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Maintenance of terrestrial nutrient loss signatures during in-stream transport

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Abstract. Small streams account for the majority of channel length in river basins worldwide and are the primary conveyors of terrestrial nutrients to rivers and ultimately the oceans. The controls of stream nutrient fluxes, however, are debated. Classical models emphasize that nutrient transport in streams integrates nutrient cycling in the terrestrial watershed while others argue that in-stream processes control nutrient flux. Recent studies have shown that in-stream cycling can be important in determining downstream nutrient fluxes, but results have not been reconciled with mass–balance calculations at the small-watershed scale. Here we use a simple analytical framework to assess nutrient cycling in streams and show that, under most conditions, longitudinally static nutrient concentrations reflect in-stream biotic balance between uptake and regeneration and groundwater inputs. Using measures of nutrient concentrations in small streams across four biomes, we provide evidence for generality of biogeochemical steady state (inputs = outputs) in stream ecosystems: overall, longitudinal profiles were flat for nitrogen and phosphorus and were similar in concentration to soil and ground waters. Deviation from flat longitudinal profiles was associated with seasonal or successional biomass growth and small groundwater inputs relative to in-stream sink strength. We conclude that streams tend strongly toward nutrient balance, allowing use of their chemistry as an integrated measure of terrestrial nutrient losses.

Key words: analytical model; biogeochemistry; nutrient cycling; nutrient spiraling; small watershed concept; streams; terrestrial nutrient losses; watershed nutrient budgets.

INTRODUCTION

The chemistry of small streams integrates biogeochemical cycling in stream channels as well as the terrestrial systems they drain, and has played a key role in the development of ecosystem ecology (Fisher et al. 2004). The small-watershed concept (Bormann and Likens 1967) advanced the study of terrestrial nutrient cycles with the idea that stream chemical loads represent nutrient losses from the wider ecosystem, and is today perhaps the most common example of forest biogeochemistry in introductory ecology textbooks. The approach has been widely applied and has generally supported the idea that vegetation and soils control nutrient export from watersheds (e.g., Vitousek and Reiners 1975, McGroddy et al. 2008).

In contrast, the nutrient spiraling concept (Webster and Patten 1979, Newbold et al. 1982) describes nutrient cycling *within* stream channels, in which local cycles are stretched unidirectionally downstream (i.e., into a spiral) by advection; thus upstream inefficiencies feed downstream biota. Recent budgetary studies (Alexander et al. 2000, Bernhardt et al. 2003, Mulholland et al. 2004, Roberts and Mulholland 2007) and isotope spiraling experiments (e.g., Peterson et al. 2001, Mulholland et al. 2008) have revealed rapid nutrient uptake and processing in small streams, and denitrification rates comparable to those in other aquatic ecosystems worldwide. Such evidence has largely falsified the notion that streams merely act to transport nutrients but has further been used to argue for a major role of headwater streams in controlling watershed nutrient balance and nutrient loading to downstream ecosystems (Peterson et al. 2001, Bernhardt et al. 2005). Here we evaluate in-stream contribution to watershed nutrient balance and export and show that, under many conditions, in-stream

cycling and the small watershed approach are reconcilable on theoretical and empirical grounds.

METHODS

Model

Consistent with spiraling theory (Newbold et al. 1982, Payn et al. 2005), we propose that longitudinal (distance) patterns in ambient stream nutrient concentrations result from the balance of in-stream uptake and regeneration occurring across benthic surfaces and the supply from groundwater sources. We apply a Lagrangian framework by following M, the mass of nutrient (e.g., nitrogen, N, or phosphorus, P) in a volume of stream water with distance [x; or time (t) with $t = x/u$, where u is velocity]:

$$\frac{dM}{dx} = Q_G[M]_G + R - U \qquad (1)$$

where Q_G is net groundwater inflow (in units of volume V per channel length increment), $[M]_G$ is groundwater M concentration, R is M regeneration (includes mineralization, nitrification, organic production), and U is uptake (assimilation, gaseous loss, or burial). We solve Eq. 1 for stream M concentrations $[M] = M/V$ and apply the derivation chain rule:

$$\frac{dM}{dx} = V\frac{d[M]}{dx} + [M]\frac{dV}{dx}$$

where $dV/dX = Q_G$. Hence,

$$\frac{d[M]}{dx} = \frac{Q_G}{V}([M]_G - [M]) + \frac{R - U}{V}. \qquad (2)$$

When the longitudinal nutrient profile is flat, $d[M]/dx = 0$, we obtain

$$Q_G([M]_G - [M]) = U - R \Leftrightarrow [M] = [M]_G - \frac{U - R}{Q_G}. \qquad (3)$$

