

## Nutrient spiraling in streams and river networks

Scott H. Ensign<sup>1</sup> and Martin W. Doyle<sup>2</sup>

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[1] Over the past 3 decades, nutrient spiraling has become a unifying paradigm for stream biogeochemical research. This paper presents (1) a quantitative synthesis of the nutrient spiraling literature and (2) application of these data to elucidate trends in nutrient spiraling within stream networks. Results are based on 404 individual experiments on ammonium ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ), and phosphate ( $\text{PO}_4$ ) from 52 published studies. Sixty-nine percent of the experiments were performed in first- and second-order streams, and 31% were performed in third- to fifth-order streams. Uptake lengths,  $S_w$ , of  $\text{NH}_4$  (median = 86 m) and  $\text{PO}_4$  (median = 96 m) were significantly different ( $\alpha = 0.05$ ) than  $\text{NO}_3$  (median = 236 m). Areal uptake rates of  $\text{NH}_4$  (median =  $28 \mu\text{g m}^{-2} \text{min}^{-1}$ ) were significantly different than  $\text{NO}_3$  and  $\text{PO}_4$  (median = 15 and  $14 \mu\text{g m}^{-2} \text{min}^{-1}$ , respectively). There were significant differences among  $\text{NH}_4$ ,  $\text{NO}_3$ , and  $\text{PO}_4$  uptake velocity (median = 5, 1, and  $2 \text{ mm min}^{-1}$ , respectively). Correlation analysis results were equivocal on the effect of transient storage on nutrient spiraling. Application of these data to a stream network model showed that recycling (defined here as stream length  $\div S_w$ ) of  $\text{NH}_4$  and  $\text{NO}_3$  generally increased with stream order, while  $\text{PO}_4$  recycling remained constant along a first- to fifth-order stream gradient. Within this hypothetical stream network, cumulative  $\text{NH}_4$  uptake decreased slightly with stream order, while cumulative  $\text{NO}_3$  and  $\text{PO}_4$  uptake increased with stream order. These data suggest the importance of larger rivers to nutrient spiraling and the need to consider how stream networks affect nutrient flux between terrestrial and marine ecosystems.

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### 1. Introduction

[2] Studies of nitrogen (N) and phosphorus (P) cycling are a cornerstone of ecosystem biogeochemistry because all biota depend on these elements for critical cellular processes. Productivity of aquatic ecosystems is often influenced by the concentration, molecular form, and stoichiometry of N and P. In excess, however, N and P can enhance rates of photosynthetic and heterotrophic productivity and result in fundamental changes to aquatic food webs. Eutrophication, the process of accelerated organic carbon production in aquatic systems, negatively affects rivers, lakes, and estuaries worldwide, and now accounts for the foremost aquatic ecosystem management problem in the U.S. [Bricker *et al.*, 1999]. Fundamental to the management of eutrophication is an understanding of how lakes, estuaries, and the coastal ocean are coupled

with nutrient export from their watersheds [Howarth *et al.*, 2002]. Not only do streams and rivers provide this hydrologic coupling, they also play a central role in modulating the concentrations and forms of nutrients exported downstream.

[3] The importance of in-stream uptake to watershed-scale nutrient loads has been demonstrated by studies in which nutrient export in streamflow has been found to be less than terrestrial inputs to the stream [e.g., Behrendt and Opitz, 2000; Stow *et al.*, 2001; Mulholland, 2004; Williams *et al.*, 2004]. While some in-stream uptake processes are permanent (e.g., denitrification and burial) others are temporary (e.g., biotic sequestration) and result in remineralization and subsequent downstream transport. Knowledge of the processes contributing to in-stream nutrient uptake is largely attributable to the concept of nutrient spiraling, a conceptual and empirical model of nutrient cycling in fluvial ecosystems. The current study is intended to provide a review and quantitative summary of data from studies of nutrient spiraling, with emphasis on the spatial variability within stream networks. In equal parts, this study is a response to (1) the lack of a quantitative summary and synthesis of nutrient spiraling data in the literature and (2) the call for increased attention to the ecological connectivity within stream networks. We begin this paper with a review of the

<sup>1</sup>Curriculum in Ecology, University of North Carolina at Chapel Hill, Morehead City, North Carolina, USA.

<sup>2</sup>Department of Geography, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, USA.

development and applications of the nutrient spiraling model.

### 1.1. Nutrient Spiraling Model

[4] Unlike other ecosystems, the spatial and temporal dimensions of nutrient cycling in streams and rivers are intimately coupled due to the continual movement of water-borne constituents downstream. This unique aspect of fluvial environments (relative to other ecosystems) was highlighted by *Webster* [1975] wherein he coined the term nutrient “spiraling” to describe the cycling of nutrients as they are assimilated from the water column into benthic biomass, temporarily retained, and mineralized back into the water column. Though this concept was mentioned briefly by *Wallace et al.* [1977] and *Fisher* [1977], *Webster and Patten* [1979] were the first to apply the nutrient spiraling concept to compare nutrient recycling in different streams. Without explicitly referring to nutrient “spiraling,” *Meyer and Likens* [1979] brought increased attention to the role of in-stream processes in modifying P inputs to Hubbard Brook, New Hampshire.

