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Precipitation control over inorganic nitrogen import–export budgets across watersheds: a synthesis of long-term ecological research

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ABSTRACT

We investigated long-term and seasonal patterns of N imports and exports, as well as patterns following climate perturbations, across biomes using data from 15 watersheds from nine Long-Term Ecological Research (LTER) sites in North America. Mean dissolved inorganic nitrogen (DIN) import–export budgets (N import via precipitation–N export via stream flow) for common years across all watersheds was highly variable, ranging from a net loss of $-0{\cdot}17 \pm 0{\cdot}09$ kg N $ha^{-1}mo^{-1}$ to net retention of $0{\cdot}68 \pm 0{\cdot}08$ kg N $ha^{-1}mo^{-1}$. The net retention of DIN decreased (smaller import–export budget) with increasing precipitation, as well as with increasing variation in precipitation during the winter, spring, and fall. Averaged across all seasons, net DIN retention decreased as the coefficient of variation (CV) in precipitation increased across all sites ($r^2 = 0{\cdot}48$, $p = 0{\cdot}005$). This trend was made stronger when the disturbed watersheds were withheld from the analysis ($r^2 = 0{\cdot}80$, $p < 0{\cdot}001$, $n = 11$). Thus, DIN exports were either similar to or exceeded imports in the tropical, boreal, and wet coniferous watersheds, whereas imports exceeded exports in temperate deciduous watersheds. In general, forest harvesting, hurricanes, or floods corresponded with periods of increased DIN exports relative to imports. Periods when water throughput within a watershed was likely to be lower (i.e. low snow pack or El Niño years) corresponded with decreased DIN exports relative to imports. These data provide a basis for ranking diverse sites in terms of their ability to retain DIN in the context of changing precipitation regimes likely to occur in the future. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS long-term ecological research; inorganic nitrogen retention; watershed budget; synthesis; disturbance; precipitation; flashiness; drought

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INTRODUCTION

Potential changes in the major drivers of watershed N retention have received considerable scrutiny in recent decades. Increases in precipitation have been documented for large areas across North America in the last 40 years (Probst and Tardy, 1987; Groisman *et al.*, 1999; Dore, 2005). Precipitation patterns are also becoming more variable, with more occurrences of extreme rain events and drought in recent decades (Tsonis *et al.*, 1996; Easterling *et al.*, 2000; Kunkel *et al.*, 2003; Groisman *et al.*, 2005). Furthermore, human activities are now responsible for 40–60% of atmospheric inorganic nitrogen (e.g. Vitousek *et al.*, 1997), and dissolved inorganic nitrogen (DIN; NH_4^+ and NO_3^-) deposition is an increasingly dominant source of total N loading in terrestrial systems throughout the world (Green *et al.*, 2004). Elevated DIN deposition rates observed in recent decades have had adverse effects on ecosystem function, including foliar nutrient imbalances (Pardo and Driscoll, 1996), soil acidification, and increased metal mobility (Nellemann and Thomsen, 2001; see also Ring *et al.*, 2006). Moreover, increased inorganic N deposition may exceed the capacity of biota to retain N in terrestrial ecosystems (Aber *et al.*, 1989; Fenn *et al.*, 1998); this DIN can move with the mass flow of water into streams (e.g. Band *et al.*, 2001), which has implications for water quality and aquatic ecosystem function.

The primary pathways of DIN transfer and export from terrestrial ecosystems are by hydrologic transport into ground water, loss to streams by soil erosion, gaseous fluxes, and surficial flow (e.g. Fenn *et al.*, 1998). Increases in water flow through watersheds due to changes in precipitation may flush more DIN and other nutrients into ground water and streams (Lewis and Grant, 1979; Mitchell *et al.*, 1996; Boyer *et al.*, 1997; Creed and Band, 1998). In addition, increased variation in precipitation alters the internal cycling and export of DIN from terrestrial systems. For example, laboratory studies have shown increased inorganic N

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mineralization (Cabrera, 1993) and increased nitrification potential (Fierer and Schimel, 2002) after successive drying and re-wetting cycles in soils. Moreover, aboveground net primary production, which is dependent on N release from mineralization, increased significantly as the magnitude of high rainfall events increased relative to mean rainfall across 11 North American ecosystems (Knapp and Smith, 2001). These findings suggest that terrestrial inorganic N retention and loss are influenced by changes in precipitation (see also Dumont *et al.*, 2005; Howarth *et al.*, 2006), but exactly how changes in precipitation affect patterns of DIN retention and loss from watersheds across biomes is still poorly understood.

There is a well established body of work exploring disturbance and climate perturbation effects on watershed DIN retention (Likens and Bormann, 1974; Vitousek and Reiners, 1975; Vitousek *et al.*, 1979, 1982), particularly with respect to the role disturbance plays in disrupting plant uptake (e.g. Houlton *et al.*, 2003). Disturbances contribute to the natural variability of a system, and therefore, provide an opportunity to understand possible changes in DIN retention under altered hydrologic conditions. For example, disturbances that increase the magnitude of runoff from terrestrial systems into streams, such as in floods (Dyrness *et al.*, 1996; Swanson *et al.*, 1998) or hurricanes (McDowell and Asbury, 1994; Schaffer *et al.*, 2000) are likely to decrease inorganic N retention within watersheds. Climate phenomena may also decrease watershed N retention, such as with increased runoff of water within a watershed after a period of high snowfall (Kane *et al.*, 1992; Stottlemyer and Toczydlowski, 2006), or after freezing conditions (Mitchell *et al.*, 1996). However, co-occurring changes in climate variables (such as a decrease in temperature with increased precipitation) can have confounded effects on ecosystem processes related to DIN retention (e.g. Greenland and Kittel, 2002; Greenland *et al.*, 2003).

In order to investigate patterns of DIN import and export across ecosystems and over time, we synthesized precipitation, stream discharge, and DIN concentration data previously published in long-term ecological research (LTER) studies from 15 watersheds across 9 sites in North America and Puerto Rico (Webster *et al.*, 1985; Meyer *et al.*, 1993). These watersheds were selected based on the availability of data, and were typically forested (non-urbanized) so as to facilitate cross-site comparisons. The objectives of this study were, (1) to examine long-term patterns of watershed N retention among sites using DIN import–export budgets, (2) to relate changes in watershed DIN imports and exports to patterns of precipitation, and (3) to explore the effect of precipitation seasonality on net DIN retention. Since watershed DIN retention can decrease during climate phenomena or disturbances, which increase the magnitude and variation of water runoff within a catchment, we predicted that observed maxima and variation in precipitation would correlate with periods when DIN exports more closely matched or exceeded imports in watersheds across the LTER network.

METHODS

Data acquisition

The LTER network was established in 1980 to further ecological understanding through long-term interdisciplinary research and the synthesis of information across broad spatial scales. Within this network, our site selection criteria required at least 3 consecutive years of data comprised of monthly means of precipitation, precipitation DIN and chloride (Cl^-) concentration, stream discharge, and stream DIN and Cl^- concentration. We identified seven LTER and two non-LTER sites that fulfilled these criteria (Figure 1; Table I). These sites were generally forested, non-urbanized watersheds representing reference conditions. Not all LTER sites collect the same data, nor have they all been monitoring for similar periods of time, so it was not possible to use all sites or the full temporal extents of data. To directly compare rates of N retention among sites, seasonal means for common years across sites were used.