Eq. 3 suggests that if organism biomass is at or near steady state ($U = R$), then $[M]_G = [M]$, dilution is irrelevant, and stream nutrient transport equals terrestrial losses, that is $Q_G[M]_G$.

Nutrient uptake rates (λ, m^{-1}) decrease and uptake lengths, S_w ($S_w = 1/\lambda$), increase with increasing ambient concentrations and increasing channel depth and velocity (Peterson et al. 2001, Payn et al. 2004). When substituting U in Eq. 3 as a linear function of $[M]$, $U = \lambda V[M]$, and R as a fraction (θ) of U to obtain $Q_G[M]_G = \{[M](Q_G + \lambda V(1 - \theta)\}$, we find in the case of the flat profile, $[M]$ can be expressed as a function of $[M]_G$ and a dimensionless modifier β:

$$[M] = [M]_G \frac{1}{1 + \lambda\dfrac{V(1-\theta)}{Q_G}} = [M]_G \times \beta. \qquad (4)$$

Eq. 4 shows how $[M]$ changes when stream biota deviates from steady state (e.g., $\theta < 1$). Whether stream concentrations are significantly altered depends on the

magnitude of any biotic uptake (or release) vs. external inputs from groundwater. There are three ways to achieve a flat longitudinal nutrient profile. First, the stream could act as a pipe ($U = R = 0$), a possibility under conditions of high flow, resulting in $[M] = [M]_G$. Second, at or near biotic steady state $U \approx R$, $\theta \rightarrow 1$ and thus $\beta \rightarrow 1$ also leads to $[M] \approx [M]_G$. Third, a flat longitudinal profile is possible if $Q_G < \lambda V(1 - \theta)$ and $\theta < 1$ with $[M] < [M]_G$ but in this case in-stream net uptake fluxes ($U - R$) are restricted to values $<$ groundwater supply ($Q_G[M]_G$). If in-stream sinks exceed this ceiling, concentrations should decline downstream (Eq. 2). Further, if $Q_G > \lambda V(1 - \theta)$, then $\beta \rightarrow 1$ even in the presence of a net sink ($\theta < 1$) and therefore $[M]$ approaches $[M]_G$. We thus expect stream nutrients to reflect watershed losses when the longitudinal profile is flat, indicating biotic steady state, or that Q_G is sufficient to mask in-stream sinks. Alternatively, deviations from a flat profile can occur when $[M]_G$ changes downstream or during periods of permanent loss or transient net biotic uptake ($U > R$, $\theta \rightarrow 0$) or regeneration ($U < R$, $\theta > 1$), particularly if Q_G is small.

Field measures

We evaluated this model and the underlying assumptions using original and published data from 144 longitudinal profiles of ambient dissolved N and P concentrations over scales (150–400 m) typical of most spiraling experiments and contributing areas of small watershed studies. Samples were collected longitudinally (3–10 transects) at arbitrary times and varying intensities in 15 small streams (mean annual discharge, $Q < 100$ L/s) draining relatively undisturbed watersheds with natural vegetation spanning four major biomes and large gradients in annual precipitation (~35–400 cm) and temperature (6–25°C; Appendix A). Original samples were collected seasonally in four streams in the Coweeta Hydrologic Laboratory, North Carolina, USA (27 surveys, 2002–2005) and two streams in the Northern Range on the island of Trinidad (10 surveys, 2007), and once during the summer in three streams in the Great Smoky Mountains National Park, Tennessee, USA (2002). Samples were obtained by collecting water at base flow with a syringe positioned mid-depth in the stream thalweg and field filtering (0.7 μm) into leached polyethylene bottles. Samples were immediately placed on ice and later frozen until chemical analysis by colorimetry or ion chromatography following Valett et al. (2008) and Brookshire et al. (2005).

