Biogeochemistry **57/58:** 375–385, 2002.

Yield of nitrogen from minimally disturbed watersheds of the United States

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Key words: dissolved organic nitrogen, nitrate, nitrogen cycle, nitrogen yields

Abstract. Watersheds of the US Geological Survey's Hydrologic Benchmark Network program were used in estimating annual yield of total nitrogen and nitrogen fractions (ammonium, nitrate, dissolved organic N, particulate N) in relation to amount of runoff, elevation, and watershed area. Only watersheds minimally disturbed with respect to the nitrogen cycle were used in the analysis (mostly natural vegetation cover, no point sources of N, atmospheric deposition of inorganic N < 10 kg ha^{-1} y^{-1}). Statistical analysis of the yields of total nitrogen and nitrogen fractions showed that elevation and watershed area bear no significant relationship to nitrogen yield for these watersheds. The yields of total nitrogen and nitrogen fractions are, however, strongly related to runoff (r^2 = 0.91 for total N). Annual yield increases as runoff increases, but at a rate lower than runoff; annual discharge-weighted mean concentrations decline as annual runoff increases. Yields of total nitrogen and most nitrogen fractions bear a relationship to runoff that is nearly indistinguishable from a relationship that was documented previously for minimally disturbed watersheds of the American tropics. Overall, the results suggest strong interlatitudinal convergence of yields and percent fractionation for nitrogen in relation to runoff.

Introduction

Transport of nitrogen in rivers on a continental or global scale can be estimated from monitoring data for large rivers (Meybeck 1982). Because transport rates have been strongly perturbed anthropogenically in many parts of the world, however, it is difficult to reconstruct global or continental transport under natural conditions. While information is available for numerous watersheds that are unaffected by anthropogenic sources of nitrogen on the ground, the widespread distribution of anthropogenically enhanced nitrogen deposition from the atmosphere has changed the nitrogen supply to many watersheds that are otherwise unperturbed (Aber et al. 1989; Howarth et al. 1996).

A recent review of nitrogen yield data for the Americas (Lewis et al. 1999) showed that exclusion of data sets potentially affected by mobilization of nitrogen either on the ground or through the atmosphere restricts the consideration of data representing background conditions primarily to the American tropics. An analysis of these data for annual nitrogen yield in relation to watershed area, elevation, and runoff showed a very strong relationship between annual runoff and annual yield of total nitrogen ($r^2 = 0.85$) and of individual nitrogen fractions. The analysis also showed secondary but significant relationships between elevation and annual yield of dissolved inorganic N, and between watershed area and ratios of nitrogen fractions. It was not clear whether background nitrogen yields from watersheds at temperate latitudes would follow trends similar to those that are characteristic of the American tropics.

Recent studies in Europe as part of the NITREX network have shown that naturally vegetated watersheds show virtually no perturbation of inorganic nitrogen yield in runoff up to a threshold of approximately 10 kg ha^{-1} y^{-1} of nitrogen deposition (Dise & Wright 1995). At deposition rates between 10 and 25 kg ha^{-1} y^{-1}, many of these watersheds show increased output of inorganic N; above 25 kg ha^{-1} y^{-1}, all watersheds show higher output of inorganic N (organic N was not included in the analysis). Thus the European NITREX studies indicate that temperate watersheds to be used in statistical analysis of yield per unit area for undisturbed conditions could in fact include those that receive some nitrogen enrichment from the atmosphere, provided that this enrichment does not exceed a threshold in the vicinity of 10 kg ha^{-1} y^{-1}. If this is the case, then the number of watersheds in North America from which data could be taken would be great enough to support a statistical analysis of nitrogen yields under background conditions.

The purpose of this paper is to use watersheds of North America having primarily natural vegetative cover, lacking point sources of nitrogen, and having nitrogen deposition below 10 kg ha^{-1} y^{-1} as a means of estimating background yield of total nitrogen and nitrogen fractions. Data for these watersheds also are analyzed for relationships between the yield of total nitrogen and nitrogen fractions in relation to variables that were used in the analysis of similar data for the American tropics (elevation, runoff, watershed area).