[5] In 1981, the nutrient spiraling concept was formalized by Newbold and colleagues who presented a mathematical framework to support a more robust conceptual model than had previously been presented [*Newbold et al.*, 1981]. The authors introduced spiraling length ( $S$ ) as the distance required for a nutrient atom to complete 1 cycle from its dissolved inorganic form in the water column (this distance being  $S_w$ ), through a particulate phase ( $S_p$ ), and finally through a consumer phase ( $S_c$ ) to be returned to the water column in a dissolved inorganic form. In this model, spiraling length is an integrated measure of water flow velocity and the influence of biochemical demand of the benthos (though subsequent studies have included chemical sorption by stream bed sediments as an uptake pathway). Further, the authors demonstrated how these spatial metrics ( $S$ ,  $S_w$ ,  $S_p$ ,  $S_c$ ) could be converted into flux measurements by incorporating data on the flux of dissolved and particulate fractions in the stream. This and subsequent publications [*Elwood et al.*, 1982] paved the way for a burgeoning field in stream ecology in which nutrient spiraling could be quantitatively compared between different streams.

[6] The first whole-ecosystem study of P spiraling was conducted in Walker Branch, Tennessee [*Newbold et al.*, 1983] using  $^{32}\text{P}$  as an isotope tracer. This was followed by a seasonal investigation of nutrient spiraling in the same stream [*Mulholland et al.*, 1985]. However, because of the difficulties entailed by using radioactive P in surface waters, the only other whole ecosystem P spiraling study performed to date was also conducted in Walker Branch [*Mulholland et al.*, 1990]. The dominant source of information regarding whole-stream N-cycling came from the Lotic Intersite Nitrogen eXperiment (LINX). Beginning in the late 1990s, the LINX project used 11 streams spanning a broad range of ecosystem types across North America to investigate stream ecosystem processes of N retention and food web transformation. Utilizing similar methods across all sites and experiments, the investigators quantified the uptake and trophic transfer of N between multiple stream compartments. The LINX project advanced understanding of the many in-stream processes affecting nitrogen uptake (summarized by *Webster et al.* [2003]), and the contribution

of trophic transfer and turnover to nutrient processing in a wide variety of streams. At the time of the present research, a LINX II study is underway to examine  $\text{NO}_3$  uptake in a diverse array of stream ecosystems.

[7] In contrast to these whole-ecosystem studies of nutrient spiraling using isotope tracers, the majority of nutrient spiraling studies have been conducted using more simplistic techniques. Bulk addition of inorganic N and P to a stream allows measurement of nutrient uptake along a stream reach. This technique has been applied since the early 1970s prior to the genesis of the nutrient spiraling model [*McColl*, 1974], but gained widespread notoriety after a review of the theory and empirical procedures was published [*Stream Solute Workshop*, 1990]. The Stream Solute Workshop publication reviewed the conceptual and empirical underpinnings of nutrient spiraling, and discussed the relative merits of using different metrics to compare nutrient uptake in streams, as well as the limitations and assumptions necessary when nutrient additions are used.

[8] There are three fundamental limitations to the nutrient addition approach. First, only one portion ( $S_w$ ) of the total spiraling length ( $S$ ) is measured using nutrient additions, providing no information on specific mechanisms of uptake or transfer between stream biota. Nutrient additions alter biochemical nutrient uptake, subsequently affecting measurements of  $S_w$  [*Mulholland et al.*, 1990, 2002] and areal uptake ( $U$ ) [*Dodds et al.*, 2002]. Second is variability in time: Despite wide recognition that spiraling varies substantially with discharge, the approach currently used limits results to a snapshot view of stream biogeochemistry, and results are only representative of a particular time and a particular discharge. Only recently have developments been made in how to account for hydrologic variability into spiraling studies [*Doyle*, 2005]. Finally is variability in space: many studies have been conducted across a range of sites, but few if any have systematically examined spiraling through a channel corridor, or more representative of watersheds, through a channel network. It is this last area in which we focus later in this paper.

### 1.2. Geomorphic Factors Affecting Nutrient Spiraling in Streams

[9] Despite these drawbacks, quantifying nutrient spiraling, specifically through the nutrient addition technique, is an important component of studying stream biogeochemistry. This focus on measuring  $S_w$  stems from early observation that  $S_w$  is the dominant component of the total spiraling length,  $S$  [*Newbold et al.*, 1981]. The numerous factors influencing nutrient uptake can be divided into two categories: biochemical (bacteria, fungi, algae, and macrophytes) and geomorphic (physical properties of the stream channel). As discussed by *Valett et al.* [1996], geomorphic stream features dictate the residence time of water moving through a stream reach while the biochemical features control nutrient uptake. Channel geomorphology, and subsequently residence time, has an indirect effect on nutrient uptake from the water column by dictating the exposure of water to the biochemically-reactive substrates. This indirect effect of geomorphology on biochemical uptake of nutrients from