We supplemented our analysis with published data for small streams for which longitudinal (<500 m) nutrient data were either available directly or could be digitized from graphs using a digitization program (Adobe distance tool; Adobe Systems, San Jose, California, USA). We used data for small streams in the desert southwest, Arizona, USA (sites 5, 6, 7, and 25 in Grimm et al. [1981]), the Hubbard Brook Experimental Forest, New Hampshire, USA (the upper 350 m of Bear Brook

in Meyer and Likens [1979]), and the Oak Ridge National Laboratory, Tennessee, USA (West Fork Walker Branch in Mulholland and Rosemond [1992]). For each original and published survey and [M] form, we tested for a flat longitudinal profile $d[M]/dx = 0$ using linear regression ($\alpha = 0.05$) analysis of concentration vs. distance using Sigma Stat (Systat Software, Chicago, Illinois, USA).

We also assessed potential groundwater nutrients by collecting original samples from point-source hill-slope surface waters (seeps and springs, $n = 10$) and mixing wells placed into stream sediments ($n = 80$) following Brookshire et al. (2005) and through the use of piezometers ($n = 4$, at Noland Divide) and published values for spring, soil lysimeter, and riparian well water (Grimm et al. 1981, Mulholland 1992, Qualls et al. 2000, Van Miegroet et al. 2001, Yeakley et al. 2003). We further explored the implications of in-stream nutrient removal for watershed nutrient balance (atmospheric input minus stream output) at sites for which long-term inorganic N budgets have been constructed and across which deposition varies from ~5 to 32 kg N·ha^{-1}·yr^{-1} (Hubbard Brook watershed 6 [Likens and Bormann 1995], mean of seven Coweeta reference watersheds [Swank and Vose 1997], Noland Divide [Van Miegoret et al. 2001], West Fork Walker Branch [Mulholland 2004]). We analyzed three scenarios: (1) stream steady state ($Q_G[N]_G = Q[N]$), where $Q[N]$ is the long-term mean N export (kg N·ha^{-1}·yr^{-1}); 2) $Q[N] = 0.8 \times Q_G[N]_G$ (following the approximate upper limit of stream denitrification losses reported in Mulholland et al. [2008]); and (3) streams remove half of terrestrial N losses annually.

RESULTS AND DISCUSSION

Despite tremendous variation in state factors and background concentrations, we found that 80% of cases examined here showed no evidence for longitudinal change in nutrient concentrations and only 15% of cases showed downstream declines across all inorganic and organic forms combined (Fig. 1). Most cases of downstream declines ($d[M]/dx < 0$) in stream N and P were associated with transient net growth of in-stream biomass, with the highest percentage of within-site declines (38%) occurring in desert streams. We also observed a total of seven cases (5%) of downstream increases in ambient nutrient concentrations. While our sites were not chosen randomly nor do sample sizes represent a balanced statistical design, our results encompass a broad array of environmental conditions under which our model and the underlying assumptions remain applicable.

Our random sampling approach suggests the intriguing possibility that U is rapidly balanced by R in the same form. For example, we found no shifts in longitudinal patterns in any N form among seasons in temperate deciduous forest streams of Coweeta or for inorganic N and P between wet and dry seasons in tropical rain forest streams, consistent with balanced U and R or quasi-balance characterized by lag times between U and R that were undetectable in our study. The magnitude of in-stream net retention and the timescale over which a downstream decline in [M] may occur depends on organism biomass and turnover rates. A scale analysis further supports and justifies assumptions of biotic steady state: in shaded watershed streams, microbial and algal biomass N averages ~ 200 mg N/m^2 (Findlay et al. 2002), and applying median U_N (~1 mg N·m^{-2}·h^{-1}) for these systems (Peterson et al. 2001, Mulholland et al. 2008) yields N turnover time of ~200 h, but in some compartments may be up to a month (Mulholland 2004). Without regeneration or significant groundwater inputs, application of gross U could in some cases unrealistically draw down watershed losses to zero or negative values. While cases where $U > R$ or $U < R$ transiently occur, high turnover rates and the relatively small biomass in streams (Findlay et al. 2002) likely severely limits the capacity to sustain such imbalances over periods of time relevant to watershed nutrient balance. With few exceptions, in-stream equilibrium is likely to occur on nearly instantaneous time scales relative to terrestrial nutrient balance.