The present analysis is based on watersheds that are part of the United States Geological Survey (USGS) Hydrologic Benchmark Network (HBN) program. Other sites could be considered as well (e.g. Williams & Melack 1997; Sickman & Melack 2002), but there are several advantages to dealing exclusively with the benchmark watersheds. First, they are sufficiently numerous and well distributed (Figure 1) to make an appropriate basis for

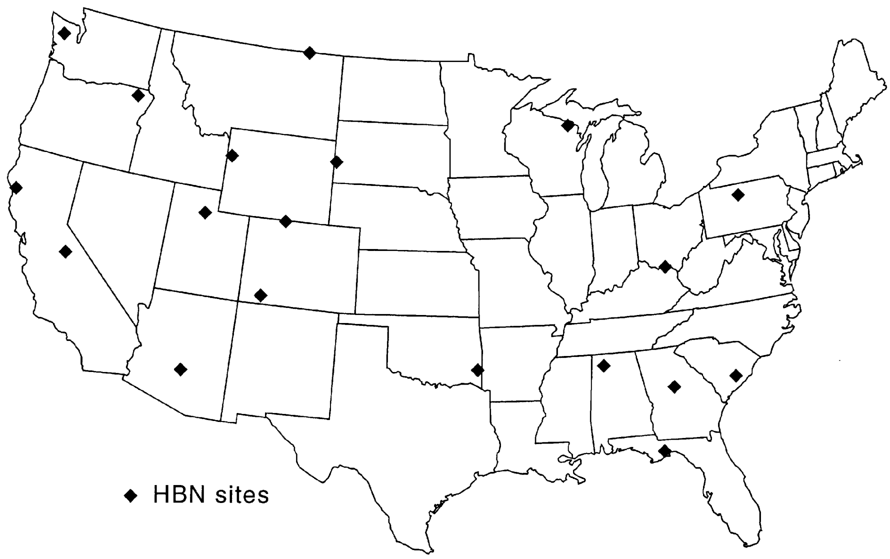

Figure 1. Location of the US Geological Hydrologic Benchmark Network watersheds that were used in the study.

statistical analysis. In addition, all of the sampling and analyses occurred through the use of the same protocols. Finally, the hydrologic documentation for these watersheds is excellent, as required for computation of annual yield of total nitrogen and nitrogen fractions.

Methods

Characteristics of the HBN data were obtained from USGS sources (Alexander et al. 1996), and then screened for combinations of sites and years for which information was available on all nitrogen fractions to be considered in this analysis: ammonium, nitrate, dissolved inorganic N (DIN), dissolved organic N (DON), total dissolved N (TDN), particulate N (PN), and total N (TN). Although the benchmark program includes 63 sites, 40 of these lack complete coverage for all nitrogen fractions over any extended interval or with sufficient frequency, and four additional ones have significant anthropogenic N sources (including atmospheric deposition, as described below). Of the remaining 19, all nitrogen fractions were measured consistently over the two years between October of 1980 and September of 1982. These 19 sites were used in the analysis (Figure 1).

Estimates were made of the nitrogen deposition for each one of the benchmark watersheds as part of the screening process for stations. The National

Atmospheric Deposition Program (NADP) monitoring site nearest to each of the benchmark watersheds was located, and the deposition at this site was considered to be representative of deposition to the benchmark watershed. Deposition records for ammonium and nitrate during the years 1981–1982 (spanning most of the months used in calculating yields) were tabulated. The NADP data do not include dry deposition or wet deposition of DON or PN.

Methods of field collection and laboratory analysis are as described by Alexander et al. (1996, 1998). Inspection of the raw data raised only a few problematic issues. Particulate nitrogen, which was estimated as the difference between paired Kjeldahl N, nitrate, and nitrite analyses on filtered and unfiltered subsamples, sometimes showed negative concentrations. This is an expected result of random error in analysis of samples that contain low concentrations of particulate nitrogen. Because elimination of the negative data points would bias the weighted means, the negative numbers were left in the data set. Two apparently erroneous, extreme concentrations of Kjeldahl nitrogen were excluded. For ammonium, mean values below the detection limit (10 μg/L) were set to half the detection limit.

Daily discharge records for the 19 watersheds under analysis were retrieved from USGS sources (Alexander et al. 1996). Individual chemical analyses then were matched with discharge data. A single chemical analysis was considered representative of a span of days midway between the most recent previous analysis and the subsequent analysis. Discharge from this interval of time was applied to the concentration data for each nitrogen constituent in the computation of discharge-weighted means for each constituent. In this manner, a discharge-weighted mean concentration for each nitrogen fraction was obtained over the entire two years for each watershed. The sampling frequency for nitrogen analysis typically was monthly (one site bi-monthly; occasional missing data for some sites).

