountainous areas have increased as much as 30-fold during the last several decades (Fahey et al. 1986). The impacts of increases in atmospheric deposition of N are beginning to be identified for aquatic ecosystems. For example, there has been a long-term shift in algal productivity in

Lake Tahoe in the subalpine Sierra Nevada from co-limitation by both N and P to overwhelming P-limitation (Goldman et al. 1993). This phenomenon may be a more general one underway in other mountainous, granitic watersheds with surface waters prone to N limitation (e.g. Paerl et al. 1990).

Terrestrial alpine ecosystems may also be affected by increased N-deposition. An increase in N deposition to alpine basins may both enhance the growth of biota that are N limited and degrade biota through acidification processes. Bowman et al. (1993) report that primary production in alpine tundra of Colorado is N-limited, and that phosphate amendments in combination with N significantly alter both species composition and primary production. Fertilization from atmospheric deposition of N may increase plant mortality by delaying senescence into late fall, when cold temperatures or autumn snowfalls may cause physiological damage to plant structures that have normally undergone winter hardening (Keigley 1987). In high-elevation areas of the Colorado Front Range, the loading of H^+ is strongly correlated with NO_3^- (Grant & Lewis 1982), and increases in the H^+ content of bulk deposition are correlated with increases in NO_3^- rather than SO_4^{2-} (Lewis & Grant 1980). Ecosystem acidification can also influence the rate and extent of several processes in the N-cycle, such as decreasing N mineralization and nitrification (Novick et al. 1984; Rudd et al. 1988).

In this paper we integrate and evaluate results from published and original data in order to: i) quantify sources and sinks of N in an alpine basin, ii) identify the important processes that transform N, iii) evaluate the effects of atmospheric inputs of N on the N-cycle, and iv) identify areas of N-cycling where additional research is needed in alpine basins. We address these objectives using studies conducted at the Emerald Lake Watershed (ELW) from 1985–1987, a headwater basin located in Sequoia National Park, southern Sierra Nevada. Statistical analyses of data from the Western Lakes survey conducted by the Environmental Protection Agency show that ELW is representative of granitic basins in the Sierra Nevada (Melack & Stoddard 1991). Therefore knowledge of the processes that control N fluxes at the ELW can be applied to the broader region of granitic basins in the Sierra Nevada.

Site description

The Emerald Lake basin is a north-facing granitic cirque located on the upper Marble Fork of the Kaweah River drainage, in the southern Sierra Nevada of California, USA (36°35′49″ N, 118°40′30″ W) (Fig. 1). Basin area is 120 ha; elevation ranges from 2800 m at the lake outlet to 3416 m at the summit of Alta Peak (Fig. 2). Emerald Lake is a 2.72 ha cirque lake at the bottom of the basin, fed by two main inflows and six intermittent streams, and drained by

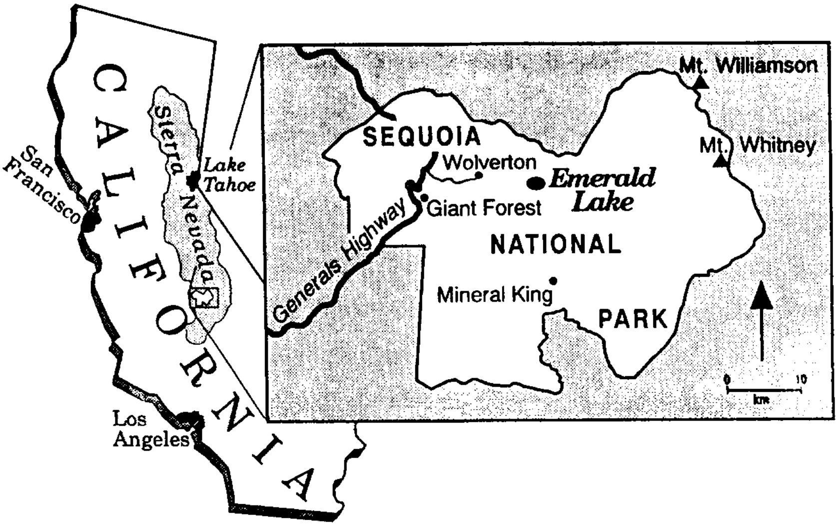

Fig. 1. Location of Sequoia National Park, Giant Forest., Wolverton, and the Emerald Lake watershed.

Table 1. Soil properties by soil type (with representative locations within watershed).

Soil type and location	Area ha	Density g cm^{-3}	Depth m	Cation exchange capacity meq kg^{-1}	Base saturation percent
Entic Cryumbrept (bench)	0.94	1.25	0.373	161	15.5
Lithic Cryumbrept (ridge)	13.08	1.38	0.337	10.0	15.5
Lithic Histic Cryaquept (inlet)	6.20	1.02	0.237	257	19.1
Cryorthod association (pine)	2.08	1.35	0.326	105	18.1
Typic Cryothent (cirque)	4.54	1.21	0.249	12.2	15.5
Total (area) or weighted mean	26.85	1.29	0.350	54.4	16.1

a single outflow (Fig. 2). Emerald Lake and the streams in its watershed are weakly buffered, calcium-bicarbonate waters (Melack et al. 1989), which are typical of high-altitude Sierran surface waters (Melack et al. 1985; Melack & Stoddard 1991).

Vegetation covers about 20% of the basin area with 3% of the basin having scattered trees (Fig. 2) (Rundel et al. 1989). Massive rock outcrops cover 33% of the basin area; unconsolidated sand, gravels, and talus cover

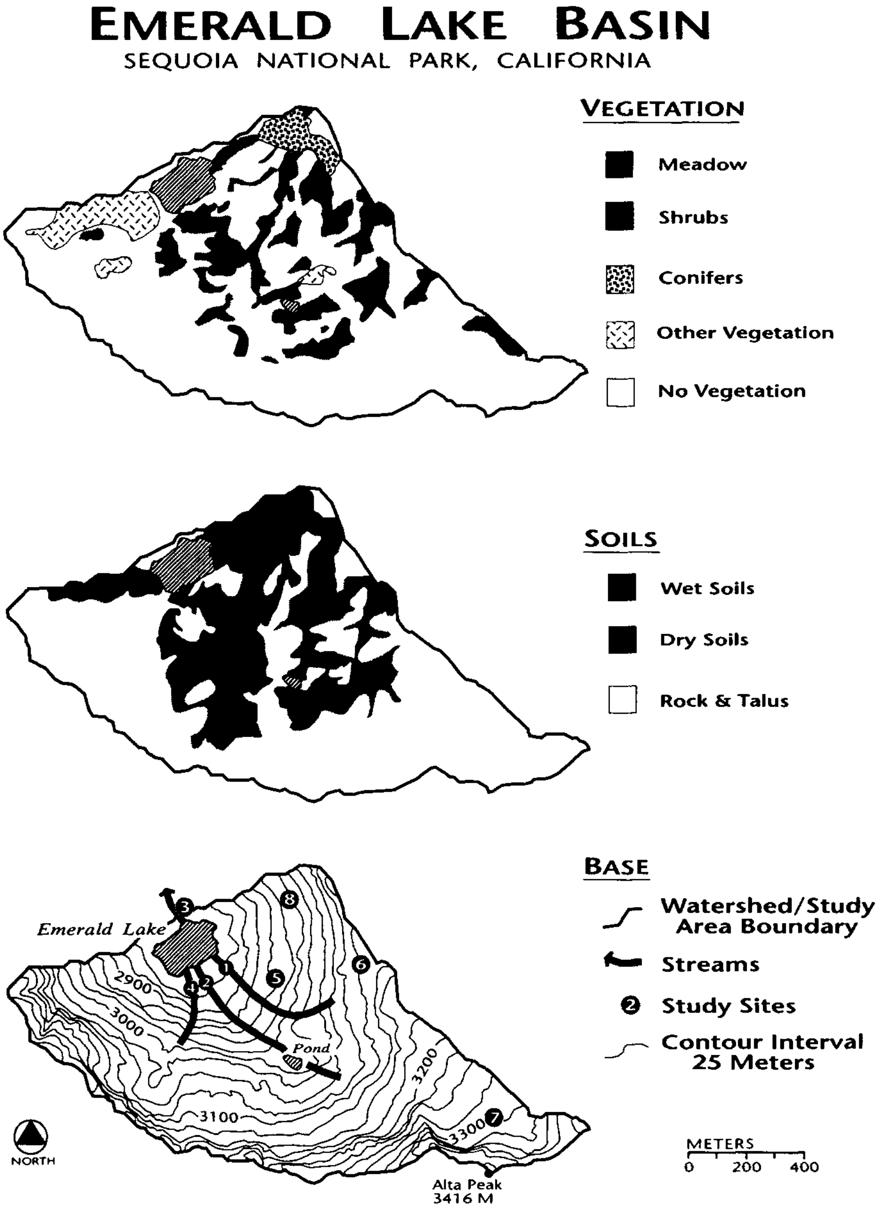

Fig. 2. Topographic, soils and vegetation maps of the Emerald Lake watershed. Location of sites are as follows: 1 inflow 1; 2 inflow 2; 3 outflow; 4 inflow 4; 5 bench; 6 ridge; 7 cirque; 8 pine stand. Discharge was measured and water samples collected immediately above the lake at 1, 2, and 4 and immediately below the lake at 3. Snowpit samples were collected in 1986 at 2, 6 and 7 and in 1987 snowpit and meltwater samples were collected at 2, 5, 6, and 7. Aerochem Metrics wet-only collector was located near 1. Soil lysimeters were located at 2, 5, 6, 7, and 8. The nine major vegetation groups have been lumped into four classes for presentation purposes.