Both theoretical analysis and data suggest that longitudinal changes of [M] are possible when groundwater inputs are small or derive predominantly from an upstream point-source, biomass is undergoing net growth ($U > R$), permanent losses occur (e.g., via denitrification), or if nutrients are quasi-permanently buried as particulates. The resulting longitudinal [M] profile will depend on the relative magnitude of competing groundwater input and nutrient sinks (Eqs. 3 and 4). For example, in desert streams nitrate declines rapidly with distance from groundwater sources (Fig. 1). Here, N accumulates during post-flood succession and potentially over several months until the next scouring flood (Grimm et al. 1981, Dent and Grimm 1999). Nutrient accumulation also occurs in some forest streams during open-canopy periods that promote net algal growth either seasonally as observed downstream of groundwater sources in Walker Branch, Tennessee (Fig. 1; Mulholland 2004, Roberts and Mulholland 2007), or following canopy disturbance as observed at Hubbard Brook, New Hampshire (Bernhardt et al. 2003). Similarly, autumn inputs of carbon-rich leaf litter can stimulate microbial N immobilization (Roberts and Mulholland 2007, Valett et al. 2008), which, in the absence of denitrification, should be balanced by R. While regeneration of N via nitrification has been examined (e.g., Peterson et al. 2001), little is known about R in general, especially as particulate and dissolved organic forms (Meyer and Likens 1979, Brookshire et al. 2005).

A challenge in quantifying in-stream contribution to watershed nutrient balance is the identification of actual terrestrial inputs ($Q_G[M]_G$) crossing groundwater–surface-water interfaces. In Fig. 2, we summarize potential
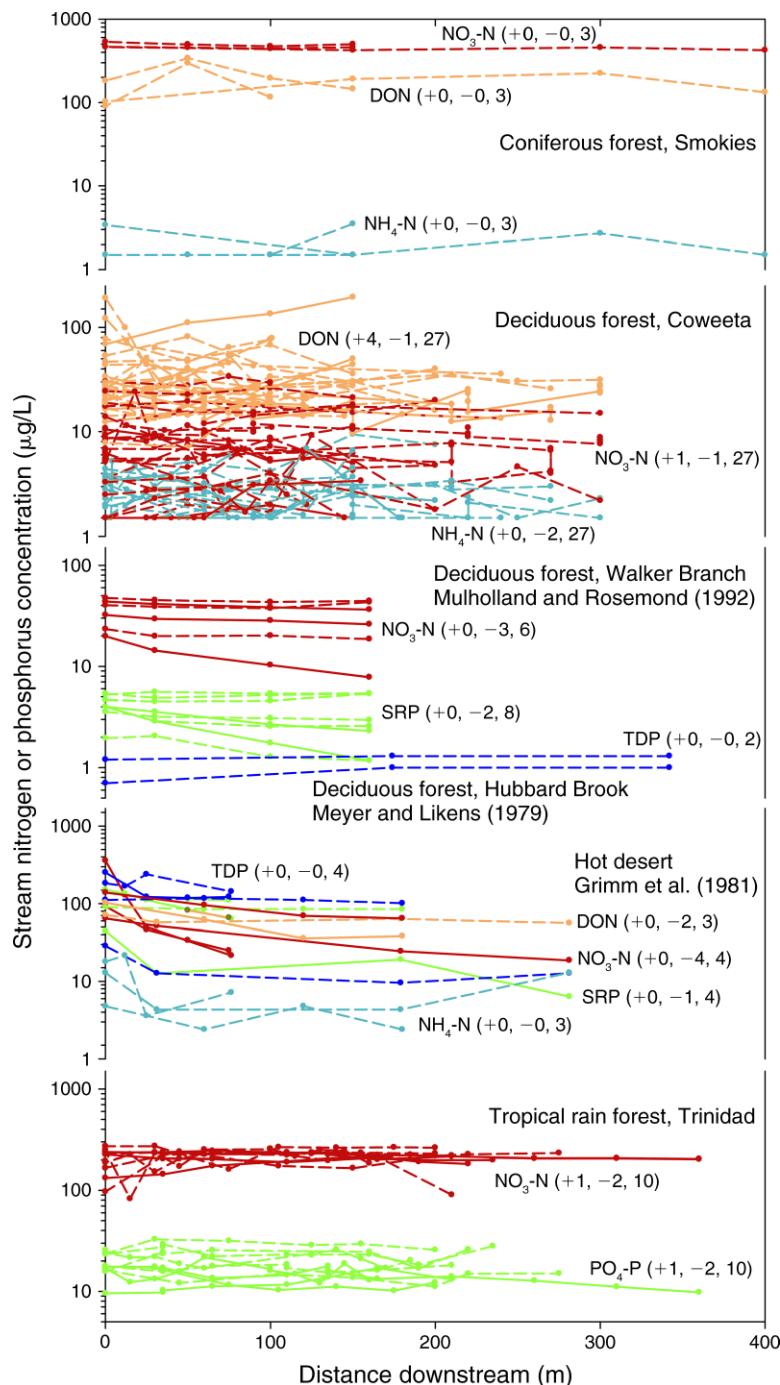
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FIG. 1.   Longitudinal profiles of ambient stream nitrogen and phosphorus chemistry collected in watershed streams. Profiles are for NO_3^- (nitrate), NH_4^+ (ammonium), DON (dissolved organic N), SRP (soluble reactive P), PO_4^{3-} (phosphate), and TDP (total dissolved P). Values are original data or are taken directly or digitized from publications. Numbers in parentheses represent, in order, (1) the number of significant ($P < 0.05$) regressions with positive (+), and (2) negative (−) slopes, and (3) the total number of longitudinal profiles. Statistically significant profiles are shown as solid lines, and nonsignificant profiles as dashed lines.