The USGS data on ammonium and organic nitrogen are biased. Over the period relevant to the present study, the USGS was using mercuric chloride tablets to preserve samples intended for ammonium and Kjeldahl analyses. In response to queries about the possibility of contamination caused by these tablets, the USGS arranged for two of its laboratories to conduct tests for bias caused by contamination. The results, which are reported along with the documentation for the HBN data set (Alexander et al. 1996) indicated that one of the laboratories found a small amount of contamination (3 to 15 μg/L) and another found negligible contamination. A detailed statistical analysis of field data for waters in Texas, however, provided strong circumstantial evidence for more significant bias caused by contamination (Schertz et al. 1994); bias was higher for Kjeldahl nitrogen analyses than for ammonium analyses.

Table 1. Characteristics of sites used in the analysis. Runoff is the mean for the two years considered in the analysis (see text)

Site	Latitude (N)	Longitude (W)	Elev m asl	Area km^2	Runoff mm/yr
Young Womans Creek, PA	41	77	238	119	541
Scape Ore Swamp, S.C.	34	80	50	249	266
Falling Creek, GA	33	83	367	186	219
Sopchoppy, FL	30	84	3	264	580
Sipsey Fork, AL	34	87	540	238	470
Upper Twin Creek, OH	38	83	538	31	245
Popple River, WI	45	88	429	360	299
Rock Creek, MT	48	106	771	850	25
Castle Creek, SD	44	103	5920	205	41
Encampment River, WY	41	106	2521	189	548
Kiamichi River, OK	34	94	270	104	775
Vallecito Creek, CO	37	107	2410	186	682
Wet Bottom Creek, AZ	34	111	707	93	94
Red Butte Creek, UT	40	111	5400	18	198
Merced River, CA	37	119	1224	469	886
Elder Creek, CA	39	123	1391	18	1333
Andrews Creek, WA	48	120	4300	57	536
Cache Creek, WY	43	110	2057	28	449
Minam River, OR	45	117	774	622	799
Mean	–	–	1574	226	473
Standard Error	–	–	412	50	76

The data for the present study were tested statistically for evidence of bias caused by contamination associated with the mercuric chloride preservation method. Mean values for ammonium concentration for each station were taken over the interval October 1980 through September 1986, when mercuric chloride preservation was used. A comparison then was made with means for each station over the interval October 1986 to September 1994, when the same protocols were used for analysis, but without use of mercuric chloride tablets for preservation. The comparison showed evidence of bias. Ammonium concentrations averaged 37 μg/L higher across all stations over the interval when mercuric chloride tablets were used (standard error, 7 μg/L). A similar analysis was conducted for the Kjeldahl nitrogen measurements leading to estimates of dissolved organic nitrogen; the mean bias was 150 μg/L (standard error, 25 μg/L). These biases are within the range reported by Schertz et al. (1994) for stations in Texas. Because handling and storage of the tablets were the probable causes of contamination, bias is expected to vary from one station to another. Therefore, mean concentrations of total nitrogen and nitrogen fractions for any given station were corrected for the bias associated with that station prior to statistical analysis of the data.

Results

As a first step in the statistical analysis, the three independent variables (elevation, area, runoff) were compared with each other. A correlation matrix showed that the independent variables are not significantly associated statistically ($p > 0.05$). As a second step, all three of the independent variables (logarithmically transformed here and in all other analyses) were entered into a stepwise multiple regression analyses of nitrogen yield. There were seven such multiple regressions: one for each of the nitrogen components listed in Table 2. In no case is watershed area or elevation significantly related to yield of total nitrogen or nitrogen fractions in these multiple regressions. For this reason, the remaining analyses focus only on runoff.

Table 3 summarizes the relationships between runoff and yield of total nitrogen and nitrogen fractions; all relationships are highly significant ($p < 0.001$) and account for high amounts of variance (Figure 2). Yield of total nitrogen and all nitrogen fractions increases with runoff. In all cases, the rate of increase in yield is less than the rate of increase in runoff (slope <1.0). The result is a decline in concentrations with increasing runoff, even though yield per unit area is increasing with increasing runoff (Table 3).

Discussion

Runoff explains a very high percentage of variance in the yield of total nitrogen and nitrogen fractions among minimally disturbed HBN watersheds. Lewis et al. (1999) reached the same conclusion for undisturbed tropical watersheds. The equations that were developed for tropical watersheds are very similar to those developed for the benchmark watersheds of the U.S. (Figures 2). Although rigorous statistical comparison of the relationships for tropical and temperate watersheds is problematic because the tropical watersheds cover a much greater span of physical conditions, the indication of the comparisons shown in Figure 2 is that tropical-temperate differences in relationships between runoff and yield are small and possibly insignificant.

