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Patterns of nitrogen transport in streams of the Lake Tahoe basin, California-Nevada

Robert N. Coats
Hydroikos Associates, San Rafael, California

Charles R. Goldman
Department of Environmental Science and Policy, University of California, Davis

Abstract. In an effort to characterize the spatial and temporal patterns of nitrogen concentration and load in streams of the Lake Tahoe basin, we analyzed 10 years of data from 10 streams, developing discharge-concentration relationships and total load estimates for nitrate-N, ammonium-N, and organic N. The results indicate that (1) most of the nitrate transport occurs early in the snowmelt season or during large winter rainstorms; (2) dissolved organic nitrogen concentrations peak early in the runoff season, decline during snowmelt, and in some streams peak again during the summer low-flow period; (3) organic nitrogen accounts for over 90% of the total nitrogen load in basin streams; (4) averaged over 10 years and the area of 10 watersheds, the nitrogen flux rates in kg ha^{-1} yr^{-1} are 0.081 for nitrate-N, 0.017 for ammonium-N, 0.58 for dissolved organic N, and 0.47 for particulate organic N; (5) the variation in annual runoff explains most of the interannual and interwatershed variability in total nitrogen load; and (6) the dominance of organic nitrogen relative to nitrate-nitrogen in Tahoe basin streams contrasts with sites in eastern North America.

1. Introduction

Human intervention in the global nitrogen cycle has increased dramatically in the last half century. The effects of excess nitrogen from fertilizer and sewage on aquatic ecosystems and groundwater supplies have long been recognized [*Vitousek et al*., 1997]. More recently, nitrogen saturation, an excess of available nitrogen over the biotic and abiotic retention capacity of terrestrial ecosystems, has led to increased attention to nitrogen cycling and to the linkages between terrestrial and aquatic ecosystems [*Aber et al*., 1989; *Fenn et al*., 1998; *Vitousek et al*., 1997; *Williams et al*., 1996]. At Lake Tahoe, the accumulation of nitrogen, over half of it originating in direct atmospheric deposition to the lake, has been sufficient to shift the primary limiting nutrient in the lake from nitrogen to phosphorus [*Chang et al*., 1992; *Goldman et al*., 1993; *Jassby et al*., 1994, 1995].

Elsewhere in the Sierra Nevada, research focused on acid deposition, and lake acidification has greatly increased our understanding of nitrogen cycling in alpine and subalpine catchments. *Sickman and Melack* [1998] found a pronounced ionic pulse of nitrate during early snowmelt in some catchments and documented a downward trend in outflow nitrate concentration at Emerald Lake. *Williams et al*. [1995] also noted an early snowmelt ionic pulse but noted that the soil beneath the snowpack is a possible source of nitrate-N during snowmelt. They found that mineralization and nitrification produced an inorganic N export of 3.5 times the atmospheric N loading. *Johnson et al*. [1997], in a study in the eastern Sierra Nevada, calculated that the N loss in wildfire and the input by symbiotic fixation far exceeded the solution losses and input from atmospheric deposition. The application of the Alpine Hydrochemical Model in the Emerald Lake basin has produced some important insights into the processes of nitrogen uptake and release in alpine catchments [*Wolford et al*., 1996; *Meixner et al*., 1998].

The database of the Lake Tahoe Interagency Monitoring Program (LTIMP) provides a unique opportunity to characterize the spatial and temporal patterns of nitrogen transport in subalpine streams. We hope to answer the following questions: (1) What is the relative importance of nitrate-N, ammonium-N, and organic N in stream loads, and how do the concentrations of different forms vary with season and discharge? (2) What are the major sources of the different forms of nitrogen in basin streams? (3) What are the major hydrological and biogeochemical controls on the flux the different forms of nitrogen to the lake? (4) How does the biological availability of particulate and dissolved organic nitrogen relate to its origin? Although the LTIMP data may not provide definitive answers to all of these questions, they do allow us to frame the questions heuristically.

2. Methods

2.1. Study Area

Lake Tahoe lies at an elevation of 1898 m in the central Sierra Nevada, astride the California-Nevada border (Figure 1). Volume of the lake is 156 km^3, and its surface area is 501 km^2, 38% of the total basin area of 1313 km^2. The eutrophication of the lake has been studied intensively since the early 1960s [*Goldman*, 1981] and has attracted considerable political attention. In spite of increased land-use controls and export of treated sewage effluent from the basin, primary productivity of the lake is increasing by more than 5% annually, and its clarity is decreasing at an average rate of 0.25 m yr^{-1} [*Reuter et al*., 2000].

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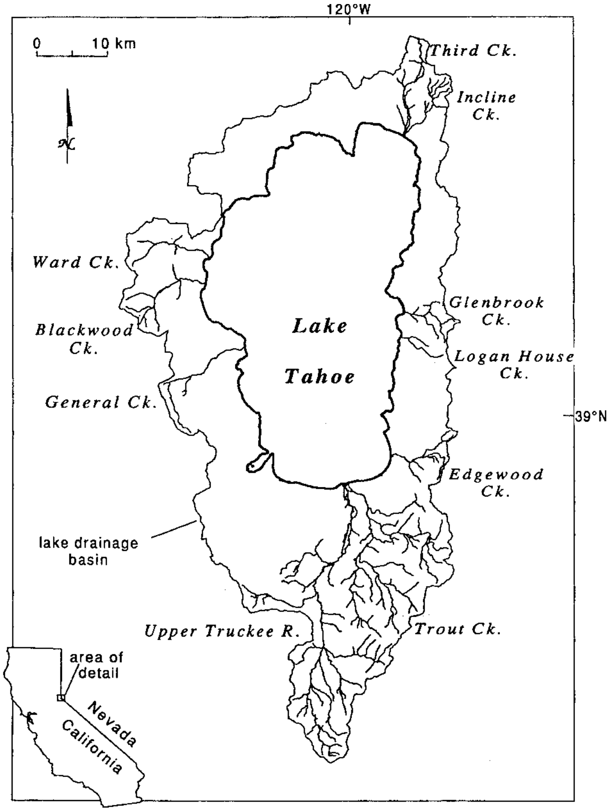

Figure 1. The Tahoe Basin. Named tributaries have been sampled by the Lake Tahoe Interagency Monitoring Program (LTIMP).