$[M]_G$ for sites where data are available. In deciduous forests, nutrient concentrations measured in lysimeters in B and C soil horizons (Mulholland 1992, Qualls et al. 2000, Yeakley et al. 2003) were very similar to stream waters, particularly for nitrate, supporting the idea that

in-stream cycling tends to maintain terrestrial nutrient losses at relatively static levels. Some nutrients were higher in riparian and stream sediment (hyporheic) waters, consistent with nutrient accumulation and vigorous internal cycling (Brookshire et al. 2005) or
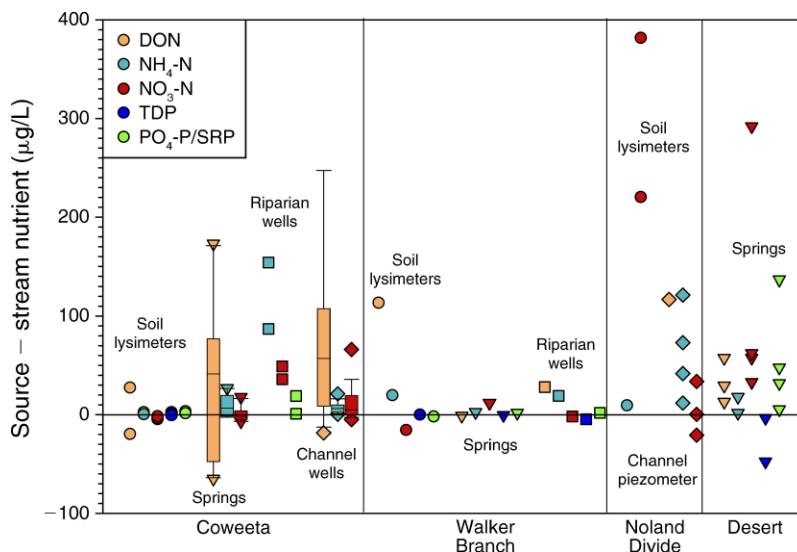
Fig. 2. Potential sources of $[M]_G$ (groundwater concentration of nutrient mass) for streams examined in this study. Samples are from zero-tension lysimeters placed below B and C horizons (circles), springs (triangles), permanent near-stream riparian wells (squares) and hyporheic wells and stream sediment piezometery (diamonds). Symbol colors in circles apply to all sample (and symbol) types. Data for desert streams represent upstream groundwater source (spring) chemistry. Data are individual samples or box plots with 95% confidence limits and outliers, displayed as potential source minus mean stream concentrations.