about 23%. The remaining area is mapped as a rock-soil complex, which is about half soil and half rock outcrop (Fig. 2). Soils are classified into five mapping units (Table 1), and are largely located along perennial or ephemeral streams (Fig. 2). Soils are strongly acidic and weakly buffered (Huntington & Akeson 1986; Brown et al. 1990). The estimated average depth for the 26.8 ha of soils covering the basin is approximately 0.35 m (Brown et al. 1990). All soils are derived primarily from weathering of the underlying bedrock. X-ray diffraction of the clay fraction collected from soil profiles at soil lysimeter sites found hydroxy-interlayered vermiculite and kaolinite to be the dominant clay minerals in all soil samples (Brown & Lund 1991). Cation exchange capacity (CEC) of soils ranges from 10 to 257 meq 1000 g^{-1} with a basin volume-weighted mean of 54 (Table 1). Calcium and K^+ dominate the exchangeable bases of soils, with weighted averages over the basin of 51% and 45%, respectively. Base saturation for the upper 200 mm of soils are typically 26–30%, and the basin weighted average is 16% (Brown et al. 1990). The total saturated water content of the basin is about 48,000 ± 13,000 m^3; laboratory measurements of the saturated hydraulic conductivity range from 0.1 to 0.01 mm s^{-1} (Williams et al. 1993a).

Data sources, methods and summary

We used the best available sources to compile our data base of hydrologic, chemical, biological and soil parameters. These sources include publications by ourselves and others at the ELW, and complimentary research at nearby sites. In addition, we present previously unpublished data on soil mineralization and nitrification. We concentrate on the 1987 water year (October 1, 1986–September 30, 1987), the water year with the most comprehensive data sets. Additional data from water years 1985 and 1986 are presented when available. Where journal publications exist, abbreviated methods and results are presented which were used to calculate catchment-scale reservoirs and fluxes of N. Where data is unpublished, methods and results are reported in more detail.

Wet deposition

Wet deposition over three water years (1985–1987) were reported in detail by Williams & Melack (1991a). In brief, all samples were analyzed for pH, conductance, major inorganic ions and reactive silicate. Total nitrogen (TN) was collected in the snowpack in 1986 and was assayed as NO_3^- after persulfate digestion; TN includes inorganic N (NO_3^- and NH_4^+), dissolved organic N and particulate N. The chemical content of rainfall was sampled at a single site near the lake inlet (Fig. 2), using a wet-only Aerochem Metrics model 301 sampler. The chemical content of snowfall was sampled using two techniques: (1) on an event basis at 1–4 sites using snowboards, and (2) at three to six snowpits during the period of maximum accumulation. The analytical precision for NH_4^+ and NO_3^- was within 6% of mean values; detection limits were 0.5 μeq L^{-1}. Detailed analytical information was presented in Williams & Melack (1991a).

Concentrations in winter snow were among some of the most dilute measurements of N recorded in wet precipitation, yet N concentrations in rainfall were comparable to areas with large anthropogenic sources of N. Nitrogen concentrations in snow of about 2 μeq L^{-1} each for NH_4^+ and NO_3^- (Table 2) are comparable to mean concentrations of 2.8 μeq L−1 for NH_4^+ and 2.4 μeq L^{-1} for NO_3^- reported by Galloway et al. (1982) for a site in central Alaska. Kennedy et al. (1979) report similar values from the sparsely populated coastal region of the Matole River in northern California. However, mean concentrations in rainwater at the ELW of about 55 μeq L^{-1} for NH_4^+ and 42 μeq L^{-1} for NO_3^- (Table 2) are comparable to N concentrations in rainfall in areas having considerable anthropogenic sources of N, such as the Adirondack and Catskill mountains of New York (Stoddard 1994). One reason for the higher concentrations of NH_4^+ and NO_3^- in rainfall relative to snow appears to be a change from dilute winter storms that originate as frontal systems over the Pacific Ocean to summer convective storms that entrap air masses from local urban and agricultural areas (Williams & Melack 1991a).

Measurements of TN from the snowpack were similar to the sum of NO_3^- plus NH_4^+, indicating that almost all N in the snowpack was inorganic.

The arithmetic average of total inorganic N (TIN) loading in wet deposition at ELW from 1985–1987 of 164 eq ha^{-1} yr^{-1} is among the lowest reported for the contiguous 48 states (Stoddard 1994). Baron (1991) reports a 40% higher value (230 eq ha^{-1} yr^{-1}) for the Loch Vale catchment in Rocky Mountain National Park (elevation 3159 m), for the period 1984–1988. For the northeastern United States, Stoddard (1994) reports N loading three-four times that of the ELW at 550–600 eq ha^{-1} yr^{-1} for the Catskills and Adirondacks.

Deposition of N in the seasonal snowpack was important, even though concentrations of N were very low. About 90% of the annual loading of NH_4^+ and $NO3^-$ from precipitation occurred as snow and was stored in the seasonal snowpack for release during the relatively short span of snowmelt runoff. Furthermore, about 80% of the NO_3^- and NH_4^+ stored in the seasonal snowpack was released in the first 20% of snow melt, an ionic pulse (Bales 1992). Maximum concentrations of NO_3^- measured in the first fraction of snowpack meltwater were 27μeq L^{-1}, or about six time that of the bulk snowpack concentrations at the same site (Williams & Melack 1991b).

Table 2. Volume-weighted mean concentrations and annual loadings of NH_4^+ and NO_3^-, by precipitation type, WY's 1985–1987.[a]

Year	Concentration, μeq L^{-1}								
	NH_4^+				NO_3^-				
	Winter snow	Autumn snow	Rain	Annual	Winter snow	Autumn snow	Rain	Annual	Total inorganic N
1985	0.9	15.1	42.8	2.6	2.3	11.8	40.4	3.5	6.1
1986	1.4	21.8	23.4	3.3	1.8	14.7	22.2	3.1	6.4
1987	3.8	44.4	63.0	14.4	4.2	25.5	48.2	11.9	26.3
Mean	1.7	20.8	55.3	5.4	2.3	14.4	42.8	5.0	10.4
					Loading, eq ha^{-1}				
1985[b]	9	14	7	30	24	11	6	41	71
1986[c]	33	46	8	87	43	31	7	81	168
1987[d]	30	8	100	138	33	5	76	114	252
Mean[e]	24.0	22.7	38.3	85	33.3	15.7	29.6	79	164

[a] Adapted from Williams & Melack (1991a).

[b] Winter snow, 1046 mm; autumn snow, 95 mm; rain, 16 mm.

[c] Winter snow, 2380 mm; autumn snow, 213 mm; rain, 32 mm.

[d] Winter snow, 780 mm; autumn snow, 19 mm; rain, 160 mm.

[e] Arithmetic average.

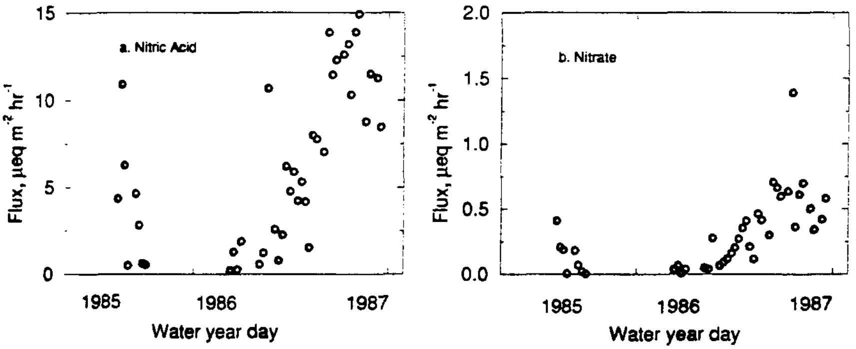

Fig. 3. Dry deposition of nitric acid (panel a) and p-NO_3^- (panel b) at Wolverton, 1985 to 1987.