Vegetation in the basin is dominated by a mixed conifer forest of Jeffrey pine (*P. Jeffreyi* Grev. and Balf.), lodgepole pine (*P. murrayana* Grev. and Balf.), white fir (*Abies concolor* Lindl.), and red fir (*A. magnifica* A. Murr.). The basin also contains significant areas of wet meadows and riparian areas, dry meadows, brush fields (with *Arctostaphylos* and *Ceanothus*), and rock outcrop areas, especially at higher elevations. *Ceanothus* is capable of fixing nitrogen, but mountain alder (*Alnus tenuifolia* Nutt.), which grows along many of the basin's streams, springs, and seeps, fixes far greater quantities, and contributes measurably to nitrate-N concentrations in some small streams [*Fleschner*, 1975; *Leonard et al.*, 1979].

Soils of the basin are derived primarily from andesitic volcanic rocks and granodiorite, with minor areas of metamorphic rock. Some of the valley bottoms and lower hillslopes are mantled with glacial moraines or glacial outwash material derived from the parent rock. Cryopsamments, Cryumbrepts, rockland, rock outcrops, and rubble and stoney colluvium account for over 70% of the land area in the basin [*Cartier et al.*, 1994]. The basin soils (in the <2 mm fraction) are generally 65–85% sand (0.05–2.0 mm) [*Rogers*, 1974].

Substantial areas of the basin have been developed for residential and commercial uses, especially along the south shore. Development of "high hazard" lands has been linked to increased concentrations of nitrate-nitrogen, phosphorus, and suspended sediment in tributary streams [*Byron and Goldman*, 1989].

Mean annual precipitation ranges from over 140 cm yr^{-1} in watersheds on the west side of the basin to ~67 cm yr^{-1} near the lake on the east side of the basin [*Marjanovic*, 1989]. Most of the precipitation falls as snow between November and April, although rainstorms combined with rapid snowmelt account for the largest floods. There is a pronounced annual runoff of snowmelt in late spring and early summer, the timing of which varies from year to year. In some years, summertime monsoonal storms from the Great Basin bring intense rainfall, especially to high elevations on the east side of the basin.

An atmospheric sampling station at lake level recorded 1.16 kg $\mathrm{ha}^{-1}\,\mathrm{yr}^{-1}$ nitrate-N and 1.08 kg $\mathrm{ha}^{-1}\,\mathrm{yr}^{-1}$ ammonium-N, in wet + dry deposition, for the period 1989–1992. Total nitrogen deposition in this period, on the basis of a ratio of dissolved inorganic nitrogen (DIN) to total nitrogen (TN) in a subsample, was ~5 kg $\mathrm{ha}^{-1}\,\mathrm{yr}^{-1}$ [*Jassby et al.*, 1994]; DIN predominated in wet deposition, and organic-N predominated in dry deposition. Although these inputs are significant, they are considerably lower than input rates reported from the eastern United States but comparable to those for the Colorado Front Range [*Baron and Campbell*, 1997].

Unsaturated shallow lateral flow accounts for most of the streamflow during summer and nonstorm periods, including snowmelt, since the soils of the basin are generally highly permeable, thin, and poorly developed [*Melgin*, 1985]. Weakly cemented silica pans in some of the better developed soils also restrict vertical percolation [*Rogers*, 1974]. Expansion of variable source areas occurs during rapid snowmelt, providing relatively direct flow paths for the routing of snowmelt water to the stream system [*Melgin*, 1985]. Fractured bedrock and basin-fill deposits; however, permit some deep percolation and contribute to discharge during the summer low-flow period [*Thodal*, 1997]. Saturation overland flow can be observed in meadows and riparian zones adjacent to streams during rapid snowmelt. Hortonian overland flow can occur during intense summer rainfall on hydrophobic forest soils, especially on the east side of the basin, but this is a localized phenomenon [*Naslas et al.*, 1994].

From 1972 to 1978, the Tahoe Research Group sampled up to four streams in the Tahoe basin; since Water Year (WY) 1980, the Lake Tahoe Interagency Monitoring Program (LTIMP) has intensively sampled up to 10 streams and measured the concentration and load of nitrate-nitrogen and (since WY 1989) of organic nitrogen. Discharge from the monitored LTIMP streams accounts for ~50% of the tributary inflow to the Lake. The samples, together with water discharge measurements, have been used to estimate the total load of nitrogen in surface runoff to the lake. [*Byron and Goldman*, 1986; *Reuter et al.*, 2000].

Figure 1 shows the Lake Tahoe basin, with the 10 LTIMP streams indicated. Table 1 shows the catchment areas of the watersheds, along with the mean annual runoff, and the ratio of the mean annual-maximum daily discharge to the mean annual-minimum daily discharge, for the water years 1989–1998. Note that the westside streams (Blackwood, General, and Ward Creeks) have a much higher ratio of high flow to low flow than the eastside streams. For Blackwood Creek at least, the mean runoff for the period 1989–1998, which we analyze here in detail, was within 1% of the mean for the 1961–1998 period of record. The 1989–1998 period included both wet years (75% above average) and dry years (65% below average). It also included a major flood (January 1997) with a recurrence interval that varied from less than 10 years to greater than 100 years for the LTIMP streams [*Rowe et al.*, 1998].

2.2. Discharge Measurement, Sampling, and Chemical Analysis

Discharge for each of the LTIMP watersheds is measured by the U.S. Geological Survey (USGS), using continuous water level recorders, together with cross-section surveys and velocity measurements for developing rating curves. Samples of stream water are collected for nutrient analysis at the stream gauging stations, according to protocols of the USGS (L. R. Kister and W. B. Garrett, written communication, 1983). Sampling frequency depends on runoff conditions. During spring snowmelt, samples are collected at least weekly, with up to two samples per day during high runoff. During large rainstorms, an attempt is made to collect two or three samples, ideally representing the rising stage, hydrograph peak, and the falling stage. During low flow periods in fall, winter, and midsummer, samples are collected approximately monthly.

Since 1988, samples have been collected with a USGS DH81 depth-integrating sampler, using the equal width increment method. Samples from intervals across the stream are composited in a churn splitter and allocated to bottles for later analysis. Prior to 1988, single grab samples were collected at each site and time.

Samples for inorganic nitrogen analysis are filtered on-site through a 0.45 μm filter, returned to a laboratory at the Lake, and stored at 4°C for usually no more than 8 days prior to analysis. Nitrate-nitrogen is determined by the hydrazine reduction method of *Kamphake et al*. [1967], and ammonium-nitrogen is determined by the indophenol method described by *Liddicoat et al*. [1975] and *Solorzano* [1969]. Samples for organic nitrogen are shipped in a cooler to a laboratory at the University of California at Davis. Usually within 8 days, unfiltered samples are subjected to Kjeldahl digestion followed by direct colorimetric determination of ammonium (as above). The Kjeldahl procedure includes ammonium initially present in the sample but not nitrate [*American Public Health Association* (*APHA*), 1995] (method 4500N).