**Table 1.** Commonly Used Metrics of Nutrient Uptake and Transient Storage<sup>a</sup>

Name	Symbol	Units	Derivation	Description
Uptake rate constant	$K_c$	$\text{time}^{-1}$	$= V_f \div h$ $= u \div S_w$	first-order uptake rate constant
Uptake length	$S_w$	length	$= u \div K_c$ $= u \times h \div V_f$	average distance traveled by a nutrient molecule in inorganic phase prior to uptake
Uptake rate	$U$	$\text{mass length}^{-2} \text{time}^{-1}$	$= V_f \times C = h \times C \times K_c = h \times C \times u \div S_w$	areal uptake rate of an inorganic nutrient into the benthos under ambient conditions; $U$ represents gross nutrient uptake (net uptake is roughly zero in a stream at steady state due to remineralization)
Mass transfer velocity	$V_f$	$\text{length time}^{-1}$	$= h \times K_c = U \div C$ $= u \times h \div S_w$	vertical velocity of nutrient molecules through the water column towards the benthos
Transient storage area	$A_s$	$\text{length}^2$	inverse modeling of observed conservative tracer breakthrough curves	average cross-sectional area of transient storage per unit length of stream
Transient storage exchange coefficient	$\alpha$	$\text{time}^{-1}$	inverse modeling of observed conservative tracer breakthrough curves	rate of water movement between the open channel and transient storage zone
Hydraulic uptake length	$S_H$	length	$= (1 \div \alpha) \times u$	average distance a parcel of water travels before entering transient storage
$F_{med}$	$F_{med}$	%	$= 1 - e^{-L(\alpha \div u)} \times (A_s \div (A_s + A))$	fraction of median travel time through a stream reach that is due to temporary retention of water in transient storage zones; $F_{med}$ can be standardized to a length of 200 m to facilitate comparisons between experiments of different lengths.

<sup>a</sup>Abbreviations:  $u$ , stream velocity;  $h$ , depth;  $L$ , reach length;  $C$ , ambient nutrient concentration;  $Q$ , volumetric flow;  $A$ , channel cross-sectional area.

the water column is a function of channel size and transient storage.

[10] Channel size (a function of depth and width) affects the ratio of benthic surface area to channel volume: As channel size increases, the surface area to volume ratio decreases. Thus a lower proportion of the solute load in a large river has contact with the benthos per length of channel than a small river. Additionally, stream velocity increases with river size, reducing the residence time within a channel reach. These geomorphic relationships have been used extensively to model nutrient uptake in river networks [Wollheim *et al.*, 2006]. From a spatial perspective, the retentive capacity of a stream network depends on its proximity to larger rivers. Allochthonous nutrients will be attenuated more completely during transport through a stream network the farther they must travel before being exported from the watershed [Alexander *et al.*, 2000]. These and many other studies emphasizing the role of headwater streams in nutrient processing are founded on this simple geomorphic relationship: Small rivers allow a larger proportion of water they transport to interact with benthic substrates than do larger rivers.

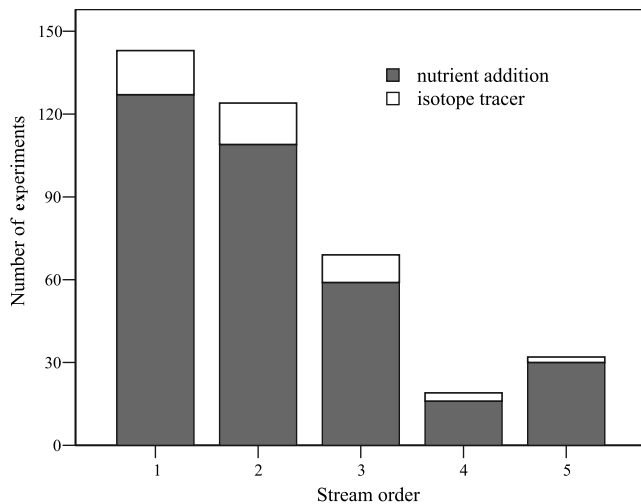
[11] Transient storage is a second geomorphic variable that affects the exposure of stream water to biochemically reactive substrates. This generic term describes the temporary retention of water-borne solutes within localized regions of slow-flowing water. Transient storage can be caused by hyporheic flow [Stanford and Ward, 1988], macrophyte vegetation and water column turbulence [Ensign and Doyle, 2005], and side pools adjacent to the main stream channel [Hall *et al.*, 1998; Gücker and

Boëchat, 2004]. These processes delay downstream transport of water, increase residence time within the stream reach, and expose a larger portion of the stream water to biochemically reactive zones [Dahm *et al.*, 1998]. While transient storage has been widely regarded as an important variable influencing nutrient uptake in streams, generic measurements of transient storage which do not identify the specific mechanisms involved (e.g., hyporheic exchange) do not support this conclusion [Hall *et al.*, 1998; Webster *et al.*, 2003] (except see Ensign and Doyle [2005]).

[12] Studies focused on geomorphic variability have often used  $S_w$  as the metric of nutrient spiraling. However, due to the influence of advection,  $S_w$  has been shown to be a poor metric for comparing the absolute demand of a stream's benthos for a nutrient. More effective comparisons of biochemical nutrient demand between streams can be accomplished by using  $U$  or uptake velocity ( $V_f$ ). These metrics of nutrient spiraling are easily calculated with data from nutrient addition or isotope tracer experiments by incorporating nutrient concentration and depth of the stream (Table 1). Since nutrient uptake from the water column ( $U$ ) is a function of nutrient concentration,  $V_f$  is the preferred metric of benthic nutrient uptake because it is independent of concentration and hydrologic characteristics of the stream.