Dry deposition

Dry deposition of N was measured using several different methods, including Bytnerowicz et al. (1991), who measured dry deposition of N to pine needles and surrogate surfaces (nylon and paper filters) during three periods from July 15 to September 10, 1987. Materials were deposited on teflon-film-coated and non-coated branches of two native conifers: Lodgepole pine (*Pinus contorta*) and western white pine (*Pinus monticola*). Samples were collected from foliage for chemical analysis by rising with deionized, distilled water. Fluxes of NO_3^- were similar to all surfaces, while NH_4^+ fluxes to surrogate surfaces varied considerably from fluxes to pines. Average fluxes to pine were 0.45 μeq m^{-2} h^{-1} for NO_3^- and 0.41 μeq m^{-2} h^{-1} for NH_4^+. Wu & Davidson (1989) measured deposition fluxes of NO_3^- to teflon plates and nylasorb filter paper set into recesses in aluminum frisbee-shaped airfoils. NO_3^- deposition to teflon and nylasorb averaged 0.54 ± 0.08 ± eq m^{-2} h^{-1} and 1.57 ± 0.90 μ eq m^{-2} h^{-1}, respectively; they assumed the difference to be HNO_3 gas (1.03 ± 0.90 μeq m^{-2} h^{-1}). Their data were reported for four two-day exposures and two one-week exposures from August 11 to September 30, 1987. Differences as compared to Bytnerowicz et al. (1991) were due in part to differing deposition surfaces and the later period that Wu & Davidson worked. Williams & Melack (1991a) estimated dry deposition of NO_3^- to the winter snowpack by comparing NO_3^- loading from cumulative event totals to NO_3^- loading in co-located snowpits and report no evidence for dry deposition of NO_3^- to winter snow.

Year-round dry deposition measurements were from a forest clearing at 2250 m at Wolverton, near the trailhead for the Emerald Lake watershed (Fig. 1); this site is part of the National Oceanographic and Atmospheric Administration (NOAA) nationwide network of dry deposition monitoring stations.

Table 3. Monthly estimates of nitrogen in dry deposition, for WY 1987.

Month	N-flux eq ha^{-1}	NO_3^- eq ha^{-1}	NH_4^+ eq ha^{-1}
October	0.95	0.50	0.45
November	1.11	0.58	0.53
December	0.32	0.17	0.15
January	0.63	0.33	0.30
February	2.06	1.08	0.98
March	1.59	0.83	0.76
April	2.86	1.50	1.36
May	4.14	2.17	1.97
June	6.21	3.25	2.96
July	7.01	3.67	3.34
August	8.12	4.25	3.87
September	4.45	2.33	2.12
Annual loading	39.45	20.65	18.80

Weekly field measurements made from 1985 through 1987 were available. While the physiographic parameters of Wolverton are different from the ELW, it is informative to analyze this extensive data set for seasonal trends. Fluxes at Wolverton were highest in June and July, dropping to 10–20% of the summer values by October; fluxes remained low until mid-February, after which they rose (Fig. 3). Trends in dry deposition at Wolverton are attributed to seasonal differences in both ambient concentrations and deposition velocities.

Dry deposition estimates at ELW were consistently lower than at Wolverton. During the 57-day period of overlapping measurements at the two sites, total NO_3^- deposition averaged 1.06 ±eq m^{-2} h^{-1} at Wolverton. The corresponding value at ELW based on Bytnerowicz et al. (1991) was 43% of that, or 0.45 ±eq m^{-2} h^{-1}. Differences in concentrations, meteorology, surface conditions, and methods are all probable explanations for differences between the two sites.

To estimate dry deposition of NO_3^- at ELW throughout the year, we applied a factor of 0.43 to the sum of monthly flux of p-NO_3^- and HNO_3 at Wolverton (Table 3). Seasonal trends in dry deposition of NO_3^- were pronounced, with the majority of dry deposition occurring during the summer months. Lacking estimates of the surface area available for dry deposition per unit watershed area, we applied the deposition fluxes to the total watershed area. While this assumption should be reasonably good for times when the catchment

Table 4. Throughfall (TF) measurements during rain events †.

	Area ha	NH_4^+ meq m^{-2}	NO_3^- meq m^{-2}	NH_4^+ eq ha^{-1}	NO_3^- eq ha^{-1}	N loading eq ha^{-1}
Chinquapin	2.76	−0.69	+0.24	−0.160	+0.055	−0.10
Western White Pine	2.01	−0.02	+1.52	−0.003	+0.255	+0.25
Willow	8.67	−0.33	−0.25	−0.238	−0.180	−0.42
Total TF loading §	—	−0.77	+1.51	−0.40	+0.13	−0.27
Summer rain‡	120	+0.8	+0.7	+8.0	+7.0	+15.0

† Fluxes to (+) and from (−) rain.

§ Total throughfall loading calculated as the sum of loading per square meter times vegetation area of basin divided by total basin area.

‡ Median annual summer rain loading from 1985–1987 ($n = 17$), for comparison.

Adapted from Brown & Lund (1994).

was covered with snow, it should result in underestimates during snow-free periods. Bytnerowicz et al. (1991) report that dry deposition of NH_4^+ was 91% of that observed for NO_3^-; we therefore calculated NH_4^+ flux to be 91% of NO_3^- dry deposition. Total N flux from dry deposition was therefore estimated to be 40 eq ha^{-1} for water year 1987 (Table 3).

These results are consistent with an independent estimate of annual N loading from dry deposition in 1987 made by Blanchard et al. (1989). They estimated dry deposition loading to the ELW using the data sets from Bytnerowicz et al. (1991) and Wu & Davidson (1989). Using average deposition values of 2.0 meq m^{-2} yr^{-1} each for NO_3^- and NH_4^+, the Blanchard et al. (1989) analysis also produced a rate of 40 eq ha^{-1} for 1987.

Throughfall

Brown & Lund (1994) investigated throughfall by comparing the chemical content of rainfall (18 collectors) with throughfall collection sites located under three dominant woody vegetation types (6 collectors per vegetation type): chinquapin (*Chrysolepsis sempervirens*), western white pine (*Pinus monticola*), and willow (*Salix orestera*). Solute composition and water depth were collected from 17 rain events in 1985, 1986 and 1987 during the summer months in 1-L polyethylene bottles with a 0.15-m diameter funnel inserted into the bottle cap. Net throughfall deposition was calculated as the difference between precipitation and throughfall, using multiple regression models (e.g. Lovett & Lindberg 1984).

At the ELW, foliar processes such as exchange, leaching, washoff of dry deposition, and adsorption have a large effect on the N concentrations of incident rain. Almost all the NH_4^+ in rainfall (0.8 meq m^{-2}) was retained by throughfall (-0.77 meq m^{-2}) on an areal basis (Table 4). Conversely, release of NO_3^- by vegetation (leaching and/or washoff of dry deposition) (+1.51 meq m^{-2}) was more than twice that of incident rain (0.7 meq m^{-2}).

However, the changes in N loading at the basin scale caused by foliar interactions with precipitation were low because: i) NH_4^+ retention tended to be compensated by NO_3^- release, and ii) only a small area of the basin is covered by vegetation. Net throughfall loading of N to the basin was calculated by adding net throughfall for each N-species by vegetation type on a per meter basis, multiplying by the areal extent of each vegetation type, summing over the area of all vegetation types, and then dividing by 120 ha to convert the result into eq ha^{-1} for the ELW. The net retention of -0.27 eq ha^{-1} of N was much less than the 15.0 eq ha^{-1} of N from summer wet deposition over the same time period. On a watershed basis, throughfall caused only a 2% change in atmospheric deposition of N during the summer months. Assuming that throughfall changes were negligible during the winter months, throughfall changes in N-deposition were much less than 1% of annual wet and dry deposition.

Dry deposition estimates from the throughfall data provided additional confidence that our estimates of dry deposition were reasonable (Brown & Lund 1994). Dry deposition estimates were calculated using three years of throughfall data from western white pine, the assumption of a 120-day summer, and a leaf area index of 5.2. The dry deposition values calculated from the regression model were not significantly different from the leaf washing data of Bytnerowicz et al. (1991) at $p < 0.05$, using a standard t-test for the comparison of means.

Biomass and litter

Rundel et al. (1989) quantified standing biomass pools, nitrogen mineral capitals, and nitrogen fluxes for the nine major vegetation groups in the watershed, which we lumped to four for ease of display (Fig. 2). Tissue assays for nitrogen were conducted using wet digestion and colorimetric total-N determination with a Technicon autoanalyzer system. Methods used to measure the various pools and fluxes are illustrated for conifers and varied slightly by vegetation group. Diameter at breast height of every tree in the basin was measured. Rundel et al. (1989) estimated total above ground biomass of conifers from regressions on diameter at breast height developed for *Pinus lambertiana* (Gholz et al. 1979). They estimated fine root (<2 mm) and woody root (>2 mm) biomasses as 6% and 20% of the total biomass, using the rationale presented in Pearson et al. (1984). Litter decay rate was estimated from the function developed for *Pinus jeffreyi*:

$$Y_t = y_0^{-0.043t)} \tag{1}$$

solving for t (years) with Y_t set equal to zeroth-year litter ash weight (Stark 1972). Standing litter biomass was estimated by summing Y_t from year zero through the residence time of the litter.