Wet deposition data for this study were either collected by the National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu) or by site representatives (i.e. USDA Forest Service; Table I). Precipitation at each station is collected weekly according to strict protocols adhering to those of the Central Analytical Laboratory in Illinois, so that trends in precipitation chemistry may be compared among different regions of the USA.

Study watersheds

The forested catchments used in this study varied considerably in their climate, dominant vegetation, and soil parent material (Table II), and encompassed a wide range in water inputs through precipitation and losses from evapotranspiration and streamflow (Figure 2). The Gila River and Bonanza (BNZ) Creek sites were among the driest examined, with mean actual evapotranspiration (AET) comprising approximately 90 and 60% of the respective precipitation inputs at these locations (Table II, Figure 2). The Luquillo (LUQ) and Coweeta (CWT) watersheds were among the wettest examined, with mean AET comprising approximately 40–30% of the respective precipitation inputs. The colder sites studied exhibit mean annual temperatures of approximately −2 C (BNZ), −3 C (NWT), and 0 C (HBR), and the warmer sites exhibit mean annual temperatures of approximately 8 C (AND), 9 C (KBS), 13 C (CWT), 15 C (WBR, Gila), and ~22 C (LUQ).

There is also considerable variation in the physical characteristics affecting retention structure and flow regime at the different LTER watersheds included in this analysis, as previously reviewed by Meyer *et al.*, 1993. The seasonal pattern of discharge ranges from sites heavily influenced by a pulse of snowmelt (e.g. NWT, BNZ, HBR, KBS), to sites where storms can lead to high variation in runoff (AND, CWT, LUQ), or sites with groundwater influence (WBR W; Mulholland, 1997). At BNZ, streams are frozen throughout the winter, and soils within the catchments can remain frozen year round, which affects the pathways for DIN export

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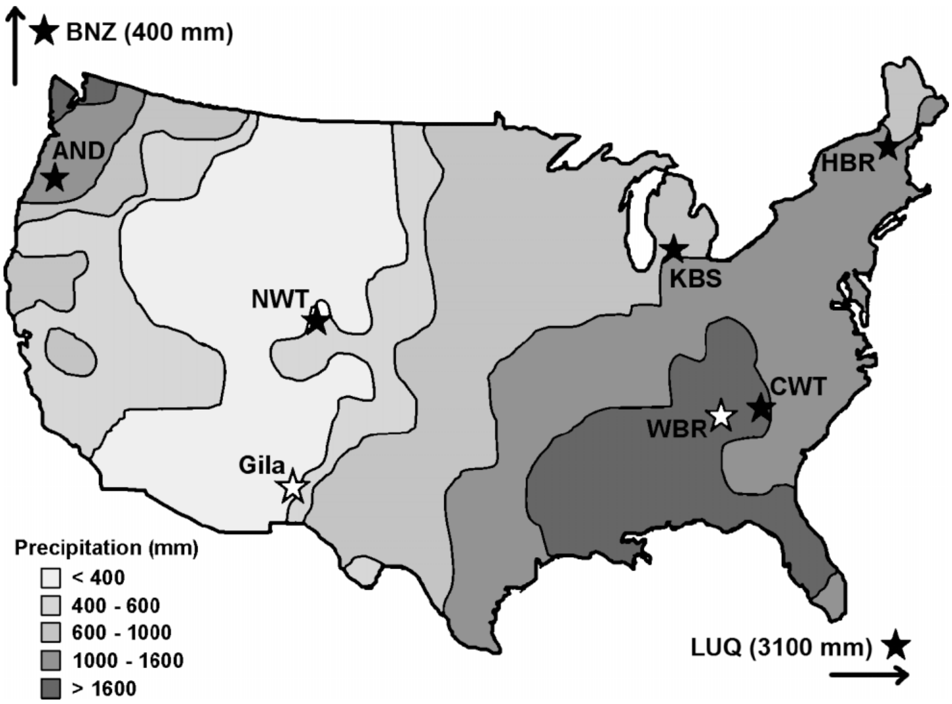

Figure 1. Map of LTER (solid shapes) and non-LTER (open shapes) watershed sites included in this synthesis. The site codes are AND (H.J. Andrews LTER (OR): watersheds Mack, 2, 9, and 10), BNZ (Bonanza Creek LTER (AK): watershed C4), CWT (Coweeta LTER (NC): watersheds 18 and 36), HBR (Hubbard Brook LTER (NH): watersheds 5 and 6), KBS (Kellogg Biological Station (MI): Bullet, Ransom, and South Eagle watersheds), NWT (Niwot Ridge LTER (CO): Albion inflow), WBR (Walker Branch River (TN): east and west forks), the Gila River (NADP AZ99), and LUQ (Luquillo LTER (PR): Quebrada Sonadora). Contour map (or inset values for LUQ and BNZ) illustrates mean annual precipitation (National Atmospheric Deposition Program, 2006).

Table I. Description and location information for the watershed sites.

Experimental Watershed	Site	Latitude and Longitude	Watershed Area (ha)	Period of Record (y)	Site Designation
H.J. Andrews	AND M	44 14′N 122 10′W	640	15	USFS/LTER NADP
	AND 2	44 14′N 122 10′W	60·3	15	USFS/LTER NADP
	AND 9	44 14′N 122 10′W	8·5	15	USFS/LTER NADP
	AND 10	44 14′N 122 10′W	10·2	15	USFS/LTER NADP
Bonanza Creek	BNZ C4	65 10′N 147 30′W	1000	3	USFS/LTER NADP
Coweeta	CWT 18	35 00′N 83 30′W	12·5	22	USFS/LTER NADP
	CWT 36	35 00′N 83 30′W	48·6	22	USFS/LTER NADP
Gila River	Gila	33 4′N 109 52′W	2×10^6	15	NADP SEV LTER
Hubbard Brook	HBR 5	43 56′N 71 45′W	21·9	27	USFS/LTER
	HBR 6	43 56′N 71 45′W	13·2	35	USFS/LTER
Kellogg Biol. Station	KBS E	42 24′N 85 24′W	1074	3	NADP/LTER
Luquillo	LUQ QS	18 15′N 65 45′W	6·3	6	USFS/LTER El Verde
Niwot Ridge	NWT	40 3′N 105 36′W	710	8	NADP/LTER
Walker Branch	WBR E	35 57′N 84 17′W	59·1	8	NADP/ORNL
	WBR W	35 57′N 84 17′W	38·4	13	NADP/ORNL

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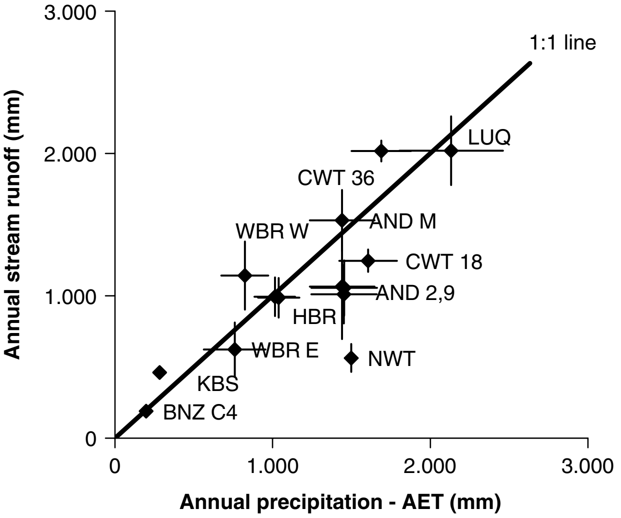

Figure 2. Annual precipitation minus published estimates of mean actual evapotranspiration (AET) increases with mean annual stream runoff across all sites, with a slope not different from 1 (linear coefficient ± SE: $\beta_0 = 127\cdot92 \pm 222\cdot57$, $\beta_1 = 0\cdot78 \pm 0\cdot17$; $r^2 = 0\cdot64$, $p < 0\cdot001$).