Method detection limits (MDL) for the three forms of nitrogen are 0.07 μmol L^{-1} for nitrate-N, 0.2 μmol L^{-1} for ammonium-N, and ~2.5 μmol L^{-1} for Total Kjeldahl Nitrogen (TKN) [*Janick et al*., 1990]. Quality assurance/quality control (QA/QC) procedures (use of field blanks, spike recovery, duplicate samples, etc.) conform to USGS protocols. Duplicates are run on 8% of the samples, and for TKN, ~95% of the duplicates meet established criteria (e.g., <15% difference between duplicates for concentrations >5 times MDL). The consistency of duplicates for inorganic nitrogen exceeds that for TKN.

On a limited set of samples from 1989–1993 ($n = 467$), organic nitrogen was determined on both filtered and unfiltered subsamples, allowing us to calculate particulate organic nitrogen by difference. For the period 1989–1998, the database includes nitrate, ammonium, and organic-nitrogen concentrations in 3758 samples.

2.3. Data Analysis

The data were analyzed in two steps. In the first step, a discharge-concentration model was used to generate a trace of daily nitrate-N concentration for 3 water years in one watershed. This synthetic record was than sampled and load calculated by two methods. On the basis of this test, a method was selected and used to calculate loads for 1989–1998 record for the 10 watersheds. Estimates of dissolved organic nitrogen (DON) and particulate organic nitrogen (PON) were derived from a smaller data set and used to estimate the fractional contribution of these constituents to the total nitrogen load.

Table 1. Watershed Area and Runoff, Water Years 1989–1998, for LTIMP Streams

Stream	Catchment Area, ha	Mean Annual Runoff, cm	Annual High Flow: Low Flow
Blackwood	2,901	114	342
Edgewood	1,425	22	17
General	1,927	78	360
Glenbrook	1,054	15	50
Incline	1,813	40	16
Loganhouse	539	8	37
Third	1,567	47	25
Trout	9,505	34	19
Upper Truckee	14,219	64	223
Ward	2,513	94	771

The ratio of annual high flow:low flow is the mean maximum annual daily discharge divided by the mean minimum annual daily discharge for the 10-year period.

2.3.1. Choosing a load calculation method. The regression model used to relate nitrate-nitrogen concentration to discharge is a modified form of the equation used successfully by *Johnson et al*. [1969] for relating ion concentrations (including nitrate) to discharge at Hubbard Brook and tried unsuccessfully for nitrate data from the Bull Run Watershed in Oregon [*Bakke and Pyles*, 1997]. Derivation of the model is given by *Hall* [1970]. It assumes mixing of precipitation or event water with baseflow in an open stream system. In order to account for the shift in the discharge-concentration relationship over the water year, we added a second variable: the cumulative water discharge as a fraction of total for the water year. To avoid the effects of algal uptake of nitrate, we used only data for fall, winter, and spring. Details of the application of this model to Tahoe basin streams are given by *Coats and Goldman* [1993].

In an effort to develop regression equations for calculating nitrogen load, the discharge-concentration model was applied by water years to Blackwood Creek (1975–1996), Ward Creek (1976–1996), and General Creek (1981–1996). The results were mixed, with R^2 values ranging from 0.21 to 0.85, and the model was judged inadequate for calculating loads for all streams and water years.

For Blackwood Creek, 1989, 1990, and 1995, however, the discharge-concentration model fit the data reasonably well, with R^2 of 0.76, 0.78, and 0.53. For these years, the "true" daily average nitrate-N concentration was estimated from the regression equations and multiplied by daily discharge to create a trace of daily load values. The daily concentrations were then "sampled" on the same days that samples were actually collected, and the synthetic data sets used to estimate load by two methods: a ratio estimator method and a period-weighted sample method [*Dann et al*., 1986; *Likens et al*., 1977]. The resulting estimates were then compared with the annual loads calculated from the synthetic daily trace.

From 1972–1987, the Tahoe Research Group used the "worked record" method [*Cohn*, 1995] to calculate total loads of sediment and nutrients. Beginning with the 1988 water year data, the worked record method was replaced with a ratio estimator method. In this method, the log of instantaneous load is calculated from concentration and instantaneous discharge, then log of load is regressed against log of instanta-

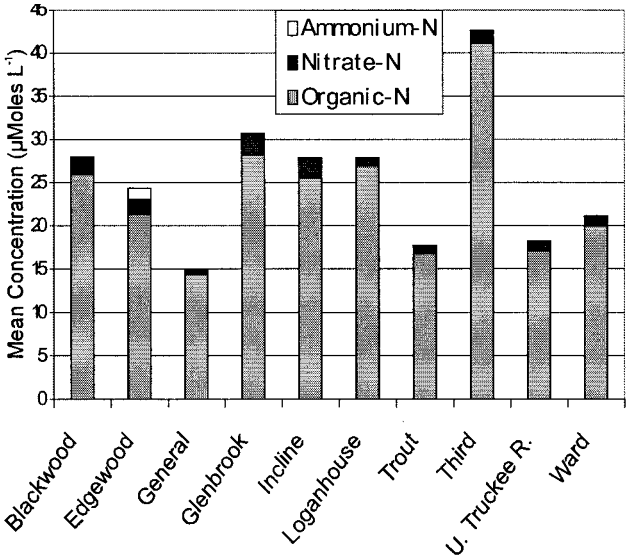

Figure 2. Discharge-weighted mean concentrations of nitrate-N, ammonium-N, and organic N in LTIMP streams, 1989–1998.

neous discharge. The resulting relationship, with a correction for retransformation bias [*Ferguson*, 1986], is used to estimate daily load from daily discharge, and the daily results are summed. With systematic sampling, the method gives unbiased results provided that (1) the relationship between load and discharge is a straight line through the origin and (2) the variance of load about the regression line is proportional to discharge. However, with event sampling, unstratified ratio estimators may be highly biased [*Preston et al.*, 1989].

Since the sampling strategy of the LTIMP is designed to sample high flow events and periods of rapidly changing discharge, the "period-weighted sample" method may be better suited for calculating total nutrient loads in Tahoe basin streams. In this method, an average concentration for each pair of successive samples is calculated, the result is multiplied by the cumulative discharge between sampling times, and the load increments summed over the water year. *Dann et al.* [1986] concluded that this method was the best of several evaluated for calculating sulfate export from a watershed because it required the least sampling, gave reproducible results, required the least conditions on the data set, and took into account the high flows in late winter and spring, when most of the ion left the watershed.