Table 2. Summary of yield data (kg ha^{-1} y^{-1}) for the benchmark watersheds and estimates of atmospheric deposition for the same watersheds (kg ha^{-1} y^{-1}, inorganic N)

Site	NH_4^+-N	NO_3^--N	DIN	DON	TDN	PN	TN	Deposition
Young Womans Creek, PA	0.05	1.72	1.77	0.87	2.63	0.65	3.28	7.5
Scape Ore Swamp, S.C.	0.06	0.48	0.54	0.86	1.40	0.14	1.54	4.5
Falling Creek, GA	0.16	0.25	0.41	0.49	0.90	0.21	1.11	3.5
Sopchoppy, FL	0.26	0.44	0.70	2.34	3.04	1.45	4.49	3.5
Sipsey Fork, AL	0.15	0.29	0.43	0.37	0.80	1.59	2.40	5.5
Upper Twin Creek, OH	0.08	1.07	1.15	0.50	1.65	0.19	1.84	5.5
Popple River, WI	0.15	0.35	0.50	1.43	1.93	0.02	1.95	4.0
Rock Creek, MT	0.02	0.11	0.13	0.11	0.24	0.12	0.37	1.5
Castle Creek, SD	0.01	0.05	0.07	0.10	0.17	0.02	0.19	1.5
Encampment River, WY	0.33	0.45	0.78	2.09	2.87	0.88	3.75	1.5
Kiamichi River, OK	0.31	0.62	0.93	2.47	3.40	0.41	3.81	4.5
Vallecito Creek, CO	0.29	1.09	1.37	2.91	4.28	1.07	5.35	1.5
Wet Bottom Creek, AZ	0.05	0.08	0.13	0.16	0.29	0.13	0.42	1.0
Red Butte Creek, UT	0.12	0.21	0.33	0.73	1.06	0.12	1.18	1.5
Merced River, CA	0.44	0.74	1.17	1.27	2.45	2.11	4.55	1.5
Elder Creek, CA	0.36	1.03	1.39	1.83	3.21	0.90	4.11	1.5
Andrews Creek, WA	0.11	0.41	0.52	2.47	2.99	0.58	3.57	1.5
Cache Creek, WY	0.32	0.47	0.79	0.99	1.78	0.42	2.20	1.5
Minam River, OR	0.22	0.59	0.80	1.53	2.34	1.42	3.75	1.0
Mean	0.18	0.55	0.73	1.24	1.97	0.65	2.62	2.8
Standard Error	0.03	0.10	0.11	0.21	0.27	0.14	0.36	0.4

Similarity in the relationships between runoff and nitrogen yield for temperate and tropical watersheds is somewhat surprising. The nitrogen cycles of tropical latitudes are, except at the highest elevations, not interrupted by prolonged periods of low temperature. The interlatitudinal comparisons of Figure 2 indicates that the temperate winter, while highly significant seasonally to the rates of many processes affecting the nitrogen cycle, is of low significance to annual mass balance of N fractions and TN.

The study of tropical watersheds by Lewis et al. (1999) indicated that ratios of DIN to DON and PN to TN were influenced by watershed size. No such trend appears in the data for benchmark watersheds, but the test for such relationships by use of the data for benchmark watersheds is weak because the range of watershed sizes is small (2 orders of magnitude) by comparison with the range of data available for the tropics (7 orders of magnitude). Unfor-

Table 3. Relationship (log-log) of yield (kg ha^{-1} y^{-1}) to runoff (mm/yr) for total N and N fractions. Predicted yields and concentrations of total N and N fractions are shown for a range of runoff values. All relationships are significant at $p < 0.001$

Function	Constant	Slope	r^2	Yield as N, kg ha^{-1} y^{-1}				Concentration as N, μg/L			
				100	250	500	1000 mm	100	250	500	1000 mm
Ammonium N	–2.93	0.81	0.74	0.05	0.10	0.18	0.32	49	41	36	32
Nitrate N	–2.19	0.71	0.66	0.17	0.33	0.53	0.87	171	131	107	87
Diss. Inorg. N	–2.12	0.74	0.77	0.23	0.45	0.75	1.25	228	179	149	125
Diss. Org. N	–2.32	0.89	0.78	0.29	0.66	1.23	2.27	292	264	245	227
Tot. Diss. N	–1.94	0.84	0.84	0.54	1.15	2.05	3.66	536	460	410	366
Part. N	–2.90	0.97	0.54	0.11	0.27	0.53	1.03	112	108	106	103
Tot. N	–1.90	0.87	0.91	0.69	1.53	2.79	5.09	692	612	558	509