(e.g. O'Donnell and Jones, 2006). Downed coarse woody debris and tree roots may afford additional structure in stream channels at some sites (AND, CWT, HBR, KBS, WBR), but are rare or absent at others (BNZ, LUQ, NWT, Gila). Moreover, the extent of the hyporheic zones across these LTER sites ranges from a depth of at least 1 m into the sediments (e.g. BNZ, LUQ) to sites with less than 0 · 1 m of sediment above bedrock within the catchments (CWT, HBR, NWT) (see review by Meyer *et al.*, 1993). There is also considerable variation in stream channel gradients across sites (Table II), which suggests changes in stream flashiness and water residence time within a catchment.

Analyses

Our general approach was to use a mass-balance model to estimate net DIN retention (import–export), and then to compare net DIN retention in watersheds from various biomes to differences in precipitation regime. We analysed both precipitation and stream chemistry data on monthly and yearly intervals. Where available data were not in the form of monthly means, we adjusted data to reflect monthly mean values through weighted averaging based on the time period of collection, either daily or weekly, within each month. We calculated the monthly import of DIN as the product of the monthly mean precipitation and the precipitation–weighted mean for wet DIN deposition. Stream export was calculated as the product of mean monthly stream discharge and flow–weighted mean for stream DIN concentration, and was standardized to a watershed area. Mean monthly DIN and Cl^- import–export budgets were then compared across all sites. A positive DIN import–export value reflects net retention of DIN within the watershed, whereas a negative number reflects a net loss. Mean annual DIN import and export were derived from flow-weighted monthly averages for a given year at 13 of the 15 watersheds with complete annual records. In cases where there were insufficient data to characterize a monthly summary period, rendering an annual record incomplete by 1 or 2 months (NWT and LUQ), we used the long-term mean for that month across all years measured.

Care has to be taken in comparing elemental import–export budgets with variability in precipitation because the amount of precipitation is used directly in import–export budget calculations. Since it is generally assumed that Cl^- does not react biologically or chemically in

Table II. Biophysical properties of the study locations.

Experimental Watershed	Climate	AET[1] (mm)	Mean channel gradient (%)[2]	Dominant Vegetation	Dominant Soil order/genesis[3]
H.J. Andrews	Maritime Wet/temperate	501	10	Coniferous forest	Inceptisols/Alfisols clay-loam, silt
Bonanza Creek	Boreal	214	1	Coniferous mixed forest	Gelisol; Inceptisol histic-organic, loess silt
Coweeta	Wet/temperate	680	19	Deciduous forest	Typic Dystrochrept sandy & clay-loam
Gila River	Arid desert	200	<1	Shrub/Deciduous	Aridisols sand, sandy-loam
Hubbard Brook	Temperate	500	28	Deciduous forest	Spodosols sandy-loam
Kellogg Biol. Station	Temperate	540	<1	Secondary growth Deciduous	Typic Hapludalfs fine- and coarse-loam
Luquillo	Tropical	1338	24	Deciduous forest	Oxisols and Ultisols clay & clay-loam
Niwot Ridge	Subalpine	546	10	Shrub/Conifer forest	Cryochrepts & Cryumbrepts sandy gravel/sandy loam
Walker Branch	Wet/temperate	610	4	Deciduous forest	Paleudults silt loam

[1] Actual Evapotranspiration.

[2] Determined from: *AND, BNZ, CWT, HBR, NWT*: (Meyer *et al.*, 1993); *Gila*: Hawley *et al.*, 2000; *KBS*: Hamilton *et al.*, 2001, pers. comm.; *LUQ*: McDowell and Asbury, 1994; *WBR*: Mulholland, 1997.

[3] Information from respective LTER websites and: *AND*: Bernsten and Rothacher, 1959; Dyrness, 1969; *BNZ*: Ping *et al.*, 2005; *CWT*: Hatcher, 1988; Walbridge *et al.*, 1991; *Gila*: Baker *et al.*, 2001, NADP AZ99; *LUQ*: Johnston, 1992; *NWT*: Williams *et al.*, 1997; *WBR*: Johnson *et al.*, 2007.

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watersheds, and that the major source of Cl^- is precipitation, we also calculated Cl^- import–export budgets for all sites in the same manner as was done for DIN. Import–export budgets of the relatively conservative Cl^- element were compared with DIN import–export budgets across all sites.

For comparisons among catchments, we chose two 3-year time periods (1989–1991 and 2001–2003). Two sites, AND and WBR (see Figure 3), contained complete datasets for both time periods; monthly estimates for these sites represent averaged values across both time periods. We examined seasonal changes in DIN import–export budgets, means, and variances, over these common years. Seasonal means were taken across 3 months for a given season, across a 3-year time period (e.g. winter: December, January, February (DJF), 1989–1991).

We estimated flashiness for each catchment over the 3-year period using the Richards–Baker (R–B) Flashiness Index (Baker *et al.*, 2004):

$$\text{R–B Index} = \frac{\sum_{i=1}^{n} |Q_i - Q_{i-1}|}{\sum_{i=1}^{n} Q_i} \qquad [1]$$

where Q is mean monthly flow (L ha^{-1} $month^{-1}$) and i is the monthly time-step ($n = 12$). The R–B index was originally developed to characterize variation in stream discharge over daily time-steps and represents oscillations in Q relative to total Q for a given time period (Baker *et al.*, 2004). We modified the R–B index to reflect variation in monthly Q relative to total Q for a yearly time-step so that the temporal scope of the flashiness index would coincide with our DIN import–export budgets. We compared a simple estimate of soil water storage plus AET (precipitation inputs : stream outflow) with DIN import–export budgets by season for common years across all sites in order to investigate any lag effects associated with the timing of solute transfer by streams relative to precipitation inputs.

Linear regression was used to analyse correlations between annual DIN import–export budgets and discharge and precipitation estimates. Differences among sites were tested using one-way analysis of variance (ANOVA) pair-wise comparisons with Scheffe error protection. Pearson correlation coefficients demonstrated relationships between variables ($\alpha = 0{\cdot}05$). The coefficients of variation in precipitation were non-normally distributed across all sites and were natural-log transformed in regression analyses. Potential outliers were investigated through examination of standardized residual errors. Descriptive statistics and regressions were calculated with Analyze-it statistical module (Analyze-it Software, Ltd. Leeds, UK) and PC SAS (SAS institute, Cary, NC).