[13] Of particular relevance to the current study are examinations of how benthic nutrient demand changes along gradients of channel size, as this will give an indication of how spiraling may vary systematically through a channel network. An investigation of 6 Alaskan





**Figure 1.** Distribution of nutrient spiraling experiments by Strahler stream order.

streams with discharge varying 4 orders of magnitude did not find a systematic change in  $V_f$  with stream size [Wollheim *et al.*, 2001]. Few other investigations have compared  $U$  or  $V_f$  across a range of stream sizes, and little is known about how or when  $V_f$  varies along a stream network. This lack of information has made stream network modeling of nutrient uptake challenging. Uptake velocity has not often been used directly to parameterize biological nutrient uptake in models (except see Ensign *et al.* [2006]). Instead, uptake rate constants ( $\text{time}^{-1}$ ) are frequently used, resulting in the unintentional variation of  $V_f$  with stream depth [Wollheim *et al.*, 2006].

### 1.3. Goals and Structure of Paper

[14] In summary, substantial advancements in stream ecology have been made via nutrient spiraling research over the past 3 decades. However, many fundamental questions remain, such as how nutrient processing changes throughout stream networks and the relative effects of geomorphology and stream biota along longitudinal gradients. The current study presents a quantitative synthesis and summary of nutrient spiraling data from the literature. Following discussion of our results, we utilize the nutrient spiraling summary data developed here to examine spatial trends in nutrient spiraling occurring within a stream network. In this discussion we integrate fundamental scaling relationships for river networks with data from the current study to derive simple models of nutrient spiraling and uptake within stream networks.

## 2. Methods

[15] Literature searches were performed to find peer-reviewed articles on nutrient spiraling in streams published prior to March 2006. To be included in this study, the paper had to report  $S_w$ ,  $U$ , or  $V_f$ , or allow calculation of one or more of these values from the data provided. Equations in Table 1 were used to calculate additional nutrient spiraling metrics if one or more was omitted in the original publication. A database was developed for cataloging data reported in the literature. The database consists of 38 fields of data

with one record created for each individual experiment in a stream. In instances where a range of values were reported for a given parameter during an experiment (e.g., stream depth, temperature, slope), the average of the values was used to represent the predominant conditions along the stream reach. Data from both isotope tracer studies, nutrient addition studies, and studies following assimilation of background nutrient concentrations (mass balance) were analyzed. Flume studies, manipulative experiments, and rivers with extremely high nutrient concentrations were excluded. Data were exported from the database to SPSS for statistical analysis.

[16] Stream parameters that could be used to represent the relative size of a stream (e.g., cross-sectional channel area, velocity, discharge) are all quantitatively related to the nutrient spiraling metrics (Table 1). Therefore Strahler stream order was used to represent the general change in channel morphology with increasing channel size [Strahler, 1952].

[17] The difference between isotope tracer and nutrient addition data were examined for each stream order using a Mann-Whitney U test (nonparametric statistics were used because the data were non-normally distributed and had large differences in sample sizes among groups). Differences in spiraling metrics among stream orders were examined using a Kruskal-Wallis test. Differences between spiraling metrics of each nutrient were examined using a Mann-Whitney U test. A critical value of  $\alpha = 0.05$  was chosen for this and all subsequent statistical tests. Nonparametric correlation analysis (Spearman Rank test) was performed between each nutrient spiraling metric and 5 different hydrologic (transient storage) parameters:  $A_s$ ,  $A_s/A$ ,  $S_H$ ,  $F_{med}^{200}$ , and channel bed slope (Table 1). Empirically,  $F_{med}^{200}$  is a measure of the fraction of the median travel time through a stream reach that is attributable to transient storage [Runkel, 2002].

## 3. Results

[18] Fifty-two papers that were included in the database, published between 1981 and 2006 (auxiliary material Text S1<sup>1</sup>). The number of nutrient addition studies performed in each stream order was 127, 109, 59, 16, and 30 for first- to fifth-order streams, respectively (Figure 1). The number of isotope tracer studies performed in each stream order was 16, 15, 10, 3, and 2 for first- to fifth-order streams, respectively (Figure 1). The 87 rivers analyzed were composed of 18, 27, 20, 9, and 3 streams of first- to fifth-order, respectively, and 10 streams of unknown order.

[19] There was wide variability in the spiraling metrics among nutrients, and among metrics used to quantify spiraling (Table 2). The interquartile range in  $S_w$  was 36 to 2917 m for  $\text{NH}_4$ , 102 to 758 m for  $\text{NO}_3$ , and 32 to 394 m for  $\text{PO}_4$  (Table 2). The interquartile range of  $U$  was 6.9 to 63.2  $\mu\text{g m}^{-2} \text{min}^{-1}$  for  $\text{NH}_4$ , 5.2 to 66.3  $\mu\text{g m}^{-2} \text{min}^{-1}$  for  $\text{NO}_3$ , and 6.2 to 34.6  $\mu\text{g m}^{-2} \text{min}^{-1}$  for  $\text{PO}_4$  (Table 2). The interquartile range of  $V_f$  was 2.2 to 10.4  $\text{mm min}^{-1}$  for  $\text{NH}_4$ , 0.5 to 4.3  $\text{mm min}^{-1}$  for  $\text{NO}_3$ , and 0.9 to 6.0  $\text{mm min}^{-1}$  for  $\text{PO}_4$  (Table 2).

[20] These metrics also varied with stream order (Figure 2 and Table 2). Significant differences between spiraling met-

<sup>1</sup>Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/jg/2005jg000114>. Other auxiliary material files are in the HTML.