Nitrogen contents of needles were means of *P. balfouriana, P. contorta,* and *P. monticola* needles produced between 1982 and 1986; N content of wood was the mean of *P. contorta* wood produced in 1982 and 1985; and N content of bark was the mean of *P. balfouriana, P. contorta,* and *P. monticola* bark produced between 1982 and 1986. Live branch N contents were estimated as simple means of wood and bark contents. Rundel et al. (1989) assumed N content of zeroth-year litter was equal to that of live needles; N content of standing litter was summed from zeroth-year litter over the residence time of litter. The assumption that zeroth-year N litter was equal to that of N in live needles does not account for translocation of N out of needles before senescence and may therefore overestimate N in litter (e.g. Chapin & Kedrowski 1983). Nitrogen concentrations of roots were averaged from samples of *P. monticola* roots collected in 1988, with woody root N contents being the sum from means of 2–5, 5–10, 10–20, and 20–50 mm size root classes.

Conifers are the dominant component of biomass and nutrient pools for vegetation in the ELW (Table 5), comprising 90% of the total above-ground biomass and 73% of the below ground biomass. Total above ground productivity was 808 kg ha^{-1} for biomass and 254 kg ha^{-1} for litter (Rundel et al. 1989).

Total N storage in vegetation is 10,093 eq ha^{-1} in standing biomass and another 1,053 eq ha^{-1} in litter (Table 5). Conifers account for most of the above-ground N storage, comprising 90% of the total above-ground storage of organic N. Plant communities other than conifers contribute a higher percentage of N storage in below-ground tissue and in litter. Conifers account for 54% of the below-ground storage of N while the plant communities of willow, wet meadow and dry meadow account for 40% of below-ground N storage. The largest amount of N storage in litter was by the willow community, 792 eq ha^{-1} or 75% of the total N stored in litter; conifers accounted for 115 eq ha^{-1} or 11%.

The net annual uptake of N in above-ground tissues and release of N from litter were both greater than atmospheric deposition of N. Rundel et al. (1989) estimated the net annual N uptake to above-ground tissues was 451 eq ha^{-1} yr^{-1} and release as litter was 336 eq ha^{-1} yr^{-1} (Table 5). Much of the

Table 5. Basin biomass, N-storage, and annual N uptake by vegetation.

		Basin biomass			Basin nitrogen storage			Net annual N uptake	
Community	Basin† area ha	Above ground kg ha^{-1}	Below ground kg ha^{-1}	Litter kg ha^{-1}	Above ground eq ha^{-1}	Below ground eq ha^{-1}	Litter eq ha^{-1}	Above ground eq ha^{-1}	Litter eq ha^{-1}
Willow	8.55	965	567	439	487	330.7	792	71.4	185
Mesic shrub	0.73	26.5	42.4	29.5	15.6	32.1	27.8	4.20	8.50
Mesic crevice	15.15	36.9	58.8	40.0	22.1	51.3	39.3	7.10	12.1
Wet meadow	4.14	130	999	47.3	157	624	51.3	133	51.4
Xeric crevice	13.4	6.0	33.0	48.7	2.12	25.0	26.9	3.50	15.0
Dry meadow	7.73	62.9	361	49.7	–	276	–	10.7	35.7
Fell field	0.84	0.4	2.1	0.3	–	1.42	–	–	–
Colluvium	3.44	1.5	8.5	1.2	–	6.42	–	1.42	0.70
Trees (1294)‡	–	16000	5630	37.7	6465	1598	115	219	27.8
TOTAL	24	17200	7710	694	7149	2944	1053	451	336

† Includes a mixture of vegetated and unvegetated groundcover.

Adapted from Rundel et al. (1989).

‡ Number of trees in basin.

biomass distribution of conifers is invested in non-productive woody tissues as contrasted with the meadow communities with very little above-ground tissues. The data on the below-ground productivity are less reliable and are not reported here. However the estimates of below-ground productivity by Rundel et al. (1989) indicate that the significance of the wet meadow, willow thicket and dry meadow communities are all disproportionately high when below-ground processes are factored in. Rundel et al. (1989) suggest that a reasonable estimate of total below-ground assimilation of N is about twice above-ground assimilation, or 900 eq ha^{-1} yr^{-1}.

Soil organic matter, mineralization and nitrification

Five soil map units within ELW were intensively sampled to determine the magnitude and spatial variability of soil physical-chemical parameters (Fig. 2 and Table 1); results are reported here for the first time. Soils were samples by total depth in 10-cm increments and air dried prior to analysis. Duplicate undisturbed cores were obtained for bulk density determinations. Soil temperature and soil moisture were monitored continuously at each of the five sites from the fall of 1986 to the spring of 1988 with thermocouple temperature probes and with resistivity moisture sensors (Williams et al. 1993a).

Total soil N was determined by micro-Kjeldahl digestion, distillation of NH_3 and titration (Lueking et al. 1986). Net N-mineralization rates and net nitrification rates in the field were obtained using the buried bag method (Eno 1960). Soil pits were excavated at four sites: the ridge, bench, meadow and pine stand. Installation dates at each of the four sites were August 5, 1986, September 3, 1986, October 28, 1986, and June 8, 1987. During excavation, soil samples were collected to measure soil moisture content, NH_4^+, and NO_3^-; soils were sampled by horizon. Part of the sample was incubated *in situ* by placing into triplicate polyethylene bags, sealing and returning the sample to the soil pit. After incubation the contents of the bags were removed and the same analyses conducted. Nitrification was calculated as the percentage of mineralization nitrogen existing as NO_3^-. The integrated temperature for the incubation period was calculated using tubes in the bags containing a buffered sucrose solution (Lee 1969). Brown et al. (1990) conducted laboratory incubations to determine optimal moisture and temperature conditions for mineralization.

Soil depth averaged 0.35 m. Storage of N in soil organic matter was almost ten times that of organic N in standing vegetation and litter and is the largest reservoir of N in the basin at 81,600 eq ha^{-1} (Table 6). The highest concentrations of total N were 5,438 mg kg^{-1} for the Lithic Histic Cryaquept at the inlet wet meadow and 2,327 mg kg^{-1} for the Entic Cryumbrept at the dry meadow (bench) site. However a large part of the N storage in soil was

Table 6. Soil organic nitrogen pool and inorganic N release in annual net mineralization, WY 1987.

Soil type	Soil mass	Organic N		Inorganic N				
		Kjeldahl pool[a]	Total organic	Mineralized N	Nitrification	Total mineralization		Total N
	10^6kg	mg kg^{-1}	10^6eq	mg kg^{-1}	%	(eq) NH_4	(eq) NO_3^-	eq
Entic Cryumbrept	5.71	2,327	0.94	8.01	5	3,104	163	3,267
Lithic Cryumbrept	79.8	310	1.76	14.15	51	39,494	41,106	80,601
Lithic Histic Cryaquept	14.9	5,438	5.80	20.80	15	18,863	3,328	22,192
Lithic Cryorthent	9.11	1,504	0.98	20.27	16	11,078	2,110	13,188
Typic Cryorthent	13.6	310	0.30	14.15	51	6,738	7,013	13,752
TOTAL BASIN	123.16	NA	9.80	NA	NA	79,279	53,723	133,000
TOTAL (eq ha^{-1})			81,600			660	447	1,108

[a] $n = 114$.

Table 7. Seasonal mineralization rates and comparison of mineralization rates for different soils, from *in situ* buried bag experiments ($n = 3$), 1987.

Site	Installation date d	Elapsed time d	Net N mineralization mg N kg^{-1} d^{-1}	Net nitrification %	Soil temp °C	Soil moisture %
Ridge	860805	29	0.626	46.4	15.3	9.2
Ridge	860903	55	0.215	46.5	5.6	4.0
Ridge	861028	224	0.014	48.2	0.2	18.1
Ridge	870608	85	0.020	100	15.0	25.0
Bench	870608	85	−0.267	2.1	13.0	105
Inlet	870608	85	−0.173	9.2	11.9	94
Cirque	870608	85	−0.044	38.1	11.1	19

in the Lithic Cryumbrept soils due to their relatively large mass compared to other soil types.