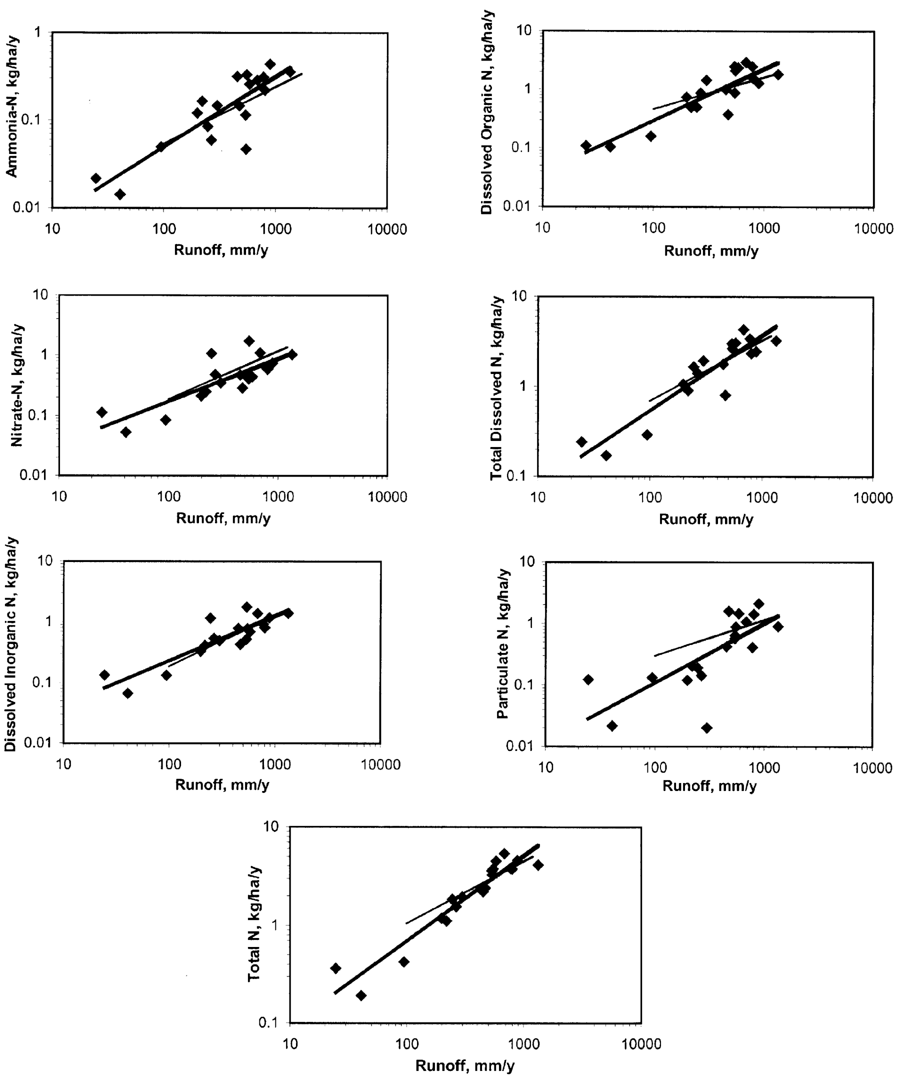

Figure 2. Relationships of runoff to total N and N fractions expressed as annual watershed yield for the 19 benchmark watersheds. The trend lines for tropical watersheds (narrow lines) from Lewis et al. (1999) are shown for comparison.

tunately, background nitrogen yields cannot be estimated empirically for very large watersheds at temperate latitudes.

Variables not included in this analysis (e.g. vegetation type, soil type, land-use history) may explain additional variance in nitrogen yields beyond what is explained by the three variables that were used here. Unfortunately, there are several impediments to the analysis of additional variables. Most important is that a large amount of variance (91% for total N) is already accounted for, indicating that an accounting of the small residual variance would require a much larger data set. Also, some of the additional variables most likely to relate to nitrogen yields (e.g. vegetation type) are categorical in nature and thus are more difficult to quantify.

The data for these watersheds confirm, along with data for the American tropics, that runoff is a master variable explaining interwatershed variance of yield for N and N fractions. The role of runoff in explaining N transport and N fractionation is remarkably insensitive to latitude.

Acknowledgements

This work was initiated as part of the International SCOPE N Project, which received support from both the Mellon Foundation and from the National Center for Ecological Analysis and Synthesis. I thank James Saunders for assistance with the statistical analysis, Sujay Kaushal for assistance with NADP data, Richard Alexander for providing me with access to and comments on the HBN data, Bob Howarth for encouragement of this project, and three reviewers for helpful comments.

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