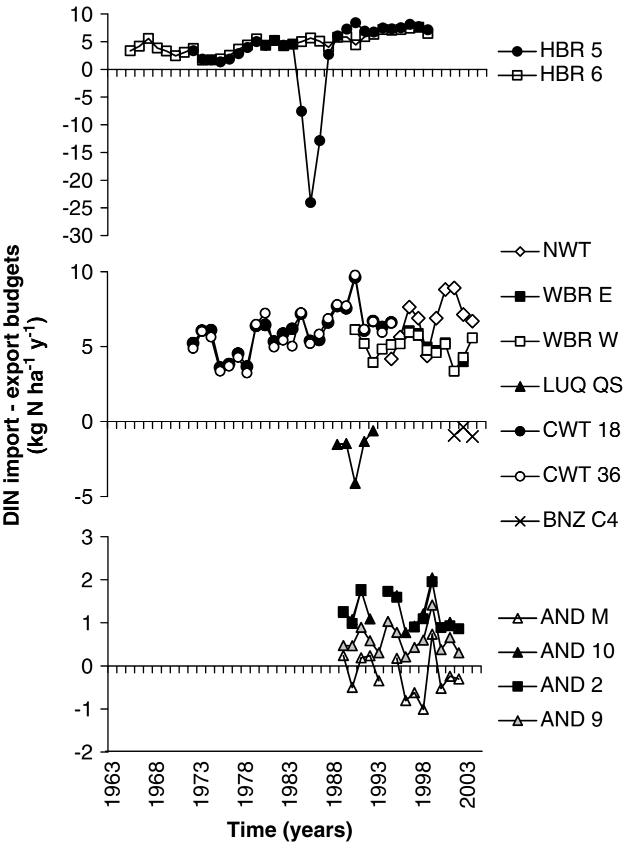

Figure 3. Patterns of annual DIN retention (import–export; kg N ha^{-1} y^{-1}) across 13 watersheds over time. Values <0 indicate DIN loss whereas positive values indicate net retention within a watershed. For clarity, panes separate watersheds into groups exhibiting similar levels of import–export.

RESULTS

Annual patterns of DIN import and export among watersheds

Across all sites and years of available data, mean import of DIN (from precipitation) ranged from 0.29 kg N ha^{-1} y^{-1} at BNZ to 7 · 33 kg N ha^{-1} y^{-1} at NWT and mean annual export of DIN (in stream outflow) ranged from 0 · 09 kg N ha^{-1} y^{-1} at CWT to 4 · 26 kg N ha^{-1} y^{-1} at LUQ (Table III). Mean DIN import–export budgets varied in magnitude among the eight watersheds and over the 39 years of study, ranging from means of −1·82 to 6 · 72 kg N ha^{-1} y^{-1}. DIN import–export budgets for individual years were highly variable across all sites, with values ranging from −24·05 to 9 · 77 kg N ha^{-1} y^{-1} (Figure 3). The lowest annual DIN import–export budgets co-occurred with years exhibiting the highest precipitation observed across all years at 6 of the 13 sites with complete annual datasets (Table IV).

In general, temperate deciduous watersheds [Hubbard Brook (HBR), Coweeta (CWT), and Walker Branch (WBR)] had higher net DIN retention than did old-growth, coniferous [H.J. Andrews (AND)], boreal [Bonanza Creek (BNZ)], and tropical [Luquillo (LUQ)] watersheds (Figure 3). Mean annual DIN exported in streams expressed as a percent of DIN imported from

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Table III. Mean and maximum annual imports and exports of DIN, Cl^- measured across the period of record (as in Table I).

Site[a]	DIN Import (kg N ha^{-1} y^{-1})			DIN Export (kg N ha^{-1} y^{-1})			Mean Chloride (kg Cl ha^{-1} y^{-1})	
	mean	max	year	mean	max	year	Import	Export
AND 10	1·3	2·1	1999	0·1	0·2	1996	5·8	22·9
AND 2	1·3	2·1	1999	0·1	0·2	1998	5·8	11·7
AND 9	1·3	2·1	1999	0·7	1·0	1991	5·8	5·2
AND M	1·3	2·8	1999	1·4	2·1	1998	5·8	12·0
BNZ C4	0·3	0·4	2002	1·1	1·3	2003	0·1	0·7
CWT 18	6·1	9·8	1990	0·1	0·2	1979	5·4	6·5
CWT 36	6·2	10·1	1990	0·3	0·5	1993	5·4	11·3
HBR 5	7·0	8·9	1990	4·1	30·4	1985	2·4	3·6
HBR 6	7·1	8·9	1990	2·4	7·2	1973	2·5	4·4
LUQ QS	2·5	3·2	1989	4·3	7·3	1990	66·7	181·8
NWT	7·3	9·2	2001	0·6	1·0	1995	1·5	0·8
WBR E	5·3	6·2	1996	0·1	0·2	1996	3·1	7·2
WBR W	5·3	6·4	1990	0·3	0·5	1991	3·0	13·3

[a] For site descriptions and DIN imports and exports reflecting the ranges shown here see: *AND* (Vanderbilt *et al*., 2003), *BNZ* (Jones *et al*., 2005), *CWT* (Swank and Vose, 1997), *HBR* (Likens *et al*., 1970; Bernhardt *et al*., 2005), *LUQ* (McDowell and Asbury, 1994; Schaffer *et al*., 2000), *NWT* (Hood *et al*., 2003; import value may be inflated by 32% owing to blowing snow; Burns, 2003), and *WBR* (Mulholland, 2004). *KBS* and *Gila* only had seasonal data, not complete annual datasets for this comparison.

Table IV. Maximum and minimum annual import—export budgets are compared to the years in which maximum precipitation occurred.

Site	Precipitation (mm y^{-1})			Import—Export (kg N ha^{-1} y^{-1})				
	mean	max	year	mean	max	year	min	year
AND 10	2142	2751	1998	1·3	2·0	1999	0·8	1996
AND 2	2142	2751	1998	1·3	2·0	1999	0·9	2002
AND 9	2142	2751	1998	0·6	1·4	1999	0·2	1996
AND M	2142	2751	1998	−0·2	0·7	1999	−1·0	**1998**[a]
BNZ C4	400	488	2003	−0·8	−0·4	2002	−1·0	**2003**[a]
CWT 18	2056	2677	1978	6·0	9·6	1990	3·6	**1975**[a]
CWT 36	2060	2739	1978	5·9	9·8	1990	3·2	**1978**[a]
HBR 5	1417	1813	1996	2·9	8·4	1990	−24·0	1985
HBR 6	1425	1825	1973	4·7	7·6	1997	1·7	**1973**[a]
LUQ QS	3100	4033	1990	−1·8	−0·6	1992	−4·1	**1990**[a]
NWT	2175	2729	1996	6·7	8·9	2001	4·2	1994
WBR E	1312	1645	1996	5·1	6·0	**1996**[a]	4·0	2002
WBR W	1407	1679	1990	5·0	6·1	**1990**[a]	3·4	2001

[a] Denotes when the year of either maximum or minimum annual retention (Import—Export) matched the year of maximum annual precipitation.
CWT_18 had the second lowest annual Import–Export in 1978.

precipitation varied widely across sites, with values ranging from 2, 3, and 34% in some of the temperate deciduous forest watersheds (CWT 18, WBR E, and HBR 6, respectively), and from means of 112, 171, and 367% in the coniferous, tropical, and boreal watersheds (AND M, LUQ QS, and BNZ C4, respectively).