**Table 2.** Mean, Median, Interquartile Range, and Number of Studies Reporting Each Nutrient Spiraling Metric by Stream Order<sup>a</sup>

Stream Order	NH <sub>4</sub>			NO <sub>3</sub>			PO <sub>4</sub>		
	<i>S<sub>w</sub></i> , m	<i>U</i> , μg m <sup>-2</sup> min <sup>-1</sup>	<i>V<sub>f</sub></i> , mm min <sup>-1</sup>	<i>S<sub>w</sub></i> , m	<i>U</i> , μg m <sup>-2</sup> min <sup>-1</sup>	<i>V<sub>f</sub></i> , mm min <sup>-1</sup>	<i>S<sub>w</sub></i> , m	<i>U</i> , μg m <sup>-2</sup> min <sup>-1</sup>	<i>V<sub>f</sub></i> , mm min <sup>-1</sup>
1	6093	93.9	10.3	416	56.3	2.8	136	51.5	4.2
	40	27.9	6.8	188	9.4	1.6	59	6.9	2.8
	23–275	5.3–52.6	2.5–17.0	101–478	5.8–19.1	0.8–4.2	24–161	3.4–15.7	1.5–6.6
2	53	53	53	53	52	52	104	57	64
	207	49.6	7.6	874	528.4	3.0	193	31.3	5.0
	120	32.4	5.1	199	9.2	1.4	61.5	17.4	2.6
3	60–266	10.6–59.1	2.6–10.0	84–1006	4.3–67.7	0.3–3.3	26–223	8.7–35.3	1.2–6.9
	68	52	53	33	29	29	98	49	64
	141	343.3	6.5	607	87.2	3.0	719	54.0	4.5
4	91	28.5	6.0	357	22.2	0.7	339	20.5	4.5
	51–190	7.7–216.2	2.0–10.3	170–996	4.9–66	0.4–2.8	99–743	9.8–88	1.4–7.1
	29	29	29	26	32	31	21	21	21
5	210	91.4	14.7	2481	172.7	3.0	525	19.5	3.1
	214	20.4	2.8	767	93.1	1.2	598	22.6	2.0
	104–278	3.6–142.5	1.3–12.8	119–4915	6.3–261.6	0.2–4.7	71–907	8.7–29.3	1.1–5.8
All	7	12	12	10	14	14	6	12	12
	2917	120.7	5.5	380	5068.8	9.3	66160	30.4	0.3
	2917	120.7	5.5	380	5068.8	9.3	33600	20.8	0.2
	475–5360	12.8–228.5	3.7–7.3	–	–	–	16175–61350	11.2–44.7	0.1–0.3
	2	2	2	1	1	1	30	30	30
	2128	125.5	8.7	727	1224.6	3.7	7772	41.0	4.0
	86	28.4	5.1	236	14.5	1.4	96	13.7	2.2
	36–250	6.9–63.2	2.2–10.4	102–758	5.2–66.3	0.5–4.3	32–394	6.2–34.6	0.9–6.0
	164	153	154	135	140	139	262	172	194

<sup>a</sup>Summary statistics for all streams include 10 rivers (17 experiments) in which stream order was unknown.

rics of the 5 stream orders were found for NH<sub>4</sub> *S<sub>w</sub>* ( $\chi^2 = 12.6$ ,  $p = 0.014$ ), NO<sub>3</sub> *U* ( $\chi^2 = 10.7$ ,  $p = 0.03$ ), PO<sub>4</sub> *S<sub>w</sub>* ( $\chi^2 = 98.5$ ,  $p < 0.001$ ), PO<sub>4</sub> *U* ( $\chi^2 = 18.5$ ,  $p = 0.001$ ), and PO<sub>4</sub> *V<sub>f</sub>* ( $\chi^2 = 63.2$ ,  $p < 0.001$ ). There were significant differences between nutrient addition and isotope tracer data for NH<sub>4</sub> *S<sub>w</sub>* in 3rd order streams ( $p < 0.001$ ), NH<sub>4</sub> *U* in second-order streams ( $p = 0.028$ ), NH<sub>4</sub> *V<sub>f</sub>* in 2nd–4th order streams ( $p = 0.008$ ,  $p = 0.001$ ,  $p = 0.013$ , respectively), and PO<sub>4</sub> *V<sub>f</sub>* in 1st order streams ( $p = 0.004$ ) (Figure 2).

[21] Significant differences were apparent between *S<sub>w</sub>* of NH<sub>4</sub> and NO<sub>3</sub> ( $p < 0.001$ ) and NO<sub>3</sub> and PO<sub>4</sub> ( $p < 0.001$ ) (sample sizes for all streams in the study are given in Table 2). Areal uptake of NH<sub>4</sub> and NO<sub>3</sub> were significantly different ( $p = 0.028$ ) and NH<sub>4</sub> *U* was significantly different than PO<sub>4</sub> *U* ( $p = 0.001$ ). Significant differences were found between *V<sub>f</sub>* of NH<sub>4</sub> and NO<sub>3</sub> ( $p < 0.001$ ), NH<sub>4</sub> and PO<sub>4</sub> ( $p < 0.001$ ), and NO<sub>3</sub> and PO<sub>4</sub> ( $p = 0.027$ ).