2.3.2. Estimate of DON and PON. For the water years 1989–1993 we have data for TKN in both filtered and unfiltered samples from 10 LTIMP streams. This allowed us to examine relationships between dissolved organic nitrogen (DON), particulate organic nitrogen (PON), and discharge. DON was calculated by subtracting the concentration of ammonium-N (usually negligible) from TKN of the filtered samples; PON was estimated by subtracting TKN in the filtered samples from that of the unfiltered samples. For a few samples, the difference was negative, owing to sampling and measurement error; these samples were assigned a value of 0. For each stream, the discharge-weighted mean concentrations of total organic nitrogen (TON) and DON were calculated. Confidence limits on the estimate of percent of TON as DON were derived by bootstrapping [*Efron and Tibshirani*, 1993].

3. Results

3.1. Concentrations of Inorganic and Organic Nitrogen

The discharge-weighted concentration of organic nitrogen was typically 10 times that of inorganic nitrogen (Figure 2). PON ranged from 22 to 81% of TON, and the percent PON varied among streams (see Table 2).

Ammonium-nitrogen concentrations were almost always less than 0.7 μmol L^{-1} in Tahoe basin streams, too low to be shown on Figure 2. An exception is Edgewood Creek, which flows through a fertilized golf course. Concentrations of ammonium-N in Edgwood Creek reached as high as 36 μmol L^{-1} during June 1992.

The discharge-concentration model showed that for Ward and Blackwood Creeks, nitrate-N concentration (during fall, winter, and spring) was positively related to discharge, with a strong "wash-out" effect; concentrations tended to be high early in the runoff season (especially during rain-on-snow events) and drop before the peak of snowmelt runoff. Figure 3 shows the concentration of nitrate-N along with daily discharge, for Blackwood, Incline, and Third Creeks and the Upper Truckee River, in WY 1989. The highest nitrate-N peaks were associated with rain-on-snow events in early March and the onset of spring snowmelt in early April. Concentrations then dropped even as snowmelt runoff increased.

3.2. Particulate and Dissolved Organic Nitrogen

Figure 3 also shows the concentrations of PON and DON. DON increased sharply with high runoff during winter rain storms, or early in the snowmelt season, then decreased as runoff progressed. In the larger streams, it increased again during the summer, as discharge dropped. PON concentrations were highly episodic and variable, with sharp peaks during high runoff events.

Concentrations of both DON and PON were related to stream discharge in some streams, but the relationships were generally weak. Log PON was correlated with log of discharge in General, Incline, Loganhouse, Third, and Ward Creeks and the Upper Truckee River; log DON was related to log of discharge in General, Glenbrook, Incline, Loganhouse, and Third Creeks. R^2 ranged from 0.1 to 0.3. The wash-out of organic nitrogen early in the runoff season may have contributed to the variability in the discharge-concentration relationships.

Table 2. Discharge-Weighted Averages of Total and Dissolved Organic Nitrogen in LTIMP Streams, WY 1989–1993

Stream	TON, μmol L^{-1}	DON, μmol L^{-1}	n	Fraction as DON Mean	s.e.	Lower	Upper
Blackwood	11	5	71	0.46	0.06	0.35	0.57
Edgewood	23	17	36	0.75	0.05	0.66	0.85
General	11	8	68	0.77	0.04	0.67	0.83
Glenbrook	14	11	34	0.78	0.03	0.72	0.83
Incline	27	9	41	0.34	0.04	0.27	0.43
Loganhouse	25	13	37	0.54	0.10	0.37	0.74
Third	43	8	45	0.19	0.04	0.14	0.28
Trout	12	9	27	0.76	0.03	0.68	0.81
Upper Truckee	25	11	36	0.43	0.10	0.29	0.67
Ward	10	5	72	0.53	0.07	0.36	0.65

Standard errors (s.e.) and confidence limits for the fractions as DON were estimated by bootstrapping. Lower and upper indicate 95% confidence limits.

DON and PON were also correlated with suspended sediment, more so in some streams than others. Table 3 shows the results of the regression of PON against suspended sediment, which is generally a stronger relationship than for DON against suspended sediment.

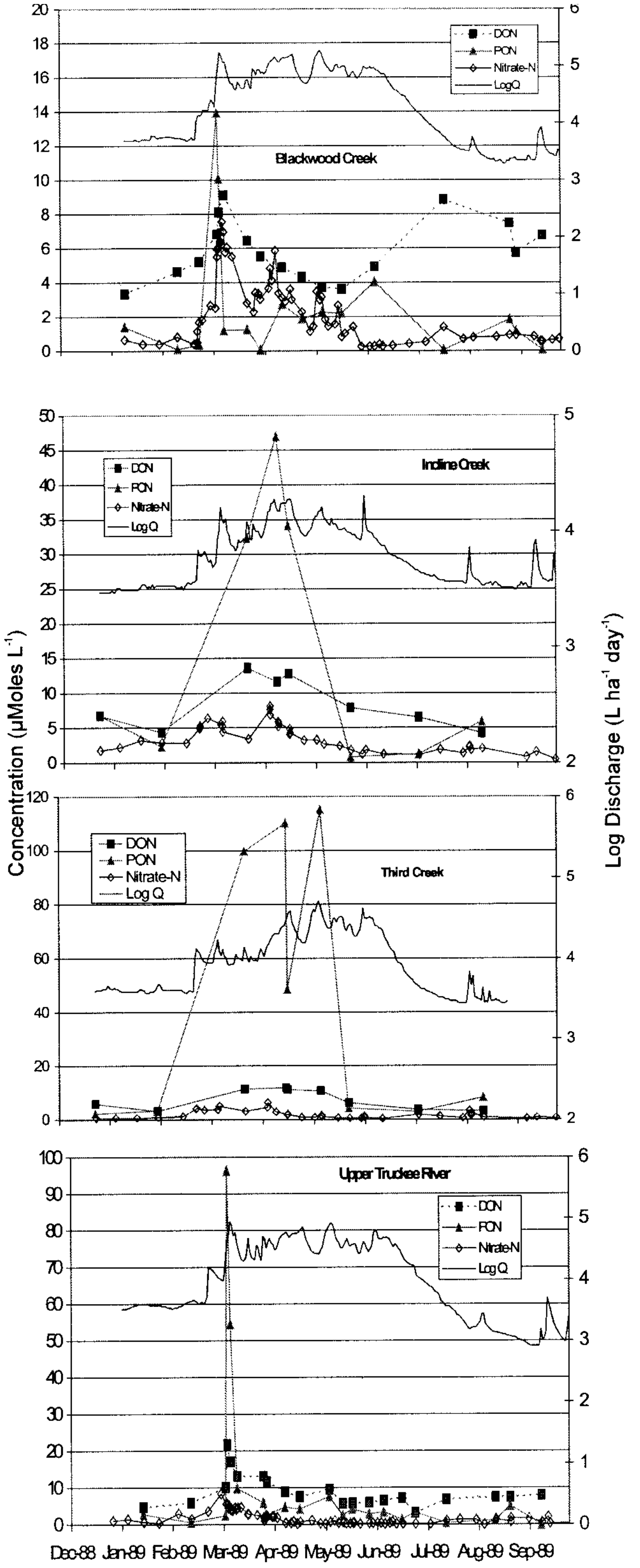

Figure 3. Concentrations of DON, PON, and Nitrate-N with mean daily discharge, WY 1989, for Blackwood, Incline, and Third Creeks and the Upper Truckee River.