Both laboratory and *in situ* field experiments indicate that temperature and not moisture was the most critical factor in nitrogen mineralization at the ELW. In laboratory studies, the quantity of nitrogen mineralized and the estimated potentially mineralizable nitrogen increased with increasing temperature in all soils; the percent moisture (range 20–80%) had no significant effect (Brown et al. 1990). Higher soil temperatures also resulted in greater amounts of *in situ* mineralization (Table 7). The lowest daily rate of *in situ* nitrogen mineralization in all four soils occurred over the winter months, when the lowest mean soil temperatures (0.2 °C) occurred. For example, net N mineralization at the ridge site (Lithic Cryumbrept) from October 28 to June 8 was 0.014 mg kg^{-1} d^{-1} with a mean temperature of 0.2 °C, compared to net N mineralization for August 5 to September 3 of 0.626 mg kg^{-1} d^{-1} and a mean temperature of 15.3 °C. However, net N mineralized was generally negative during apparently optimum growing conditions in June, July and early August (Table 7). Soil temperatures and moisture were generally highest during this time period, yet nitrogen was consumed rather than released, resulting in a net negative mineralization rate (Table 7). The consumption of nitrogen is most likely due to the incorporation of nitrogen into microbial biomass in the short term. Not all NH_4^+ produced by mineralization was converted to NO_3^-. Nitrification rates were generally lowest during the period of winter incubation (Table 7). About 50% of the NH_4^+ mineralized in the Entisol was converted to NO_3^- while less than 10% of the NH_4^+ in the Inceptisols was converted to NO_3^-.

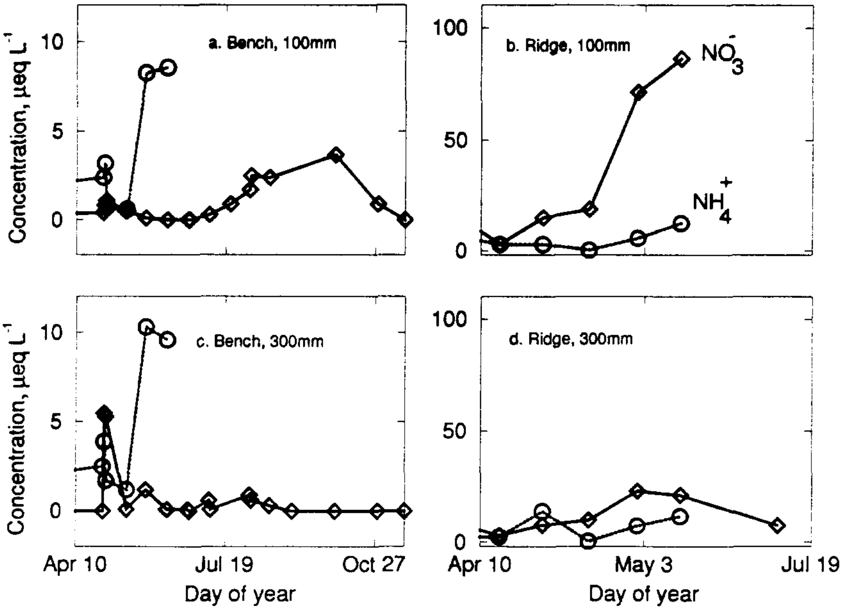

Fig. 4. Time series of NO_3^- and NH_4^+ concentrations in the soil solution at the bench and ridge sites, water year 1987.

Annual N mineralization for each soil type was estimated in water year 1987 by *in situ* bag experiments, from September 3, 1986 to August 27, 1987 (360 days) (Table 6). The amount of net N mineralized per soil unit was multiplied by the mass of each soil unit. Soil mass for each soil unit was calculated as mean density times mean soil depth times area of each soil unit. Mineralization in 1987 resulted in a net production of 660 eq ha^{-1} of NH_4^+ and 447 eq ha^{-1} of NO_3^-. The net N mineralized of 1,108 eq ha^{-1} in 1987 was almost four times the wet and dry deposition inputs of 290 eq ha^{-1} in 1987.

Soil solution

Williams et al. (1993a) reported results for soil solution, collected using tension lysimeters (membrane-covered porous polyethylene plates) which were installed in 1985 and 1986 at the five soil sites in the ELW (Fig. 2). Duplicate samples of soil solution were collected at depths of about 100 mm and 300 mm, at weekly to biweekly intervals from April to November 1987. Sample storage, analytical techniques, precision and detection limits are reported in Williams et al. (1993a).

Williams et al. (1993a) report that NO_3^- concentrations at the bench site were generally near or below detection limits for most of the year (Fig. 4).

There were small increases in NO_3^- concentration to about 5 ± eq L^{-1} at the initiation of snowmelt runoff at depths of 100 and 300 mm; and again in the autumn months at a depth of 100 mm. Ammonium concentrations also increased during the initiation of snowmelt runoff, from below detection limits to about 10 ±eq L−1. Analysis for NH_4^+ at the bench site was suspended in July. Nitrate concentrations in the soil solution at the bench site were always below NO_3^- concentrations in precipitation and snowmelt. In contrast to the bench site, NO_3^- and NH_4^+ concentrations in the soil solution at the ridge varied with the season (Fig. 4). Concentrations of NO_3^- were near detection limits at the initiation of snowmelt runoff and then increased with time. Ammonium concentrations followed a similar pattern but concentrations were much lower than NO_3^- concentrations. At a depth of 100 mm, NO_3^- concentrations increased to a maximum of 87 μeq L^{-1} compared to an NH_4^+ maximum of 12.5 μeq L−1. A similar but attenuated pattern of higher concentrations of NO_3^- relative to NH_4^+ was observed at a depth of 300 mm.

Groundwater

Groundwater was sampled for chemical analysis using two methods and reported in Melack et al. (1989) and Williams et al. (1990). First, minipiezometers and seepage meters based on the design of Lee & Cherry (1978) were installed at several locations within Emerald Lake, both in fine-textured sediments of shallow water and also in deep sediments and sampled in July of 1987 (Melack et al. 1989). A groundwater seep located on a 30° slope about 1–5 m above the lake was sampled 11 times between July 9 and October 25, 1987. Direct seepage of groundwater into or out of the lake does not appear to be an important loss of water or N from the catchment. Piezometers, seepage meters, and temperature measurements showed no discernible seepage into lake sediments (Melack et al. 1989; Williams et al. 1990). Furthermore, during August 1985 and September 1987, periods of minimum streamflow, the volume of water entering the lake could be accounted for by the lake outflow and estimated evaporation from the lake surface (Kattelmann 1989).

Subsurface release of solutes into inflowing streams does control the content of NO_3^- and NH_4^+ in stream and lake waters during the period of low-flow from about July to the following March (Williams et al. 1990). Groundwater collected at the shoreline seeps from July to October had a mean NO_3^- concentration of 6.5 μeq L^{-1} ($n = 11$), intermediate in concentration between that of the two inflowing streams and similar to lake concentrations of NO_3^- for this period. Ammonium concentrations in the groundwater seep and in inflowing streams was always at or below detection limits. Analyses of hydrologic pathways using natural tracers shows that groundwater discharge was the primary source of streamflow during the low-flow period (Williams et al. 1993a).

Denitrification

Brown et al. (1990) estimated denitrification in the field using an *in situ* technique based on acetylene blockage (Ryden et al. 1978; 1979). Denitrification products effluxing from the soil were trapped in metal enclosures (0.5 × 0.1 m) inserted in soil to a depth of 100 mm. Rates of N loss measured in two Entisols were on the order of 0.071 to 0.19 meq N_2O m^{-2} d^{-1}, during May and June of 1987. Maximum denitrification rates occurred immediately after rain events; rates were near zero in July when soils became dry and also at one site in May because of frozen soils. Even if we assume N_2 emissions were slightly greater than the measured N_2O emissions, denitrification losses were only about 10 eq ha^{-1} in 1987, about 5% of deposition inputs. This estimate of N_2 flux provides a lower boundary of potential N_2 emissions. Recent research shows that N_2O emissions under the seasonal snowpack in alpine (Brooks & Williams 1995, in press) and subalpine (Sommerfeld et al. 1993) environments can be equal to or greater than N_2O emissions during the snow-free season.

Stream waters

Stream discharge was reported in Kattelmann & Elder (1991) and inorganic chemical composition was reported in Williams & Melack (1991b) for two complete water years, October 1985 to September 1987. Grab samples of surface waters were collected from all inflows and the outflow in acid-washed polyethylene bottles for chemical analyses approximately weekly at the start of snowmelt runoff and through the summer months, and monthly during the winter period. Sample storage, analytical techniques, precision and detection limits for inorganic solutes were reported in Williams & Melack (1991b).