[22] Significant correlations were found in 14 of the 36 correlations performed between spiraling metrics, transient storage, and slope (Table 3). Transient storage area (*A<sub>s</sub>*) was positively correlated with *S<sub>w</sub>* and *U* for NH<sub>4</sub> and PO<sub>4</sub>. However, it was difficult to assess the meaning of these correlations since *A<sub>s</sub>* was closely related to stream size; a more informative transient storage metric is *A<sub>s</sub>/A*. Negative correlations with *A<sub>s</sub>/A* were apparent for NH<sub>4</sub> *S<sub>w</sub>*, PO<sub>4</sub> *S<sub>w</sub>*, and NO<sub>3</sub> *V<sub>f</sub>*. Phosphate *U* and *V<sub>f</sub>* were positively correlated with *A<sub>s</sub>/A*. The most robust metric of transient storage,  $F_{med}^{200}$ , was negatively correlated with NH<sub>4</sub> *V<sub>f</sub>*, NO<sub>3</sub> *S<sub>w</sub>*, and PO<sub>4</sub> *S<sub>w</sub>*. Uptake length for NH<sub>4</sub> in high gradient streams was shorter than for low gradient streams, suggesting a larger demand for NH<sub>4</sub> in streams draining steep terrain relative to their lower gradient counterparts (Table 3). In contrast, PO<sub>4</sub> *U* was lower in high gradient streams than in low gradient streams (Table 3).

[23] A positive relationship would be expected between the spiraling metrics *U* and *V<sub>f</sub>* and transient storage metrics if transient storage exerted influence on nutrient uptake. A

negative relationship between *S<sub>w</sub>* and these metrics would further indicate a coupling of nutrient spiraling to transient storage. Given the four significant correlations between NH<sub>4</sub> spiraling and transient storage, there was equal evidence for and against the hypothesis that increased transient storage positively influences NH<sub>4</sub> uptake. The trend of correlations for NO<sub>3</sub> and transient storage were equally ambiguous. However, 5 correlations between PO<sub>4</sub> spiraling and transient storage supported the idea that nutrient uptake occurs as a function of increased transient storage.

[24] In a final attempt to reconcile these ambiguous results concerning the relationship between transient storage and nutrient uptake, we analyzed the hydraulic uptake length (*S<sub>H</sub>*). The transient storage metric *S<sub>H</sub>* describes the length of channel required for stream water to enter transient storage zones, and examination of the ratio *S<sub>H</sub>:S<sub>w</sub>* can indicate whether nutrient uptake occurs at the same spatial scale as water uptake into transient storage. A value of *S<sub>H</sub>:S<sub>w</sub>* greater than 1 indicates that nutrient removal occurs in surficial biofilms prior to water entering transient storage [Webster *et al.*, 2003]. The *S<sub>H</sub>:S<sub>w</sub>* ratio for NH<sub>4</sub> in this study averaged 9.5 with a median of 2.9, NO<sub>3</sub> averaged 1.5 with median of 0.6, and PO<sub>4</sub> averaged 4.2 with a median of 2.9. These data indicate that NH<sub>4</sub> and PO<sub>4</sub> spiraling occurred at a shorter spatial scale than the water entering transient storage zones, and suggests transient storage is a less important factor in nutrient uptake. Nitrate *S<sub>w</sub>* is closer to the spatial scale of transient storage exchange, suggesting NO<sub>3</sub> uptake may be more closely coupled with transient storage zones.

## 4. Discussion

### 4.1. Effects of Study Methods on the Summary Results

[25] The artifacts imparted to nutrient spiraling experiments by the use of nutrient addition are well known: uptake length increases relative to ambient con-