Monthly and seasonal patterns of DIN retention among watersheds

River flashiness estimates on monthly time-steps did not explain any of the variance in DIN import–export across sites ($p = 0·73$, $n = 14$; Figure 4). Average monthly river discharge was significantly higher in winter and spring across all watersheds (ANOVA, $F_{3,56} = 5·29$, $p = 0·003$), though there were no seasonal differences in mean monthly precipitation across all watersheds (ANOVA, $F_{3,56} = 1·99$, $p = 0·13$). Mean monthly DIN imports varied widely for common years across all sites, ranging from relatively low imports of 0·03 ± 0·01 (BNZ) and 0·08 ± 0·01 (AND) to relatively high imports of 0·47 ± 0·08 (CWT) and 0·48 ± 0·13 (KBS). DIN import–export budgets relative to changes in imports across sites [(DIN import–export)/DIN import] declined as the coefficient of variation (CV) in mean monthly precipitation increased across sites [logarithmically transformed; $r^2 = 0·36$, $p = 0·02$ (LUQ removed, standardized residual $= -2·5$)]. Net DIN retention (import–export) also decreased as the CV in mean monthly precipitation increased across all sites ($r^2 = 0·32$, $p = 0·03$).

Logarithmically transformed DIN import–export budgets decreased as the CV in mean monthly precipitation increased across all sites in the winter ($r^2 = 0·28$,

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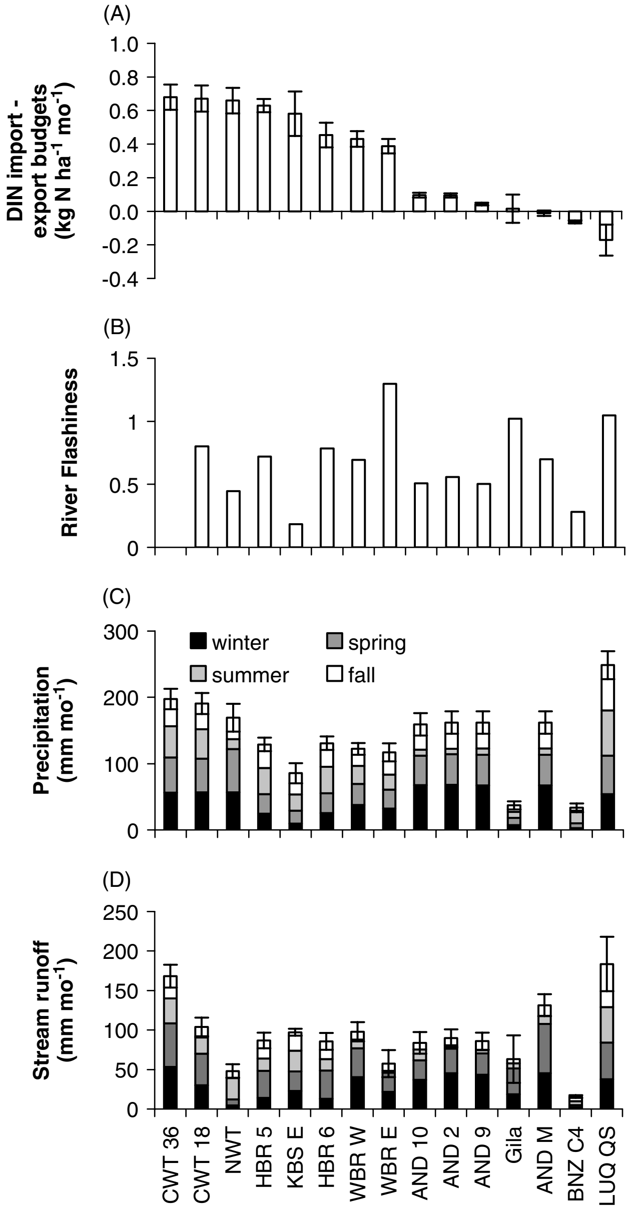

Figure 4. (A) Mean monthly DIN import–export (kg N ha^{-1} mo^{-1}), (B) river flashiness (monthly R–B Index), (C) mean monthly precipitation (mmmo^{-1}) and (D) mean monthly stream runoff (mmmo^{-1}) are presented for the periods between 1989–1991 and 2001–2003. If a site is represented in both time periods (AND and WBR W), the data presented are means from both time periods. Error bars are standard errors of the mean. Stacked bars represent proportion of total discharge or total precipitation occurring in each season (Winter: DJF, Spring: MAM, Summer: JJA, and Fall: SON).

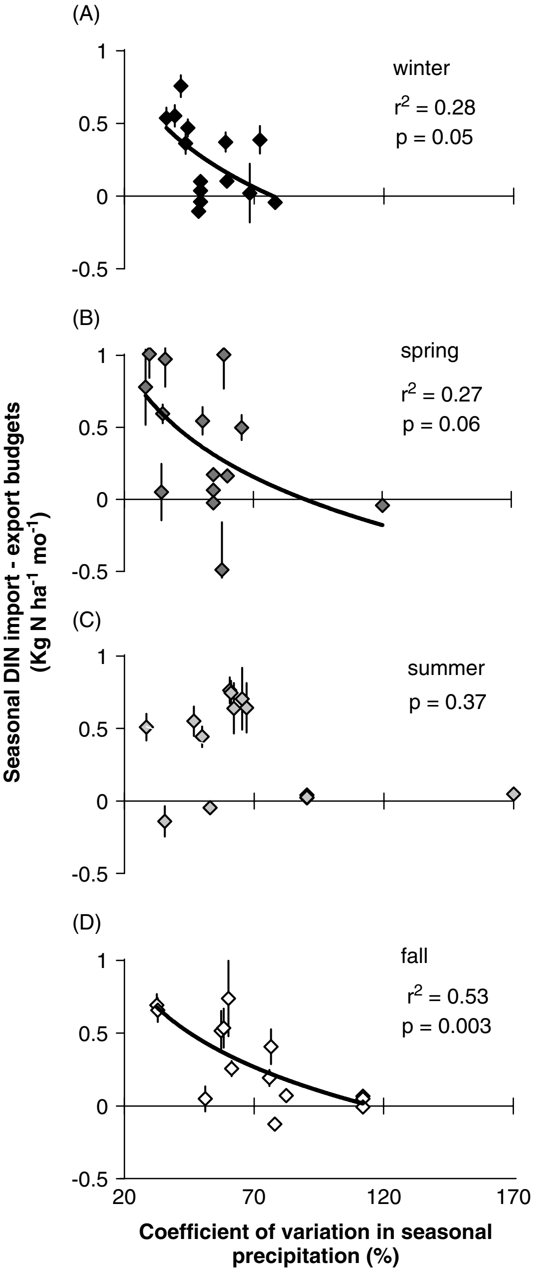

Figure 5. The relationships between coefficient of variation in precipitation and monthly DIN import–export are presented by season across common years (1989–1991 and 2001–2003; Winter: DJF, (A) Spring: MAM, (B) Summer: JJA, (C) Fall: SON, (D) Shading corresponds to seasonal changes presented in Figure 4(C),(D). Error bars are standard errors of the mean values.