permanent (gaseous) loss from waters leaving these zones (Hedin et al. 1998). At the "N-saturated" Noland Divide watershed, soil but not hyporheic waters were elevated in nitrate, suggesting denitrification losses along soil-to-stream flow paths at this site (Van Miegroet et al. 2001). In contrast, desert streams show evidence for $[M]_G > [M]$ during algal growth (Grimm et al. 1981). Directional change in $[M]_G$ (i.e., $d[M]_G/dx \neq 0$) is possible where vegetation and soils (Bernhardt et al. 2003) or flow path lengths (McGuire et al. 2005) change longitudinally. We tested the possibility of longitudinal change in $[M]_G$ in two Coweeta streams with high rates of Q_G and hyporheic exchange using longitudinally distributed in-channel mixing wells following Brookshire et al. (2005). Across seasons and N forms (42 profiles), we documented a single case of decline in $[NH_4]$ with distance, with no corresponding change in stream water N (Appendix B).

We suggest our results are robust to within-reach variation in $Q_G[M]_G$ and in-stream processing. While nutrient uptake length (S_w) increases directly with increasing discharge (Peterson et al. 2001) and expression of U and R depends on travel time, stream size and reach length used here (Appendix A) were similar and within the range of mean Q and S_w reported in a recent synthesis (Ensign and Doyle 2006) of N and P spiraling for first- through third-order streams. If spiraling length is shorter than the distance to weir, then our model applies, and if not, then U and R are less relevant to weir fluxes. Also, most spiraling experiments are conducted during base-flow and thus do not account for high flow periods that contribute to watershed export. It is also possible that within-reach heterogeneity in $Q_G[M]_G$ or

inertia in stream chemistry given small changes in Q_G or $[M]_G$ could obscure any longitudinal signal from U and R imbalance. However, because $[M]$ detection ability (which must be $<(U - R)/Q_G$) is, for most nutrients, quite small (i.e., <3 µg/L), error within this range would likely represent a small effect on watershed nutrient balance. Recapitulating Eq. 3, if $Q_G \gg \lambda V(1 - \theta)$ then $\beta \rightarrow 1$ even if $\theta < 1$ and therefore $[M] \approx [M]_G$.

Denitrification can remove nitrate-N permanently from stream ecosystems, and can therefore violate the
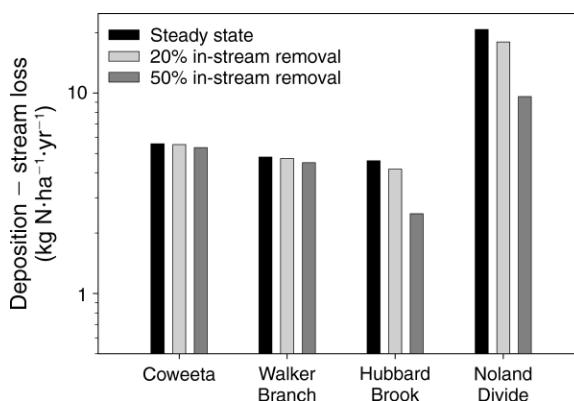

Fig. 3. Potential contribution of in-stream N removal to watershed N balance for sites with long-term N budgets. We consider three scenarios: (1) at steady state, $Q_G[N]_G = Q[N]$ (where Q_G is net groundwater inflow, $Q[N]$ is the long-term mean N export, and $[N]_G$ is the groundwater concentration of N) and therefore watershed balance equals observed atmospheric N deposition minus observed stream N losses; (2) $Q[N] = 0.8 \times Q_G[N]_G$, or 20% removal; and (3) streams remove half of terrestrial N losses.