Nitrate concentrations in stream waters showed seasonal trends. An annual maximum occurred during the first part of snowmelt runoff (Fig. 5), with maximum concentrations in inflow 2 near 20 μeq L^{-1}, four times the mean precipitation value of 5.0 μeq L^{-1} for the period of 1985–1987. During the summer months concentrations of NO_3^- decreased to near or below detection limits as discharge also decreased. Concentrations of NO_3^- slowly increased during the fall and winter months to about 6 μeq L^{-1}, reflecting the contribution of groundwater to streamflow. Ammonium concentrations were always near or below detection limits and showed no seasonal or interannual trends (Fig. 5). The low concentrations of NH_4^+ in stream waters is consistent with the low concentrations of NH_4^+ in the soil solution and strongly indicates that

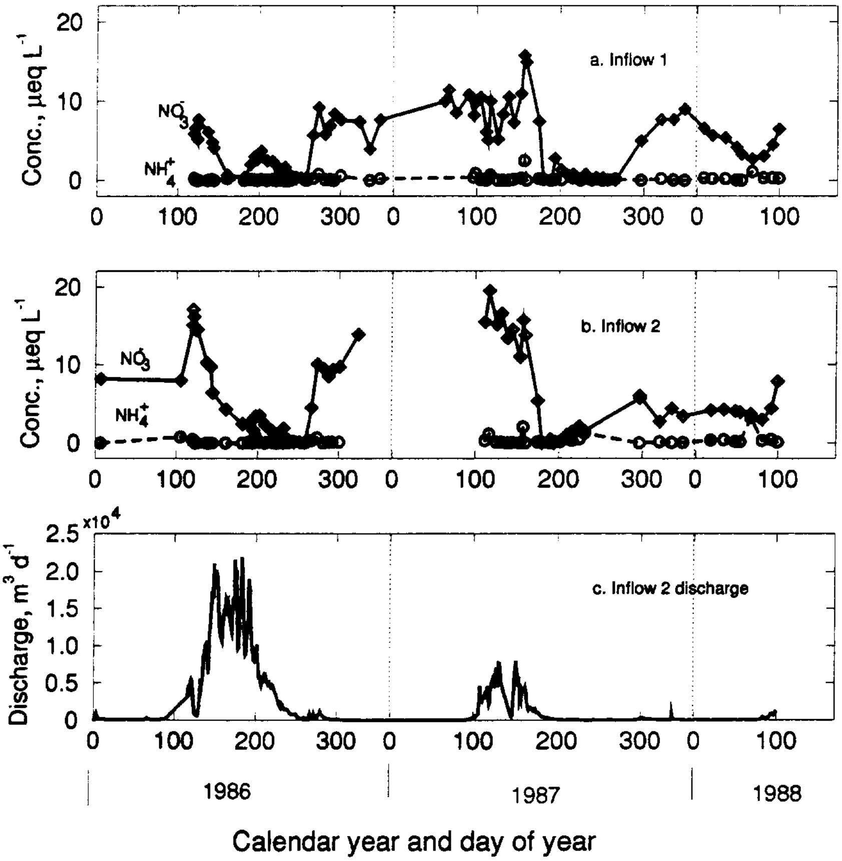

Fig. 5. Concentrations of NH_4^+ and NO_3^- from inflow 1 (panel a), inflow 2 (panel b) and discharge from inflow 2 (panel c), 1986–1988.

snowmelt runoff and rainfall interact with the basin in some manner and that NH_4^+ in precipitation is removed during this interaction.

Total N measurements ($n = 28$) were collected from inflowing streams during the summer and autumn from 1983 through 1986; these results have not been previously published. Average concentrations of TN for the four years were 2.5 times the sum of NO_3^- and NH_4^+. Export of organic N (dissolved plus particulate) in stream waters was thus 1.5 times greater than inorganic N.

Discussion

We used a conceptual mass-balance model to organize and integrate data on N pools and fluxes for the 1987 water year (Fig. 6). Inputs of total inorganic

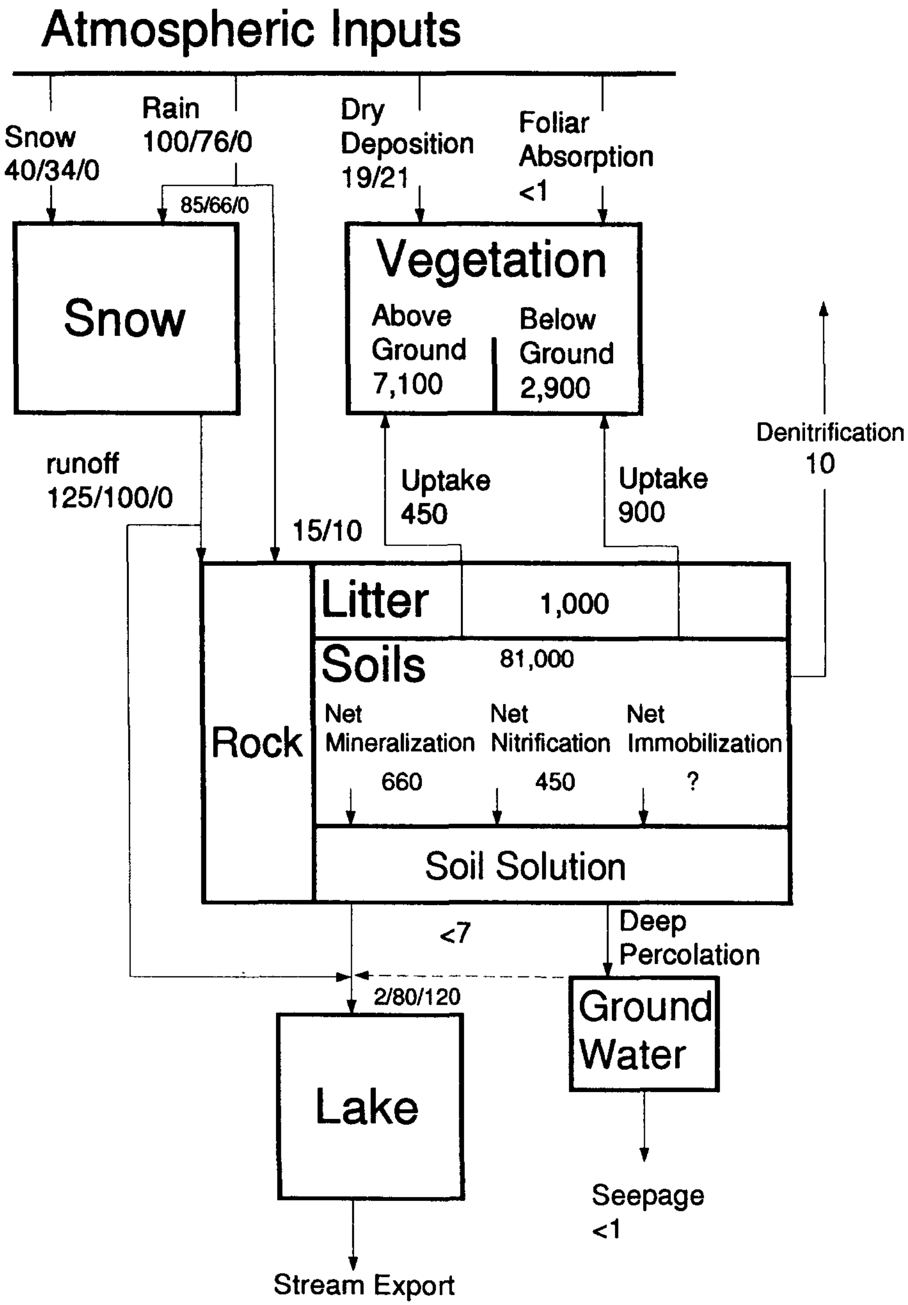

Fig. 6. Conceptual mass balance of nitrogen pools and fluxes, water year 1987. Pools are eq ha^{-1} and fluxes are eq ha^{-1} yr^{-1}. Single values are total N; where possible N values are separated into NH_4^+/NO_3^-/TN minus inorganic N.

N (TIN) to the basin were dominated by wet deposition, which accounted for 250 eq ha^{-1}. About 225 eq ha^{-1} of wet deposition of N were stored in the seasonal snowpack in 1987; most of the wet deposition as rain occurred as rain-on-snow events (Fig. 6). Dry deposition of TIN at 40 eq ha^{-1} was about 15% of wet deposition, for a TIN content in wet and dry deposition of 290 eq ha^{-1} in 1987. Throughfall changes in deposition of −0.27 eq ha^{-1} were insignificant when compared to TIN in deposition. Nitrogen fixation was not measured and was assumed to be zero. This assumption is supported by the research of Wojciechowski & Heimbrook (1984) at Niwot Ridge in the Colorado Front Range, who report typical values for biological fixation of N of 2 μeq N ha^{-1} d^{-1} during the growing season, or about 1% of the annual wet deposition flux to the ELW. Furthermore, there are few leguminous plants at the ELW that are known to have symbiotic N_2 fixers. However, the importance of free-living N-fixers is unknown (e.g. Bormann et al. 1993) and the role of N-fixation in high-elevation catchments is deserving of more research.