$p = 0{\cdot}05$), spring ($r^2 = 0{\cdot}27$, $p = 0{\cdot}06$), and fall ($r^2 = 0{\cdot}53$, $p < 0{\cdot}003$), but not in the summer ($p = 0{\cdot}37$; Figure 5). Import–export budgets relative to changes in imports across sites [(DIN import–export)/DIN import] also declined with increased precipitation CV in the winter ($r^2 = 0{\cdot}32$, $p = 0{\cdot}04$) and spring ($r^2 = 0{\cdot}46$, $p = 0{\cdot}008$). In the summer months, DIN import–export increased marginally with AET across all sites ($r^2 = 0{\cdot}25$, $p = 0{\cdot}07$), but our estimates of AET could not explain any of the variation in net DIN retention across all seasons ($p = 0{\cdot}19$). Net DIN retention investigated across just the watersheds influenced by a winter snow pack (BNZ C4, HBR 5, HBR 6, KBS E, NWT) was negatively related to increased precipitation CV in the winter ($r^2 = 0{\cdot}85$, $p = 0{\cdot}03$, $n = 5$), and across the means for all seasons ($r^2 = 0{\cdot}75$, $p = 0{\cdot}06$, $n = 5$). Net DIN retention during the snow-free seasons (spring and summer) was also negatively related to increased precipitation CV across all sites when LUQ QS was removed from the analysis (standardized residual >2; $r^2 = 0{\cdot}51$, $p = 0{\cdot}006$).

Mean DIN import–export across all seasons decreased as the CV of seasonal precipitation increased across all watersheds ($r^2 = 0{\cdot}48$, $p = 0{\cdot}005$). This relationship

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became stronger when the tropical watershed (LUQ QS) was removed from the analysis (standardized residual = −2·8; Figure 6(A); $r^2 = 0{\cdot}81$, $p < 0{\cdot}001$, $n = 14$), and also when the other disturbed watersheds (AND 10, HBR 5, KBS E) were removed from the analysis ($r^2 = 0{\cdot}80$, $p < 0{\cdot}001$, $n = 11$). There were no apparent threshold relationships between DIN import–export and variability in precipitation, either within a season (Figure 5) or across all seasons (Figure 6(A)). Trends were logarithmically transformed to meet assumptions of normality and standardized residuals were normally distributed (Shapiro Wilk = 0·9, p ≥ 0·3).

In contrast with DIN, Cl^- exports were conservative relative to imports across sites, with exports only significantly exceeding imports at the LUQ and Gila watersheds (Figure 6(B)). Cl^- import–export budgets did not change with changes in precipitation, or with increasing CV of seasonal precipitation across all watersheds (Figure 6(B)).

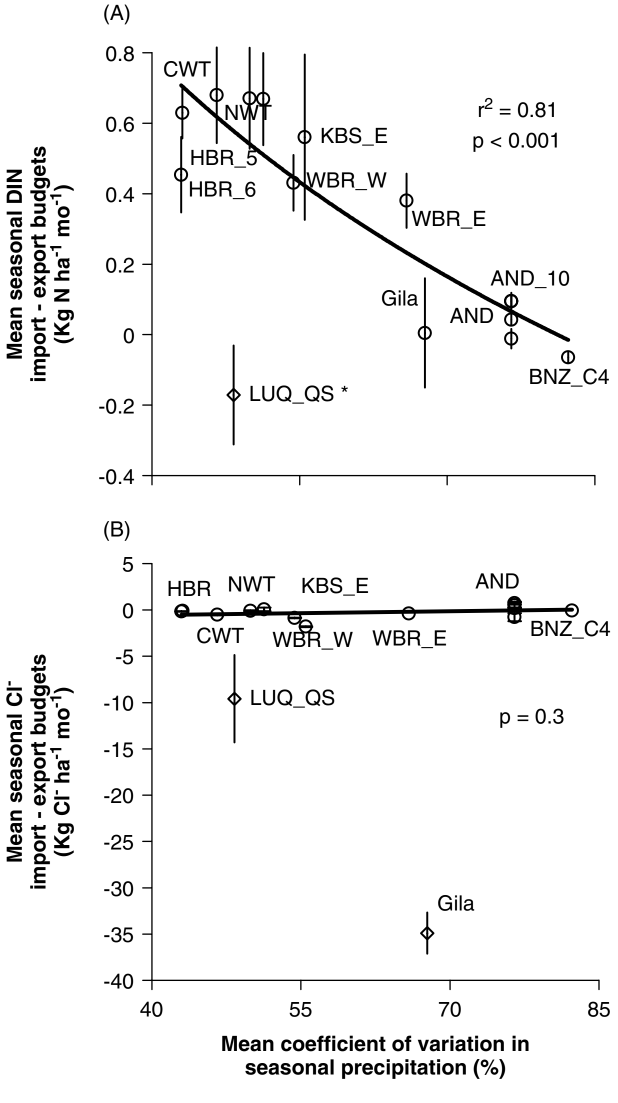

Figure 6. (A) Mean DIN import–export budgets across seasons decreased with increasing coefficient of variation in seasonal precipitation across all watersheds. (B) Mean Cl^- import–export budgets were only different at the LUQ and Gila sites, and did not change with precipitation across all sites. Figures reflect data collected between 1989–1991 and 2001–2003. If a site is represented in both time periods (AND sites and WBR W) the data presented is the mean of the means for both time periods. Asterisk denotes an outlier not included in the logarithmic regression in (A) (standardized residual for LUQ QS = −2·8). Coefficients describing the logarithmic regression (A) are $\beta_0 = 4{\cdot}89 \pm 0{\cdot}63$, $\beta_1 = -1{\cdot}11 \pm 0{\cdot}15$. Error bars are standard errors of the mean values.

DIN import–export budgets after disturbances

While many studies have shown changes in DIN retention following disturbance within a watershed, we feel it is valuable to highlight some of the relationships across sites, as high and low periods of net DIN retention coincided with discrete climate perturbations within the different watersheds studied. At NWT, net DIN retention was significantly higher during the low snow pack years of 2000–2001 (1-way ANOVA between subjects, $F_{1,7} = 7{\cdot}72$, $p = 0{\cdot}02$). Net DIN retention increased at AND (2 and 9) during the El Niño events of 1991 and 1994 (1-way ANOVA between subjects, $F_{3,20} = 4{\cdot}77$, $p = 0{\cdot}04$). However, interpreting any changes in DIN import–export during the El Niño event of 1997 at AND is obscured by the extensive flooding that had occurred there in 1996–1997 (Dyrness *et al.*, 1996), which coincided with a peak in DIN loss. A spike in DIN loss from the LUQ QS watershed coincided with Hurricane Hugo in 1989, with net DIN retention declining by a factor of three following the disturbance (Figure 3). In all cases, DIN import–export returned to pre-climate anomaly levels in <2 years.