Table 3. Regression Summary, PON Versus Suspended Sediment

Stream	n	R^2	Significance Level	Percent N in Suspended Sediment
Blackwood	65	0.05	$p < 0.001$	0.31
Edgewood	19	0.01	n.s.	1.58
General	65	0.45	$p < 0.001$	0.53
Glenbrook	32	0.17	$p < 0.01$	1.00
Incline	41	0.24	$p < 0.001$	0.59
Third	43	0.01	n.s.	0.39
Trout	25	−0.02	n.s.	1.75
Upper Truckee	35	0.95	$p < 0.001$	0.47
Ward	69	0.41	$p < 0.001$	0.67

The average concentrations of PON in suspended sediment are discharge weighted.

Table 3 also shows the discharge-weighted average nitrogen concentrations in suspended sediment. These concentrations are generally higher than in the <2 mm fraction of the top 5 cm of basin soils, where nitrogen typically ranges from 0.1 to 0.25% [*Soil Conservation Service*, 1973, 1970; *Zinke*, 1974].

Although summer rainstorms do not contribute appreciably to the total precipitation in the Tahoe basin, they can create pulses of both organic and inorganic nitrogen in basin streams, delivering nutrients to the lake during periods of rapid algal growth. Streams on the eastside of the basin, with relatively small and steep watersheds, are more affected than the westside streams. Table 4 shows the discharges and concentrations of nitrate-N, ammonium-N, and organic-N in four streams on the eastside, during a storm in August 1989. Rainfall amounts measured at Incline (near lake level) were 0.94 and 1.42 cm on August 7th and 8th, respectively. Streams on the westside were apparently unaffected by this event. The highest concentration

Table 4. Nitrogen Concentration in Four Eastside Streams During a Summer Rainstorm

DATE	TIME, PST	Q, L s^{-1}	NO_3-N, μmol L^{-1}	NH_4-N, μmol L^{-1}	TON, μmol L^{-1}
		Edgewood Creek			
Aug. 7, 1989	15:45	26	0.36	0.14	31
Aug. 8, 1989	10:20	161	4.14	2.36	49
Aug. 22, 1989	9:45	24	0.5	0.36	29
		Glenbrook Creek			
July 20, 1989	12:30	5	2.64	1.43	13
Aug. 7, 1989	13:30	14	0.5	0.5	32
Aug. 8, 1989	13:00	37	0.93	0.43	133
Aug. 18, 1989	8:20	3	2.57	0.79	14
		Incline Creek			
Aug. 3, 1989	11:10	88	1.43	0.14	6
Aug. 7, 1989	12:40	142	2.29	1.86	137
Aug. 7, 1989	15:25	108	2.43	0.36	79
Aug. 8, 1989	12:30	255	1.93	0.29	94
Aug. 15, 1989	9:35	96	2.07	0.14	10
		Third Creek			
Aug. 3, 1989	13:00	51	0.64	0.14	7
Aug. 7, 1989	13:55	91	3.5	0.36	198
Aug. 8, 1989	11:00	170	2.29	0.21	89
Aug. 8, 1989	13:25	150	1.64	0.21	89
Aug. 8, 1989	16:05	127	2.5	0.29	332
Aug. 16, 1989	9:00	74	0.93	0.36	12

Discharge (Q) is the discharge measured at the time of sampling.

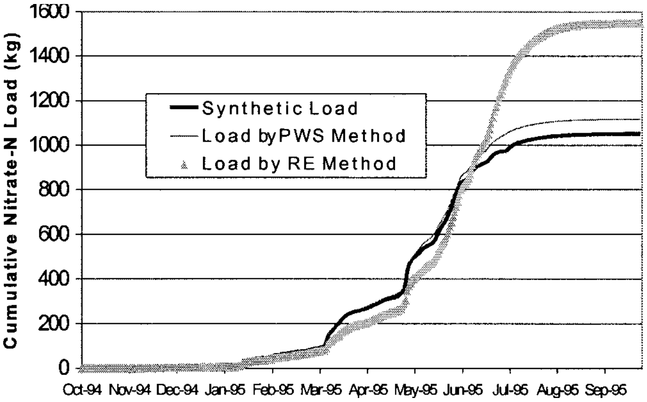

Figure 4. Comparison of two methods for calculating total nitrate-N load, Blackwood Creek, 1995. Daily load was synthesized using a discharge-concentration model combined with daily discharge records, and daily concentration data "sampled" on the same days that samples were actually collected. The period-weighted sample method (PWS) tracks the synthetic load more closely than the ratio estimator method (RE).

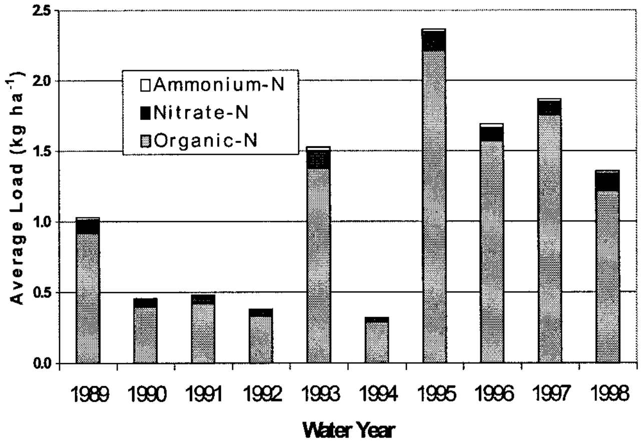

Figure 6. Total annual nitrogen loads, by water year, in 10 Tahoe basin streams.

of organic nitrogen recorded in the sampling program, 1700 μmol L^{-1} in Third Creek, was associated with a summer rainstorm on July 16, 1990 (1.02 cm at Incline). High rates of runoff during summer rainfall in these eastside streams may result in part from land development.