Basin storage of N was dominated by soils, about 81,000 eq ha^{-1}. The next largest reservoir of N was vegetation and litter, about 13% that of soils. Storage of N in the soil solution, groundwater and seasonal snowpack was less than 1% of N storage in soils. Fluxes to and from the soil solution were dominated by net mineralization of soil organic matter and biological uptake (Fig. 6). Net immobilization was unknown but may be an important sink for gross mineralization. The release of 1,450 eq ha^{-1} yr^{-1} of N from mineralization and litter decay was slightly greater than N assimilation by vegetation of 1,350 eq ha^{-1} yr^{-1}. Given the high amount of uncertainty associated with these measurements, it appears that internal sources and transformations of N within the basin about balance that N requirements of vegetation.

The export of N from the basin was 210 eq ha^{-1}, primarily as NO_3^- and organic N in streamflow. Export of N as NH_4^+ in stream waters and as N_2 and N_2O through denitrification was less than 2% of NO_3^- and organic N export in stream waters. Organic N in streamwaters was the single largest source of N export from the basin, accounting for about 60% of all N loss. Nitrate does become a mobile ion in the ELW; about 60% of NO_3^- in wet and dry deposition in 1987 was exported form the basin as NO_3^- in stream waters. Ammonium was not exported from the basin as NH_4^+; less than 1% of the NH_4^+ in deposition was exported from the basin as NH_4^+.

The ELW appears to be accumulating N. Atmospheric inputs (290 eq ha^{-1}) exceeded basin export (210 eq ha^{-1}) by 80 eq ha^{-1}, a basin accumulation of 27% of atmospheric input.

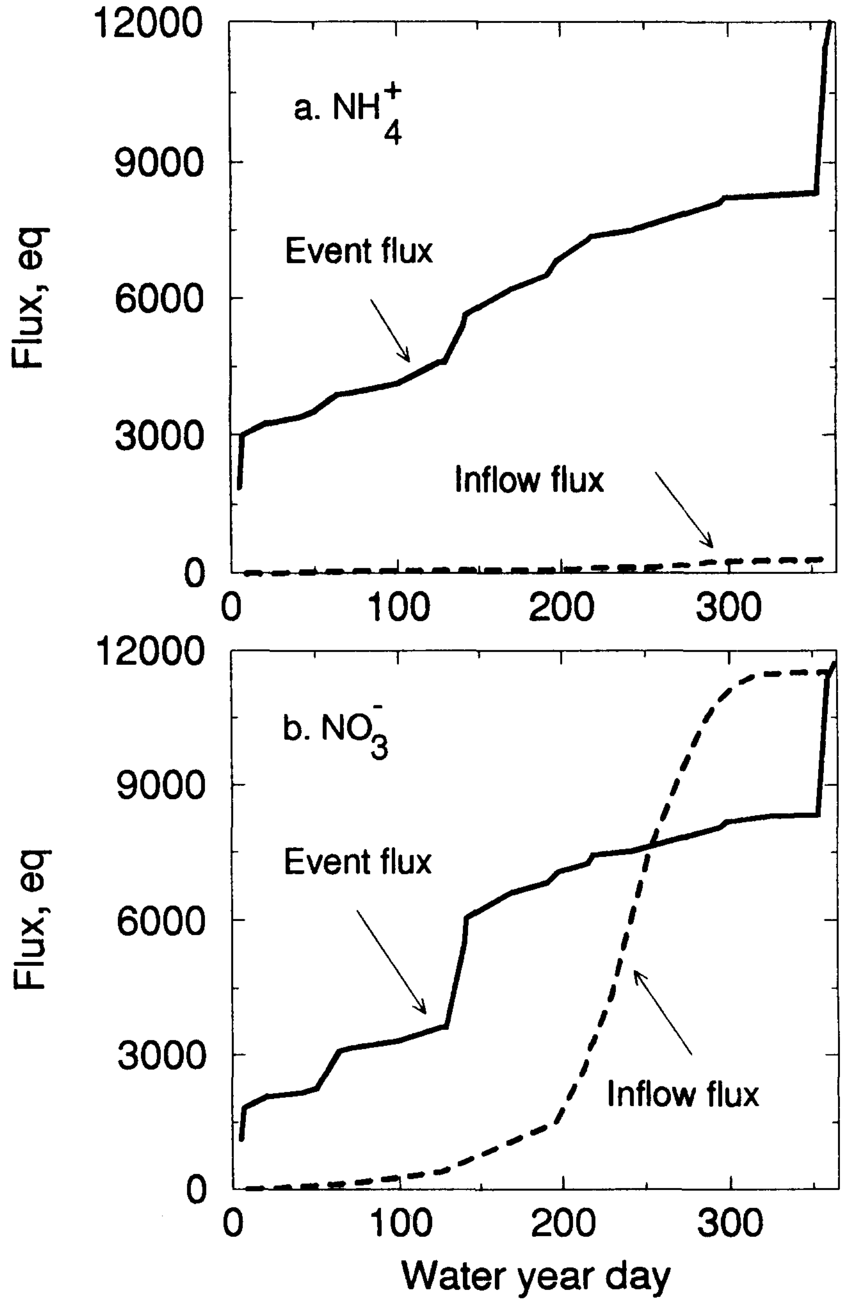

Fig. 7. Cumulative NO_3^- and NH_4^+ loading of inflowing streams compared to cumulative loading in precipitation, 1986.

Snowmelt runoff

Snowmelt runoff controls NO_3^- export in surface waters from alpine basins. To illustrate, cumulative input of NO_3^- and NH_4^+ in wet deposition for water year 1986 is compared to cumulative export in stream waters (Fig. 7). Cumulative export of NO_3^- and NH_4^+ in stream waters was calculated as the running sum of concentration times daily discharge, and plotted on a daily time step. The majority of NO_3^- and NH_4^+ loading in wet deposition occurred during the winter months, where it was held in storage in the seasonal snowpack. However, about 90% of annual NO_3^- export in stream waters occurred during the approximately 100 days of snowmelt runoff. As discharge decreased through the summer months, export of NO_3^- in surface waters also decreased.

The source of NO_3^- in surface waters during snowmelt runoff is unknown. However, release of inorganic N from the snowpack can explain both the amount and concentrations of NO_3^- in surface waters. For example, from May 5 to June 27, 1986, the sum of NO_3^- and NH_4^+ released from the seasonal snowpack was estimated at 4,800 eq and the yield of NO_3^- in all inflowing streams was estimated at 4,600 eq (Williams et al. 1991). This mass balance congruency between snowpack release of inorganic N and the export of NO_3^- in stream waters is consistent with the hypothesis that snowmelt was the source of NO_3^- in stream waters. These results also raise the possibility that the NH_4^+ stored in the snowpack may be oxidized or otherwise changed to NO_3^-.

Nitrate concentrations in stream waters were consistent with the release of inorganic N from the snowpack in the form of an ionic pulse. Maximum concentrations of NO_3^- measured in surface waters during snowmelt runoff (18 μeq L^{-1}) where similar to maximum NO_3^- concentrations in meltwater before contact with the ground (28 μeq L^{-1}). Furthermore, all inflows contributed a large fraction of their annual mass of NO_3^- with the first fractions of seasonal discharge in 1986 (Fig. 8), again consistent with the release of N from the snowpack in the form of an ionic pulse. Figure 8 shows the running sum of discharge divided by annual discharge on a daily time step and the running sum of NO_3^- loading (concentration times discharge) divided by annual loading on a daily time step. The 1:1 line represents uniform concentrations throughout the year, e.g. the mass flux of NO_3^- in stream flows occurs at the same rate as mass flux of water. In water year 1986, from 40 to 60% of the NO_3^- mass was carried by the first 20% of the annual discharge of inflowing steams and 65 to 85% of the annual NO_3^- mass was transported by the first 40% of discharge of inflowing streams. The large proportion of annual NO_3^- export in the first export in the first fractions of annual discharge is consistent with the ionic pulse in snowpack meltwater supplying the majority of NO_3^- in stream waters.