expectation of equilibration via regeneration. However, denitrification fluxes appear to be low in low-N streams where nitrate availability and oxygen-rich conditions severely limit the process (Mulholland et al. 2008) and where N-limited assimilatory pathways should exhibit strong competition for nitrate (Valett et al. 2008). For example, in low N Coweeta streams, denitrification fluxes were either undetectable or varied from ~3 to 13 mg·m^{-2}·d^{-1} in a recent study (Mulholland et al. 2008). The higher estimates could potentially double watershed N losses without affecting longitudinal nitrate profiles, a possibility which we cannot entirely reject, but we find little evidence for $[NO_3^-]_G > [NO_3^-]$ in these systems (Fig. 2). In our analysis, only 20% of nitrate profiles showed declines (Fig. 1) across streams varying >100-fold in background nitrate (5–500 μg N/L), and this number drops to 10% when desert streams are excluded. These results are similar to a recent cross-biome study (Mulholland et al. 2008) in which denitrification was found to account for ~16% of in-stream nitrate removal. We stress, however, that in order to affect terrestrial N budgeting any U vector must be of sufficient magnitude and timing to compete with groundwater inputs according to Eqs. 3 and 4 [i.e., $Q_G < \lambda V(1 - \theta)$]. For example, in the Coweeta case, Q_G/V (~0.0014 m^{-1}; derived from Brookshire et al. 2005) is more than threefold higher than λ for denitrification (~0.0004 m^{-1} [Mulholland et al. 2008]), suggesting that gaseous losses here are simply too small to compete with groundwater dilution.

Across sites with N deposition of ~5–32 kg N·ha^{-1}·yr^{-1}, and displaying net accumulation of N, we analyzed three hypothetical scenarios of how in-stream U could affect watershed inorganic N balance: (1) biomass steady state (no effect); (2) streams remove 20% of terrestrial N losses; and (3) streams remove half of terrestrial N losses annually (Fig. 3). For scenario 2, we find marginal differences in estimates of terrestrial N balance relative to observed fluxes of 0.8% (0.04 kg N·ha^{-1}·yr^{-1}) at Coweeta to 11% (2.3 kg N·ha^{-1}·yr^{-1}) at the highly N-polluted Noland Divide watershed. For scenario 3, reduction in potential terrestrial N accumulation was <4% to 55% (0.2–11 kg N·ha^{-1}·yr^{-1}). We note that these estimates require levels of in-stream N removal which our results indicate are highly implausible, but also point to the increasing relative importance of stream processing as watersheds approach N balance.

Our results challenge the idea that headwater streams naturally regulate annual watershed nutrient exports, but are also consistent with rapid cycling by stream biota. Without large gaseous losses or burial flux, the major implication of longitudinal constancy in stream nutrients is that, over the spatial scale of small watershed streams and temporal scales that address transient deviations, stream chemistry should represent losses from the terrestrial ecosystem ($[M] = [M]_G$), thus validating the classical small watershed approach. If Eq. 3 holds and $U = R$ or $U = R = 0$ (e.g., during storm

flows), then this must be true. Critically, however, high levels of nutrient accumulation and gaseous loss may occur along soil-to-stream flow paths (Mulholland 1992, Hedin et al. 1998, Fisher et al. 2004) and therefore stream losses may not equal losses from rooting zones of upland ecosystems but rather from ground–stream-water interfaces. Our results also point to conditions under which stream nutrient loads may not equal terrestrial losses: single-source nutrient inputs, low ground-water inflow, periods of high light and net biomass growth, and high rates of denitrification or burial. We suggest, however, that these cases may represent the exception and not the norm for small watershed streams. Given increasing nutrient loading from human activities globally, we emphasize the research need to address the full continuum of plant, soil, near-stream, and stream processes that determine nutrient balance in watershed ecosystems and nutrient export to downstream rivers and estuaries.

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APPENDIX A

A table showing characteristics of study sites (*Ecological Archives* E090-020-A1).

APPENDIX B

A figure showing longitudinal and seasonal patterns in surface and subsurface nitrogen concentrations in Coweeta streams (*Ecological Archives* E090-020-A2).