DISCUSSION

Controls on seasonal flushing of DIN

Considerable seasonal variation in stream DIN concentration has been documented across a wide range of catchments in temperate biomes (e.g. Likens *et al.*, 1977; Hill, 1986; Brooks *et al.*, 1998). In spring, an increase in stream NO_3^- concentration often occurs in watersheds dominated by snowmelt hydrologic regimes (Mitchell *et al.*, 1996; Sickman *et al.*, 2002; Hood *et al.*, 2003; Stottlemyer and Toczydlowski, 2006; Judd *et al.*, 2007). While the magnitude of the increase in stream NO_3^- concentration is a function of the timing of snowmelt or rainfall relative to the size of the soil DIN pool, the hydrological connectedness of the watershed also plays a major role in DIN export and retention within a catchment (Creed and Band, 1998; Stieglitz *et al.*, 2003).

In this study, variability in seasonal precipitation explained most of the variation in DIN import–export budgets across watersheds for all seasons except in the summer months. The widening gap between exports and imports may be related to a disconnect in the hydrologic connectivity of hill slopes to streams by sub-surface flow (Stieglitz *et al.*, 2003). One potential mechanism that is consistent with the observed relationships is that only during wet states are hill slopes connected to streams through sub-surface flow, resulting in a relatively high export of nutrients. During drier periods (i.e. summer), connectivity declines and the export of nutrients from

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catchments to streams decreases. Increased AET in the summer reduces soil water storage relative to the cooler, wetter months (with lower AET), thereby decreasing the period in which water inputs exceed soil water holding capacity within a catchment. Moreover, heightened uptake of DIN by vegetation during the growing season could obscure trends between net DIN retention (import–export) and precipitation variability during the summer months. For example, Knapp and Smith (2001) observed a strong correlation between above-ground net primary production and precipitation across 11 diverse LTER sites in North America. Similarly, we observed a positive relationship between net DIN retention and mean precipitation only during the growing season across the LTER sites in this study ($r^2 = 0{\cdot}48$, $p = 0{\cdot}006$, $n = 14$; LUQ removed: standard residual >2). This might suggest that a higher potential for net primary production (owing to higher precipitation; Knapp and Smith, 2001) is conducive to higher net DIN retention during the growing season, when making comparisons across diverse sites.

Across watersheds, net DIN retention decreased as precipitation variability increased. Periods when DIN exports increasingly exceeded imports corresponded with periods of high rainfall relative to the mean. In many cases, periods of the lowest net DIN retention co-occurred with periods with the highest precipitation measured (e.g. Table IV). This suggests that monthly precipitation maxima encompassed both the fast and slow leaching pathways for solutes when there was more likely to be a higher degree of hydrologic connectedness of lateral flows within the catchments. Other possible predictor variables for DIN export, such as stream flashiness (Baker *et al*., 2004; Gustafson *et al*., 2004), reflect shorter-term changes in stream flow based on daily mean flow, and thus, may not address the slower leaching pathway or the hydrological connectivity of the catchment.

Physical attributes and DIN retention

Climate, topography, land use, catchment dimensions, geology, soils, and vegetation influence pathways and delivery rates of water to streams (Baker *et al*., 2004). Collectively, these factors strongly influence the flow regime of a stream, which is defined as the pattern of variation in stream flow over time (Poff *et al*., 1997). In this study, the R–B flashiness index (Baker *et al*., 2004) was used as an integrator of physical attributes within a watershed in describing flow regimes on monthly time-steps.

The degree of stream flow flashiness is inversely related to catchment area as a consequence of hydrograph mixing, flow routing and other scale-dependent runoff factors (Baker and Richards, 2000), which have direct consequences for how DIN is exported from, or retained within, a watershed. Caraco *et al*. (2003) demonstrated that smaller watersheds (<100 km^2) retained more NO_3^- than did mid-sized or large ($>10,000$ km^2) watersheds through use of a simple NO_3^- loading model incorporating temperate watersheds. In this study, we did not see a relationship between stream flashiness, channel gradient, or watershed area and DIN import–export on monthly time-steps. It is likely that R–B indexed flashiness on the coarse time-steps investigated did not adequately capture the behaviour of DIN transport within different catchments, and that biophysical characteristics related to catchment vegetation, physical composition, climate variability, and land use history exert more control over changes in DIN import–export budgets across diverse watersheds (Campbell *et al*., 2003).

While we did not directly investigate the effects of changes in soil texture on net DIN retention within catchments in this study, general patterns between soil order and texture (Table II) and DIN import–export appeared across diverse sites. Numerous studies have established general relationships between soil texture across diverse soil types and soil organic matter accumulation (e.g. Burke *et al*., 1989; Vogt *et al*., 1995), inorganic N mineralization (Franzluebbers *et al*., 1996; Cote *et al*., 2000) and plant production (Reich *et al*., 1997); these factors affected by soil texture likely exert strong control over DIN retention in riparian areas (Bechtold and Naiman, 2006). In general, organic matter and vegetation production are higher in temperate/cold Ultisols, Alfisols, and Inceptisols, and are lower in temperate Spodosols, tropical Oxisols, tropical Ultisols, and boreal Inceptisols (Vogt *et al*., 1995; Reich *et al*., 1997). In this study, we observed the lowest net DIN retention (import–export) at sites with tropical Oxisols/Ultisols (LUQ) and boreal Inceptisols (BNZ), and the highest net DIN retention at sites with temperate Inceptisols (CWT, NWT) and Alfisols (KBS). While perhaps not surprising, these data suggest that soil orders and climate regimes capable of supporting the most vegetation and soil organic matter accumulation also correspond with higher net DIN retention.

Watershed climate variability, disturbance, and DIN import–export

The effect of a given climate anomaly on watershed DIN import–export budgets can vary considerably between different ecosystems, and depending on the nature of the disturbance, we observed both increases and decreases in net DIN retention. For example, we observed a decline in net DIN retention at AND M coinciding with extensive flooding in the area in the winter of 1996 (Grant *et al*., 1996; Swanson *et al*., 1998); it is plausible that DIN was flushed from this watershed in the large flooding event. Net DIN retention increased at NWT following a period with low snow fall (2000–2001; Sno Tel Data Network; Niwot Ridge; C-1), and net DIN retention increased during El Niño years at AND, owing to below-average precipitation (Greenland, 2003). El Niño events have been shown to influence seasonal changes in precipitation across the LTER network (Greenland *et al*., 2003), and also have been related to changes in stream water quality (Jones *et al*., 1996; Scarsbrook *et al*., 2003). These data suggest that net DIN retention within a watershed is lower during years with high wet deposition or during climate

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phenomena that can flush solutes from a watershed. However, seasonal trends within a given site can vary widely (e.g. during El Niño years, LUQ has increased rainfall in May but decreased rainfall in October (Schaffer, 2003) (see outlier in Figure 6), which precludes determining any straightforward relationships between climate variability and DIN import–export across sites.