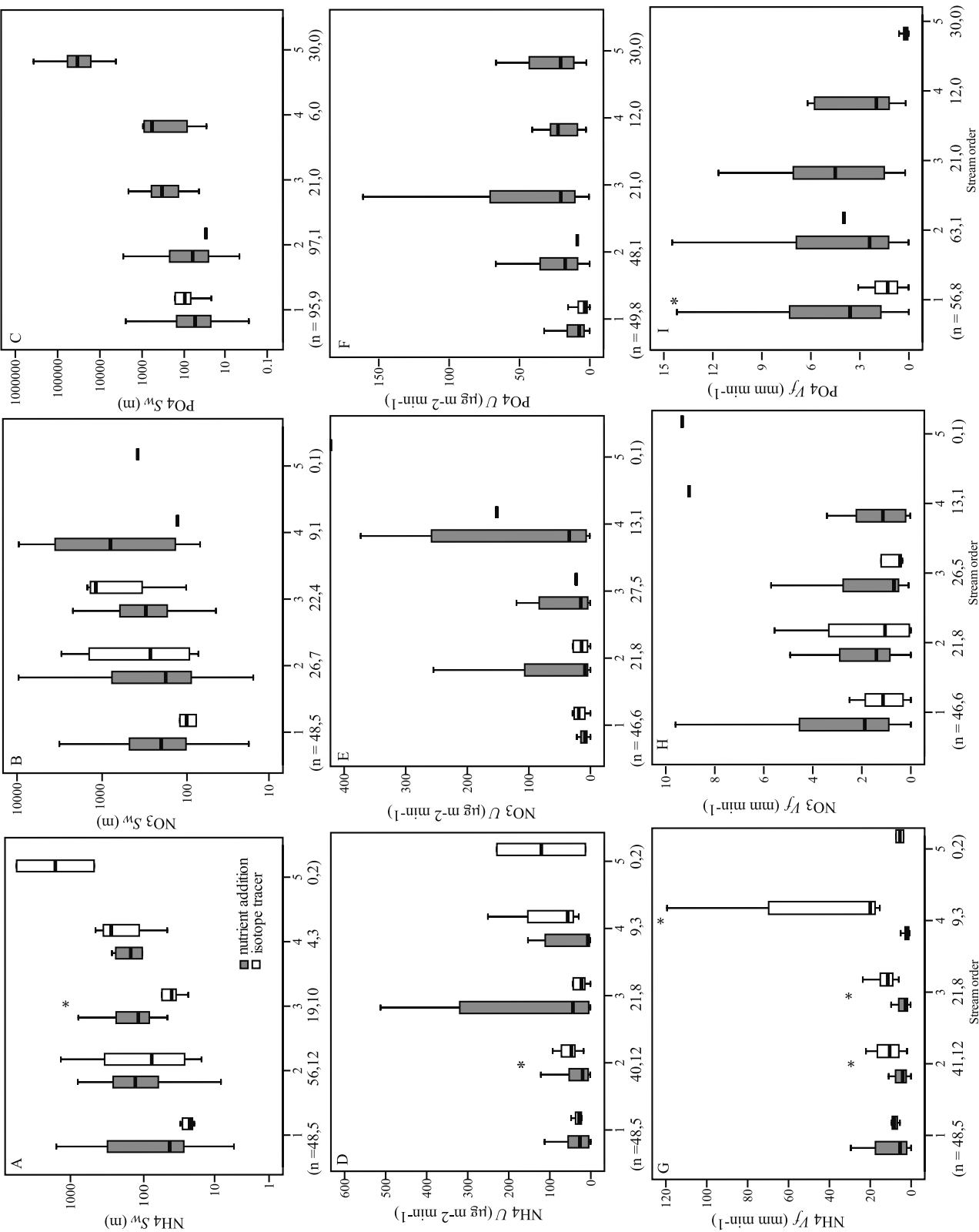


Figure 2

ditions (as measured using isotope tracers) [Mulholland *et al.*, 2002], and the stream's ambient  $U$  and  $V_f$  are underestimated [Dodds *et al.*, 2002]. Nutrient addition studies estimate the ambient  $U$  based on the ambient concentration of nutrient in the stream [Stream Solute Workshop, 1990], which results in a threefold underestimation of the ambient uptake rate [Dodds *et al.*, 2002]. In contrast, isotope tracer experiments do not increase nutrient concentrations, and thus reflect the ambient rate of nutrient cycling in-stream. Payn *et al.* [2005] developed a more sophisticated method for estimating ambient  $S_w$  and  $U$  from multiple nutrient addition experiments.

[26] We examined how these differences in methodology may have affected our results by testing for differences between the isotope tracer and nutrient addition data within each stream order. We did not intend this analysis as a rigorous examination of the influence of nutrient additions on spiraling metrics relative to isotope tracer studies, since the data included a wide range of study sites comprising diverse environmental conditions. Instead, we provided the statistical analysis of differences between isotope tracer and nutrient addition to investigate how our summary statistics provided in Table 2 may have been affected. Since most of the data summarized here was derived from nutrient addition experiments, we expect that the summary statistics are affected to some extent by the methodological problems described above regardless of the outcome of the statistical analysis. In 6 instances the groups of isotope tracer and nutrient addition data were different, and  $\text{NH}_4$  spiraling metrics were most affected. Figure 2g shows that in second- to fourth-order streams,  $\text{NH}_4$   $V_f$  from isotope tracer studies is greater than data from nutrient additions. In conclusion, interpretation of the summary statistics in Table 2 requires consideration for the inherent biases imparted by the nutrient addition methodology.

[27] Another factor affecting this and other cross-site comparisons of nutrient uptake is the influence of flow velocity on the thickness of the diffusive boundary layer (DBL) surrounding biofilms. Thickness of the DBL is proportional to the inverse of the square root of water velocity; thus higher velocities reduce boundary layer thickness and accelerate delivery of nutrients from the surrounding water to underlying cells [Riber and Wetzel, 1987; Losee and Wetzel, 1988]. In laboratory flumes, higher flow velocity reduced the thickness of the diffusive boundary layer (DBL) and enhanced uptake rates of  $\text{NO}_3$  and  $\text{PO}_4$  by periphyton [Larned *et al.*, 2004]. For the purposes of the current study, we anticipate that comparison of streams grouped by stream order alleviated some of the difficulty of cross-site comparison of nutrient uptake rates because flow velocity increases as a function of stream discharge, and therefore stream order [Knighton, 1998].

## 4.2. Influence of Geomorphology and Transient Storage on Nutrient Spiraling

[28] The results of the current study offer little evidence of a causative relationship between transient storage and nutrient uptake. Correlations for  $\text{NH}_4$  and  $\text{NO}_3$  provided conflicting results. While 5 of the 6 significant correlations between transient storage metrics and  $\text{PO}_4$  spiraling suggest transient storage positively affect  $\text{PO}_4$  uptake, the  $S_H:S_w$  relationship suggested that uptake occurred prior to water entering transient storage. Previous summaries of generic transient storage data have also not been able to find a relationship [Hart *et al.*, 1992; Webster *et al.*, 2003], and others have expressed doubt that such a relationship exists [Hall *et al.*, 1998].