3.3. Total Loads of Nitrogen in Basin Stream

Figure 4 shows the cumulative daily nitrate-N load calculated by two methods, compared with the synthetic cumulative daily load, for 1995 WY (a high runoff year with relatively few samples). The period-weighted sample method (PWS) tracked the simulated loads much better than the regression estimator (RE) method.

For the 3 years tested, the regression estimator method overestimated annual nitrate-N load (from simulated daily values) by an average of 39%, whereas the period-weighted sample method overestimated annual load by an average of 3.1% (1.3, 0.7, and 6.3% for 1989, 1990, and 1995, respectively). For the 10 water years and 10 streams, the ratio estimator method produced higher total load estimates than the period-weighted sample method by 17% for nitrate-N, 34% for ammonium-N, and 19% for TON. On the basis of these results as well as theoretical considerations, we decided to use the period-weighted sample method to calculate total nitrogen loads in the basin streams.

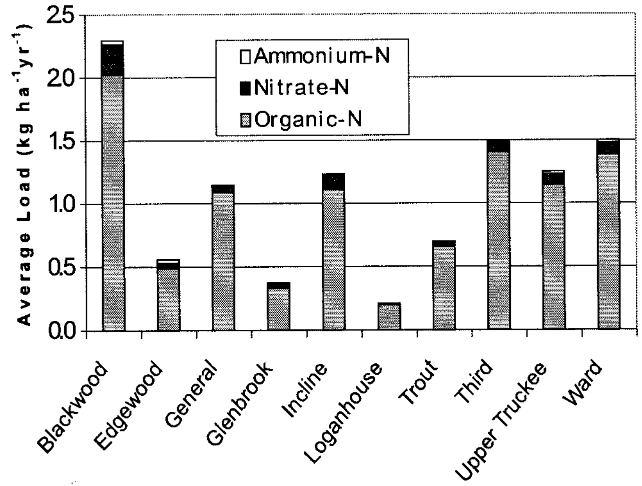

Figure 5. Mean annual nitrogen loads, by tributary, for 10 Tahoe basin stream, 1989–1998.

The total average annual export rate for the 10 LTIMP streams (in kg ha^{-1} yr^{-1}) amounted to 0.081 for nitrate-N (7% of TN), 0.017 for ammonium-N (1.5% of TN), and 1.05 for TON (91.5% of TN). Of the latter, ~55% is dissolved, and 45% is particulate (see Table 2). Figure 5 shows the mean annual loads for the 10 streams, averaged for the period 1989–1998; Figure 6 shows the loading rate summed over the 10 watersheds, for each water year.

The average loading rates for total nitrogen shown in Figures 5 and 6 are closely related to discharge. Table 5 shows the results of regressions of mean annual total nitrogen load (in kg ha^{-1} yr^{-1}) versus mean annual runoff (cm), with averages calculated by summing over area and over years.

4. Discussion

4.1. Inorganic Nitrogen Concentrations

A pulse of nitrate during early snowmelt is characteristic of Tahoe basin streams and is well recognized in catchments elsewhere in the Sierra Nevada [*Sickman and Melack*, 1998]. The increase has been attributed to ion concentration phenomena in the snowpack during freeze-thaw cycles [*Johannes-*

Table 5. Regression Results of Mean Annual Load of Total Nitrogen Versus Mean Annual Runoff

	Dependent Variable	
	10-yr Average By Watershed	Aerial Average By Year
Intercept	0.242	−0.08
Coefficient	0.016	0.022
Adjusted R^2	0.79	0.96
s.e.	0.28	0.14
Significance level	$p < 0.001$	$p < 0.0001$
n	10	10

The 10-year average load by watershed is shown in Figure 5, and the aerial average by year is shown in Figure 6. Nitrogen is given in kg ha^{-1} yr^{-1}, and runoff is given in centimeters.

sen and Henriksen, 1978; *Rascher et al*., 1987; *Williams and Melack*, 1989; *Williams et al*., 1995]. Isotopic studies in New England and in the Rocky Mountains, however, have shown that the soil is the primary source of nitrate in streamwater during early snowmelt [*Kendall et al*., 1995]. In the Tahoe basin, the soil is both a source and sink for nitrate during snowmelt. Nitrate concentrations are generally higher in snowfall than in the soil solution of the A1 or A2 horizon, at least beneath well-stocked conifer stands [*Coats et al*., 1976; *Johnson et al*., 1997]. Soils (or stream gravels) beneath mountain alder and soils in disturbed or decadent conifer stands, however, are sites of significant nitrification and may contribute to the early season nitrate pulse [*Coats*, 1975]. There is evidence that autotrophic nitrification is active in a wide range of coniferous forest soils but difficult to detect owing to rapid microbial uptake [*Stark and Hart*, 1997].

The generally positive relationship between nitrate-N concentration and discharge in Tahoe basin streams contrasts with results for the Como Creek watershed in the Colorado Rockies. *Lewis and Grant* [1979] found a negative relationship between discharge and concentration for nitrate-N and no relationship for organic N. *Lewis and Grant* [1980] also found a "spectacular" increase in streamwater nitrate associated with soil freezing (which rarely occurs in the Tahoe Basin) during a year of low snow cover. They attributed the nitrate release to disruption of plant uptake and soil microbiological processes. Clearly, regional differences in hydrology and climate exert a strong influence on patterns of nitrate transport in alpine and subalpine streams.

Catchment hydrology must exert at least as important an influence on nitrate transport as does nitrogen mineralization and uptake. The most hydrologically active zones, stream side wetlands, floodplains, riparian, and hyporheic zones, are also the most biogeochemically dynamic areas [*Cirmo and McDonnell*, 1997]. *Creed and Band* [1998a, b] showed that the variation in nitrate production in vegetationally similar watersheds of Ontario is related to catchment topography. The flushing behavior was found to be related to the rate of change in variable-source area during snowmelt; the slower the rate of increase of variable source area, the longer the flushing time, and the greater the ultimate nitrate production. Other studies have shown that much of the discharge of both water and nitrate-nitrogen during a given event may originate from "old" water and from nitrogen stored in the soil from a previous year [*Kendall et al*., 1995; *Pearce et al*., 1986].

In a study of nutrients in surface runoff from experimental plots on the northeast side of the basin, *Naslas et al*. [1994] found a pulse of nitrate in the first few minutes of artificial rainfall, with concentrations as high as 107 μmol L^{-1} nitrate-N. Runoff from plots on the Umpa series (a Cryochrept derived from volcanic parent material) showed higher concentrations than that from plots on the granitic Meeks (a Cryumbrept) soil, and open plots produced higher concentrations of nitrate than forested plots. With nitrate added to the applied rainfall, however, the Umpa (but not the Meeks) showed rapid uptake of nitrate, suggesting anion adsorption on organic and mineral surfaces [*Burcar et al*., 1997].