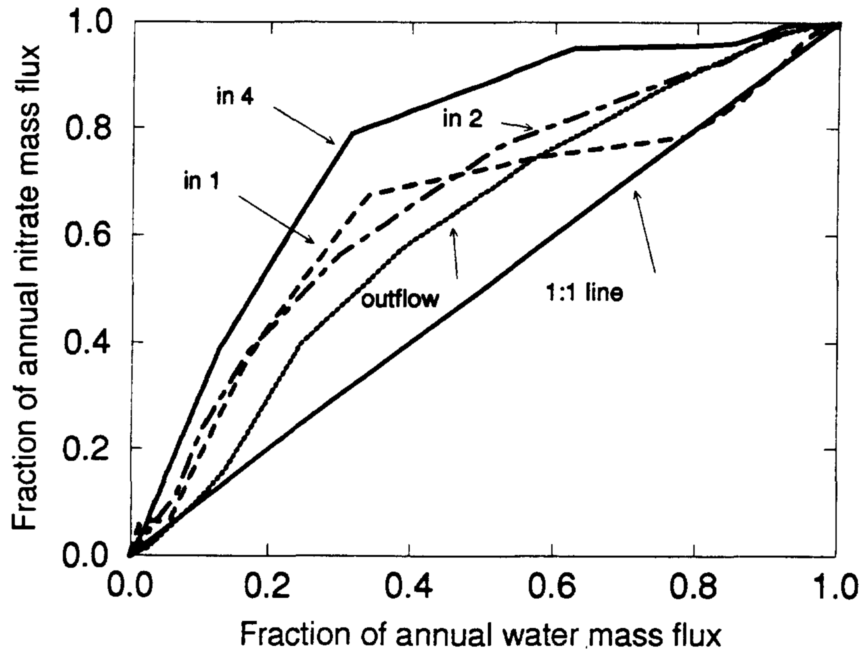

Fig. 8. Fraction of NO_3^- flux vs fraction of discharge in all streams, water year 1986.

The snowpack is thus an important component of N-cycling in the ELW and serves to illustrate the strong seasonality of N-processes in high-elevation granitic basins of the Sierra Nevada. Up to 90% of annual wet deposition was stored in the seasonal snowpack. As a result of the ionic pulse, about 90% of the annual wet deposition of N was delivered to terrestrial and aquatic ecosystems in a time span of days to weeks and concentrations of N in meltwater were magnified several fold relative to bulk concentrations in the snowpack. More research is needed to understand what processes determine the magnitude of the ionic pulse in snowpack meltwater (e.g. Bales et al. 1993) and how spatial variations in snowmelt (Williams & Melack 1989) affects the release of N from the snowpack to the basin.

Alternatively, microbial activity in soils may be a source of some of the NO_3^- in surface waters during snowmelt runoff. To illustrate, Rascher et al. (1987) report that NO_3^- pulses in stream waters during snowmelt runoff in the Adirondack were from snowmelt infiltrating soils and transporting NO_3^- produced by mineralization and nitrification processes under the winter snowpack from these soils to streams. At the ELW, net nitrification processes under the winter snowpack in 1987 produced about 100 eq ha^{-1}, sufficient NO_3^- to explain the annual export in 1987 of 80 eq ha^{-1} in stream waters.

However, concentrations of NO_3^- in the soil solution at the initiation of snowmelt were too low to be consistent with the hypothesis that nitrification processes under the seasonal snowpack supplied the NO_3^- in surface waters.

A better understanding of snowpack-soil interactions is needed. The largest gap in our understanding of N-cycling in this high-elevation catchment is the process or combination of processes that sequester NH_4^+ in the basin during snowpack runoff. It is possible that NH_4^+ contained in infiltrating precipitation is retained by ion exchangers for subsequent use by biota when physical conditions are no longer limiting to the biota. The role of talus and rock fractures is also unknown but may be important to N-cycling in high-elevation basins. The lack of NH_4^+ in stream water, even during periods when soils are saturated and infiltration capacity is exceeded (Wolford 1992) and overland flow occurs (Williams et al. 1993a) suggests that microbial assimilation and/or ion exchange in talus and rock fractures may be occurring and should be investigated.

The importance of soils to N-cycling is surprising given that soils cover only 22% of the basin and that soils are thin and slightly acidic. Soils are the largest reservoir of N in the basin by an order of magnitude and also cycle the most N through mineralization and nitrification processes. Where snowmelt runoff goes after release from the snowpack is poorly understood and yet integral to our understanding of N-cycling in high-elevation catchment. Recent research by Williams et al. (1993a) suggests that more than 50% of snowmelt runoff in the ELW infiltrates soils, interacts with soil processes, and then is released to streamflow as saturated return flow. Caine (1989) suggests similar rates of snowmelt infiltration and return flow for the Green Lake Valley in Colorado. Hydrologic flowpaths during the period of snowpack runoff merit continued attention.

Episodic acidification

Basin loss of nitrogen has resulted in episodic acidification of surface waters during snowmelt, where acidification is defined as a decrease in acid neutralizing capacity (ANC) greater than that caused by dilution. Williams & Melack (1991b) have shown that minimum concentrations of ANC are temporally coincident with both the maximum concentrations of NO_3^- and dilution of base cations. Annual minimum concentrations of ANC at the ELW occur during snowmelt runoff and are generally near 10 μeq L^{-1}. Twice in the last ten years, episodic increases in NO_3^- concentrations of surface waters from deposition events have been sufficient to drive ANC to zero at the ELW (Stoddard 1994).

The release of H^+ during biological assimilation of NH_4^+ appears to consume about 25% of the alkalinity produced by geochemical weathering. Using a variation of the steady-state geochemical weathering model developed by Garrels & Mackenzie (1967), Williams et al. (1993a) report that all of the base cations in stream waters could be accounted for by back-reacting these solutes with secondary minerals to produce the bedrock minerals found in the basin, for annual basin yields of these solutes. However, the weathering model generated a 25% excess of the measured alkalinity (50,800 mol yr^{-1}) compared to modeled alkalinity 65,200 mol yr^{-1}), with the largest discrepancy occurring during the period of spring runoff.

Wet deposition to the ELW is not acidic, in part because NO_3^- and SO_4^{2-} in rain and snow are balanced by NH_4^+ (Williams & Melack 1991a). However, transformations of NH_4^+ within the basin appear to be a cause of episodic acidification of surface waters. We have modified the geochemical modeling results by adding a nitrogen module. We make the assumption that all NH_4^+ retained in the basin was due to biological assimilation and that one mole of H^+ was produced for every mole of NH_4^+ assimilated. The model also assumes that each mole of NO_3^- retained in the basin produced one mole of OH^-. About 10,900 mol of ANC were neutralized by the net production of H^+ from assimilation of N in 1986. Subtracting this amount from the ANC generated by the weathering model leaves a residual ANC of only 3,540 mol, or within 7% of the measured ANC. Combining the weathering and N stoichiometry models for 1987 with 1986 results in an ANC residual that is within 2% of the measured ANC for this 2-year period. The 25% excess alkalinity produced by the geochemical model is balanced by production of H^+ from N assimilation. Episodic acidification driven by N dynamics has apparently resulted in increased leaching of base cations from the basin in excess of cation production from geochemical weathering.

Nitrogen saturation

Williams et al. (1993b) have recently suggested that alpine basins may act as early warning indicators of N saturation for downstream forested basins. Nitrogen saturation is defined by Stoddard (1994) as 'a situation where the supply of nitrogeneous compounds from the atmosphere exceeds the demand for these compounds on the part of the watershed plants and soil microbial communities ... and there is export of N during the growing season.' The concept was developed for forested and agricultural catchments (e.g. Aber et al. 1989; Aber 1992); its application to alpine basins has not been evaluated. In alpine systems, it is possible that the combination of a snowmelt pulse, short growing season, and limited soils and vegetation may never result in sufficient N-consumption ability to keep N from appearing in aquatic systems.

The importance of soils and the patterns of NO_3^- concentrations in surface waters at the ELW suggest that biota in the ELW currently have the capacity to use all available N during the growing season. Net mineralization rates under apparently optimal conditions during the growing season were often low or negative, suggesting that available N was utilized by vegetation or immobilized in microbial biomass. Similarly, nitrification rates were also low at this time, perhaps because there was little available NH_4^+ for nitrification. The pattern of NO_3^- concentrations in surface waters provides additional evidence that N was in demand by vegetation during the growing season. Nitrate concentrations reached a seasonal maximum during snowpack runoff when vegetation was not active and then declined to detection limits during the growing season. There was no leakage of N from the terrestrial ecosystem to surface waters during the growing season when vegetation was active. When vegetation activity was reduced in the fall and winter months, NO_3^- concentrations in surface waters increased to the mean annual concentrations in wet deposition of about 5 μeq L^{-1}. Furthermore in 1987, mass balance calculations shows that the ELW basin retained 27% of N in atmospheric deposition with most of the loss occurring during the non-growing season.

Our results suggest that alpine basins in the Sierra Nevada currently assimilate all atmospheric sources of N during the growing season and are not N-saturated at this time. However, given the multiple stresses typical of alpine ecosystems, these basins may have less capacity for N retention than downstream ecosystems. Modeling work on N dynamics conducted by Baron et al. (1994, in press) for the high-elevation Loch Vale catchment in Rocky Mountain National Park of the Colorado Front Range suggests that alpine tundra there has become N-saturated and that forested sections of the Loch Vale catchment are still N-limited. Alpine basins may thus provide an early-warning system for N saturation in downstream forested catchments of western North America.

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