Disturbance within a watershed has often been shown to reduce plant nutrient uptake and lead to the export of DIN and other nutrients in stream water, and the patterns of decreased net DIN retention coinciding with disturbances to terrestrial vegetation observed in this study (harvesting at HBR and a hurricane at LUQ; Figure 3) are in agreement with prior studies (Likens *et al.*, 1970; Bormann *et al.*, 1974; Schaffer *et al.*, 2000). Though significant increases or decreases in DIN retention coincided with different climate anomalies or disturbances, DIN import–export returned to pre-disturbance levels within two seasons in all cases in this study. Recovery was rapid even when DIN import–export following disturbance declined by more than 7 times (HBR 5 had mean pre-harvest DIN retention of 3 kg ha^{-1} y^{-1} and a post-harvest retention of -24 kg ha^{-1} y^{-1}). The degree to which DIN retention within these ecosystems returned to pre-disturbance levels suggests that N transport and cycling processes within these watersheds are somewhat resilient to climate anomalies and disturbances.

Caveats of the mass balance approach

The mass balance approach for ascertaining solute retention within a watershed (storage = input − output; Likens *et al.* (1977)) is not designed to address the relative importance of N inputs or losses outside of those measured in precipitation or stream export. For example, while dry deposition of N has rarely been measured, it may be an important consideration in some watersheds (e.g. Neff *et al.*, 2002). The southwestern region of the USA containing the Gila watershed has dry N deposition inputs of approximately 1.5–1.7 kg N ha^{-1} y^{-1} in areas not heavily influenced by cities (Grossman-Clarke *et al.*, 2002; Fenn *et al.*, 2003). At NWT, inorganic N in dry-fall has been estimated to comprise between 25–50% of precipitation DIN (Sievering *et al.*, 1992; Williams *et al.*, 2001). Another N input we could not account for at all sites was N fixation from the atmosphere, which represents a significant input of DIN to some watersheds. For example, Sollins *et al.* (1980) have shown that cyanophycophilous lichens within the canopy at AND fix approximately 2·8 kg N ha^{-1} y^{-1}, and N fixation at LUQ accounts for approximately 3·3 ± 0·3 kg N ha^{-1} y^{-1} (Cusack *et al.*, 2006). In addition, retention at some sites with potentially high denitrification rates could be overestimated (e.g. denitrification at HBR is approximately equal to wet deposition rates; Groffman *et al.*, 2001; Judd *et al.*, 2007). Notwithstanding, the mass balance approach has a proven history of providing a basis for ranking diverse sites in terms of their ability to retain N under different climate and disturbance regimes (Likens *et al.*, 1977; Campbell *et al.*, 2003; Ito *et al.*, 2005; Nelson *et al.*, 2007).

In the import–export approach used in this study, precipitation is used directly in elemental import calculations and is also correlated with stream flow (e.g. Figure 2). Therefore, it is possible for the negative relationship between DIN import–export budgets and precipitation variability across sites to be spurious. To examine the validity of this relationship, we compared Cl$^-$ import–export to precipitation variability. Since Cl$^-$ import is largely conservative in watersheds, a significant relationship between Cl$^-$ import–export and precipitation variability may indicate spurious trends. No trend was observed between Cl$^-$ import–export budgets and precipitation variability (Figure 6(B)). Exports only significantly exceeded imports at two sites, owing to Cl$^-$ weathering and aeolian deposition (Gila: Mast and Clow, 2000) or dry deposition and evaporative concentration (LUQ: Schellekens *et al.*, 2004). The marked differences between the net retention of DIN and Cl$^-$ occurring as precipitation variability changed across sites asserts that the negative trend between DIN import–export budgets and precipitation variability is not an artifact of the mass balance approach.

Dissolved organic nitrogen. Dissolved organic nitrogen (DON) often dominates total N export from catchments that have not experienced recent natural disturbances or significant effects from human activities (Triska *et al.*, 1984; Hedin *et al.*, 1995; Perakis and Hedin, 2002). While DON data were not available at all sites used in this study, a comparison of DON with DIN data at a subset of our sites (available for the AND sites) is useful in evaluating role of DON in overall catchment N dynamics. Annual DON input (wet + dry deposition) was significantly correlated with annual DIN inputs ($r = 0{\cdot}52$; $p = 0{\cdot}04$; $n = 15$), and annual export of DON composed 64 ± 7%, 78 ± 6%, and 66 ± 10% of total dissolved N exported from AND 2, AND 9, and AND 10, respectively, during the period of record from 1989–2003. Only at the largest catchment (AND Mack) did DIN dominate annual losses, with DON averaging 25 ± 5% of annual export. Recent studies at HBR, BNZ, and CWT, which also measured DON with DIN concentrations in streams, also show that DON may comprise a large fraction of total nitrogen exports. DON : DIN ratios measured in stream water from watersheds adjacent to C4 at BNZ ranged from 1 to 2 · 3 (Petrone *et al.*, 2007), and stream DON : DIN measured during the growing season at HBR 6 ranged from 1·3 to 6·9 (mol L^{-1}) (Dittman *et al.*, 2007). Similarly at CWT (watershed 2), annual stream DON exports exceeded DIN exports (0·19 kg ha^{-1} y^{-1} vs 0·05 kg ha^{-1} y^{-1}, respectively; Qualls *et al.*, 2002). Qualls *et al.* (2002) suggest that the mechanisms controlling the loss of DIN ($NO_3{}^-$) and DON are largely hydrologic (and biologic), and that the loss of DON may also be controlled by such geochemical mechanisms as dissolution and sorption. These studies and the observed correlation

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patterns at AND suggest that DON and DIN export are linked through common pathways, and that DON could comprise a significant amount of total N retained or lost from some watersheds.

CONCLUSIONS

A simple mass balance approach provided a basis for ranking diverse sites in terms of their ability to retain N under different precipitation regimes measured within the LTER network. DIN exports were similar to or exceeded imports in wet coniferous, tropical, and boreal watersheds, whereas exports were consistently much lower than imports in temperate deciduous watersheds. In general, perturbations in the climate regime that enabled increased magnitude of water import to a watershed (i.e. hurricanes or floods) corresponded with periods of reduced DIN import–export, and periods of decreased water throughput within a watershed (i.e. low snow pack or El Niño years on the west coast) corresponded with increased net DIN retention.

Net DIN retention decreased with increasing variation in precipitation across 8 diverse sites (15 distinct watersheds) within the LTER network. Net DIN retention decreased with increasing precipitation variance during all seasons except in the summer months, likely owing to diminished connectivity between precipitation inputs and stream exports from a catchment during warmer and drier periods. The coefficient of variation in precipitation explained most of the seasonal variation in net DIN retention across all sites (logarithmically transformed; $r^2 = 0{\cdot}48$, $p = 0{\cdot}005$), with the tropical (LUQ), boreal (BNZ), and maritime/temperate watersheds (AND) having the lowest import–export DIN budgets.

Extreme precipitation events have increased over the last century in the continental USA, and model projections indicate that this trend will continue because of increases in atmospheric water vapour content. If there are more periods of high rainfall relative to mean precipitation over the next century, our analyses indicate watersheds may become less DIN retentive.

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