Hourly sampling of basin streams during snowmelt has shown a pronounced diel cycle in nitrate-N concentration. Concentration rises and falls with discharge, with its maxima and minima lagging an hour or two behind those of discharge [*Leonard et al*., 1979]. This phenomenon, however, could be consistent with both a snowmelt and a soil organic matter source for nitrate. For now, whether the soil or the melting snowpack is the source of the nitrate pulse in streams of the Tahoe basin remains an open question. An investigation of nitrogen and oxygen isotopes in streamwater nitrate might prove helpful in sorting out the sources and flow paths of inorganic nitrogen.

The generally low concentrations of ammonium-N in Tahoe basin streams probably reflect effective retention of ammonium ions by the soil, as well as a highly-oxygenated stream and shallow subsurface environment, with little contribution from wetlands or anoxic groundwater. Temperate rainforest streams [*Hedin et al*., 1995; *Edmonds et al*., 1995] and boreal forest streams [*Ford and Naiman*, 1989] sometimes have more significant ammonium-N concentrations and loads.

4.2. Organic Nitrogen Concentrations

Leaching experiments with intact soil cores [*Marcus et al*., 1998], field experiments with artificial rain [*Rhea et al*., 1996], and lysimeter sampling during and after snowmelt [*Coats et al*., 1976; *Marcus et al*., 1998] have all shown that the soil solution in the coniferous forest soils of the Tahoe basin soils is generally dominated by DON, with low concentrations of inorganic N. In soils of riparian zones, however, nitrate concentrations are often comparable to those of DON, owing in large part to the influence of alder.

Our data show a weak but highly significant positive correlation between DON and DIN, both for all streams combined and for individual streams ($R^2 = 0.16$; $p < 0.00001$ for all streams). Excluding the summer season samples from the regression did not much improve the fit. *Hood and Williams* [1998] measured DON and DIN concentrations in streams at the alpine-subalpine transition in the Rocky Mountains of Colorado. They found a negative correlation between DON and DIN, reflecting differences in nitrogen dynamics between tundra, talus, and forested areas. The difference between our results and those of Hood and Williams is probably a result of differences in sampling; the LTIMP samples were collected at tributary mouths over a wide range of flow conditions, whereas their samples represented synoptic longitudinal stream profiles.

Three processes might explain the apparent N enrichment of suspended sediment relative to basin soils. First, direct input of litter from riparian vegetation must contribute PON directly to the streams. This hypothesis is consistent with the generally higher N concentrations in suspended sediment for the smaller streams, which would have a greater detritus input from the riparian zone per unit of channel area. Second, streambank erosion accounts for much of the sediment load of basin streams [*Nolan and Hill*, 1991], and soils of the riparian zone are generally richer in organic nitrogen than upland soils [*Zinke*, 1974]. Third, fine nitrogen-rich organic matter may be winnowed out during transport, with inorganic sand transported as bedload.

The interesting bimodal seasonal pattern of DON concentrations in the larger basin streams (Figures 3–6) is consistent with results from other regions [*Arheimer et al*., 1996] and raises some questions: (1) What are the sources and forms of the DON at different seasons? (2) What controls its release from the soil and transport in the fluvial system? (3) How available and biologically reactive is it? (4) Does the biological availability vary with season and dominant source? Recent research on dissolved organic matter in forest soils and streams provides partial answers to these questions.

Most of the dissolved organic matter originating in forest soils consists of hydrophobic (fulvic and humic) acids, bases, and neutrals and hydrophilic acids, bases, and neutrals [*Thurman*, 1985]. Fulvic acids contain ~1–2% nitrogen by weight, and hydrophyllic acids contain 1.7–2.5%; together these fractions account for most of the dissolved organic matter in coniferous forest streams [*McKnight et al*., 1992; *Hedin et al*., 1995].

The retention of dissolved organic nitrogen in forest soils is influenced by the phenolic and tannic acid production in pine litter. On low-nutrient sites, the formation of insoluble complexes of proteins with tannin and polyphenols is thought to be an important mechanism limiting the production of mineral nitrogen (ammonium and nitrate) and conserving nitrogen onsite [*Northrup et al*., 1995].

The mobility of dissolved organic matter, however, is strongly influenced by its interaction with hydrous iron and aluminum oxides [*McKnight et al*., 1985, 1992]. Most of the soils of the Tahoe basin are relatively poorly developed, dominated by conifers and lacking in significant accumulations of iron and aluminum oxides [*Soil Survey Staff*, 1975]. They are also coarse-textured and porous, with relatively little reactive surface area. It is thus not surprising that organic nitrogen is the predominant form in basin streams.

Using carbon isotope analysis, *Schiff et al*. [1997] identified two major pools of dissolved organic carbon (DOC): (1) a microbially labile pool released by the early stages of litter decomposition that reaches the stream via shallow flow-paths during the autumn following leaf-fall; (2) a recalcitrant pool of longer residence time in the soil that reaches the stream via deeper flowpaths. *Easthouse et al*. [1992] found that in their Spodosols, the hydrophobic acids dominated in the organic horizon but were effectively removed as water moved through the soil, so that hydrophilic acids dominated in the B horizon. They showed that DOC type varies consistently enough with soil horizon and flowpath that the concentrations of hydrophobic and hydrophilic acids can be used in end-member mixing analysis [*Christophersen et al*., 1990] to identify water sources and flowpaths in a stream.

On the basis of these considerations, we hypothesize that (1) the "first flush" of DON during fall storms and early snowmelt is relatively biologically available, representing the contribution of leachate from fresh litter of riparian zones; (2) the DON in winter low-flow, representing longer flow-path sources, is relatively unavailable; (3) streamwater DON during peak snowmelt comprises mostly fulvic and humic acids from the coniferous forest floor and is relatively unavailable; and (4) autochthonous DON in summer streamflow is relatively available but contributes little to the total annual load.

4.3. Total Loads

The record of atmospheric deposition at Tahoe provides an interesting comparison with the loads in streamflow. An atmospheric sampling station at lake level, near the mouth of Ward Creek, recorded 1.16 kg ha^{-1} yr^{-1} nitrate-N and 1.08 kg ha^{-1} yr^{-1} ammonium-N, in wet plus dry deposition, for the period 1989–1992 [*Jassby et al*., 1994]. The retention efficiency, defined as 100 (1-yield/deposition), for inorganic nitrogen in this period thus averaged 97% for Ward Creek and 90% for Blackwood Creek. Measurement of deposition at lake level underestimates watershed input, since precipitation in upper Ward Valley and Blackwood Canyon is greater than at the lake. For a small stream on the east side, *Brown et al*. [1988] reported near total stripping of nitrate from snowmelt water.

Taking into account the input (both wet and dry deposition) and yield of organic as well as inorganic nitrogen, the retention efficiency for total nitrogen averaged 88% for Ward Creek and 80% for Blackwood Creek. These estimates, however, do not take into account some important sources of N-input, such as nitrogen fixation by alder and ceanothus.

Runoff has a strong influence on total nitrogen load, both spatially and temporally. In fact, total annual runoff accounts for 96% of the interannual variance in total nitrogen load, and mean annual runoff accounts for 79% of the variance in mean annual total nitrogen load among watersheds. At the basin and decadal scales, hydrology dominates over biogeochemistry in controlling stream nitrogen loads, whereas biogeochemistry dominates over hydrology in controlling the form of nitrogen.

Table 6 compares the average nitrogen loads of Tahoe basin streams with those draining forested watersheds at a number of other sites in North and South America. The importance of DON relative to nitrate-N in Tahoe basin streams and soils is consistent with results from sites in California, Oregon, Washington, and southern Chile [*Hedin et al*., 1995] but contrasts with sites from the eastern United States, where anthropogenic atmospheric deposition of nitrogen is much higher [*Aber et al*., 1989]. Our results also contrast with results from Loch Vale (Rocky Mountains), where dissolved nitrogen loads are dominated by nitrate [*Baron and Campbell*, 1997]. The tropical streams surveyed by *Lewis et al*. [1999] carried relatively high loads of both nitrate-N and DON.

5. Summary and Conclusions

The Lake Tahoe Interagency Monitoring Program (LTIMP) samples 10 streams in the Lake Tahoe basin and analyzes the samples for (among other things), nitrate-nitrogen, ammonium-nitrogen, and total Kjeldahl nitrogen. Analysis of the LTIMP data reveal interesting patterns in the concentration and total loads of different forms of nitrogen in basin streams.

A simple two-member mixing model with an added factor to account for the "wash-out effect" was used to simulate daily nitrate-N concentrations for 3 water years in one stream in the basin. Load estimates by two methods were then compared with the loads from this simulation. The results showed that the "period-weighted sample" method is more accurate and better suited to the LTIMP sampling program than a "ratio estimator" approach. Using the former, we calculated total loads for the 10 streams and 10 water years. We also calculated discharge-weighted mean concentrations, for nitrate, ammonium, and organic nitrogen and estimated the fractions of particulate and dissolved organic nitrogen, on the basis of a subset of samples.

Both the concentration and total loads of nitrogen in basin streams are dominated by organic nitrogen. Nitrate-nitrogen accounts for ~7% of the nitrogen load, and ammonium-nitrogen accounts for only ~1.5%. On average, ~55% of the organic nitrogen is dissolved, although this fraction varies widely among streams. Dissolved organic nitrogen (DON), like nitrate, is highest at high discharge early in the runoff season. It typically drops during late snowmelt but increases again during the summer low-flow period, probably owing to in-stream biological activity. Intense summer rainstorms, especially on the eastside of the basin, are responsible for the highest peaks in organic nitrogen. Because of the complex

Table 6. Nitrogen Flux in Streams Draining Forested Watersheds in North and South America

Site	Source	Soils and Vegetation	Period	Streamwater Nitrogen Export, kg ha^{-1} yr^{-1}				
				NO$_3$-N	NH$_4$-N	DON	PON	TON
Tahoe basin	This study	mixed coniferous; entisols, inceptisols, alfisols	1989–1998	0.081	0.017	0.58	0.47	1.05
Bear Brook, New Hampshire	*Meyer et al.* [1981]	northern hardwoods; spodosols	1968–1969	2.74	0.17	0.42	0.024	0.46
Central Ontario	*Dillon et al.* [1991]	northern hardwood; mixed coniferous; spodosols, histosols	1976–1984	0.72	0.24	⋯	⋯	1.85
H. J. Andrews Forest, Oregon	K. Vanderbilt and K. Lajtha (Annual and seasonal patterns of nitrogen dynamics at the H. J. Andrews Experimental Forest, OR, submitted to *Biogeochemistry*, 2000)	20-year old Douglas fir; cryumbrepts, haplorthods	1969–1996	0.14	0.07	0.25	0.14	0.39
		450-year Douglas-fir; low elevation	1969–1996	0.029	0.079	0.42	0.251	0.671
		150-year old Douglas-fir; high elevation	1969–1996	0.042	0.085	0.246	0.143	0.389
Olympic National Park	*Edmonds et al.* [1995]	old-growth Douglas-fir/western hemlock; dystochrepts	1987–1988	2.25	0.3	4.58	⋯	>4.58
Emerald Lake watershed, S. Sierra, California	*Williams et al.* [1995]	subalpine, alpine; cryumbrepts, cryochrepts	1987	1.12	0.28	⋯	⋯	1.68
Blue Mountains, East Oregon	*Tiedemann et al.* [1988]	mixed conifer; vitrandepts, cryandepts	1971–1976	⋯	0.06	1.68	⋯	⋯
Loch Vale, Colorado	*Baron and Campbell* [1997]	alpine tundra; talus and subalpine forest	1984–1993	1.7	Trace	0.002	0.31	0.31
Average of 11–23 sites	*Lewis et al.* [1999]	tropical watersheds	varies	2.43	0.39	2.37	1.52	3.89

Note the dominance of organic nitrogen in streams of California, Oregon, and Washington compared to other areas.

relationships between discharge and concentration, neither particulate nor dissolved organic nitrogen is closely related to log discharge, except at short timescales.

At the basin and decadal scales the temporal and spatial variation in total nitrogen load is explained largely by variation in annual runoff. The relationship between annual runoff and total annual nitrogen load is good enough that annual runoff alone could now be used to estimate total annual nitrogen load to the lake from the 10 LTIMP streams.

Future work on nitrogen in Tahoe basin streams might focus on (1) relationships between watershed characteristics (soils, vegetation, hydrogeology, and land use) and nitrogen yield; (2) concentrations of PON, DON, and DIN in relation to hydrologic flowpaths and runoff events; (3) the sources and biological availability of DON in streamwater; (4) methodologies for calculating total load; and (5) the contribution of urban runoff to the nitrogen load of the lake.

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R. N. Coats, Hydroikos Associates, 1 Piombo Place, San Rafael, CA 94901. (coats@hydroikos.com)

C. Goldman, Department of Environmental Science and Policy, University of California, Davis, CA 95616.

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