[29] Alternatively, some studies have observed a strong effect of transient storage on nutrient uptake. Triska *et al.* [1989] found that transient storage of  $\text{NO}_3$  accounted for 10% of the  $\text{NO}_3$  added over 10 days to Little Lost Man Creek, California. Mulholland *et al.* [1997] found transient storage to be responsible for 43% of  $\text{PO}_4$  retention in Hugh White Creek (North Carolina). In another North Carolina stream, Snake Den Branch, transient storage was found to be responsible for slightly less than half the  $\text{NO}_3$  retention during an experimental injection [Thomas *et al.*, 2003]. Furthermore, modeling and mesocosm experiments clearly demonstrate that transient storage affects nutrient uptake [DeAngelis *et al.*, 1995; Mulholland *et al.*, 1994], although these models are structured on the a priori assumption that nutrient retention occurs in transient storage.

[30] It is important to highlight the fact that the transient storage data reviewed here represent generic, reach scale measurements in which specific mechanisms of storage (hyporheic, in-channel dead zones, biofilms, etc.) were not identified. Transient storage is most commonly quantified by inverse modeling of time series data from conservative tracer injections such as those accompanying all nutrient spiraling experiments. To develop a better understanding of transient storage in stream ecosystems, measurements of generic transient storage must be supplemented with measures of the relative importance of various stream features such as hyporheic exchange and turbulence on transient storage [see Ensign and Doyle, 2005]. Measures of generic transient storage alone provide little information about the relationship between geomorphology and nutrient uptake.

[31] Despite a general lack of consensus regarding the role of transient storage in nutrient retention, the conceptual model in which residence time (a function of stream geomorphology) indirectly influences nutrient uptake remains conceptually sound [Valett *et al.*, 1996]. Indeed, nutrient recycling within lakes and streams is predominantly a function of hydrologic residence time [Essington and

**Figure 2.** Distribution of  $S_w$  for (a)  $\text{NH}_4$ , (b)  $\text{NO}_3$ , and (c)  $\text{PO}_4$ ,  $U$  for (d)  $\text{NH}_4$ , (e)  $\text{NO}_3$ , and (f)  $\text{PO}_4$ , and  $V_f$  for (g)  $\text{NH}_4$ , (h)  $\text{NO}_3$ , and (i)  $\text{PO}_4$  experiments in the database. Sample size (n) of nutrient addition and isotope tracer experiments for each stream order is displayed below the x-axis. Whiskers represent the minimum and maximum values that are not outliers, the box represents the 25th to 75th percentile, and the black bar represents the median. Outliers (greater than  $1.5 \times$  interquartile range from the 75th and 25th percentile) are not shown. An asterisk above a pair of boxes represents a significant ( $p < 0.05$ ) difference between the isotope tracer and nutrient addition data.



**Table 3.** Nonparametric Correlations Between Nutrient Spiraling Metrics and Geomorphic Stream Parameters<sup>a</sup>

	Metric	$A_s$	$A_s/A$	$F_{med}^{200}$	Slope
NH <sub>4</sub>	$S_w$	0.575	−0.285	−0.231	−0.323
		<0.001	0.007	0.081	0.015
		60	90	58	56
	$U$	0.368	−0.040	−0.049	−0.021
		0.004	0.700	0.713	0.882
	$V_f$	58	93	58	53
NO <sub>3</sub>	$S_w$	−0.026	−0.160	−0.282	0.207
		0.844	0.123	0.032	0.137
		58	94	58	53
	$U$	0.186	−0.162	−0.372	−0.047
		0.293	0.169	0.043	0.799
		34	74	30	32
	$V_f$	0.092	0.101	−0.159	−0.106
		0.588	0.384	0.377	0.557
		37	77	33	33
PO <sub>4</sub>	$S_w$	−0.008	−0.241	−0.075	0.116
		0.963	0.035	0.680	0.520
		37	77	33	33
	$U$	0.336	−0.415	−0.552	0.174
		0.026	<0.001	<0.001	0.208
		44	86	44	54
	$V_f$	0.650	0.262	−0.139	−0.403
		<0.001	0.017	0.427	0.002
		35	82	35	55
		0.019	0.283	0.014	−0.054
		0.914	0.009	0.935	0.694
		35	83	35	55

<sup>a</sup>Values are Spearman's rho test statistic, significance value, and sample size.

Carpenter, 2000]. The greatest hurdle in development of an empirical, unified relationship between transient storage and nutrient uptake in streams is identification and quantification of the various mechanisms influencing transient storage.

[32] In addition to the metrics of transient storage used here, we included stream bed slope in this study because it was commonly reported in nutrient spiraling studies and is an important geomorphic factor of streams. Stream bed slope was negatively correlated with NH<sub>4</sub>  $S_w$  and PO<sub>4</sub>  $U$ . Like other geomorphic variables which are related to stream order, slope decreases as a function of discharge and stream order [Knighton, 1998], and concomitantly affects other geomorphic variables such as flow velocity and sediment grain size. Higher channel gradient can induce hydraulic pumping of stream water into the hyporheic zone, thus increasing transient storage and associated nutrient retention [Hester and Doyle, 2005]. This explanation applies to the relationship between slope and NH<sub>4</sub>  $S_w$  observed here, but not to PO<sub>4</sub>. Lacking other significant relationships between slope and nutrient spiraling, it is difficult to suggest how slope may affect PO<sub>4</sub> uptake.

## 5. Synthesis: Nutrient Spiraling Through Stream Networks

[33] The nutrient spiraling model has advanced the broader field of stream ecology most significantly because it integrates biogeochemical fluxes occurring within whole stream ecosystems, or at least representative reaches within them. Subsequently, we have learned much about the connectivity between streams, their hyporheic and parafluvial zones. In summary, the nutrient spiraling model has served as a unifying paradigm for the examination of

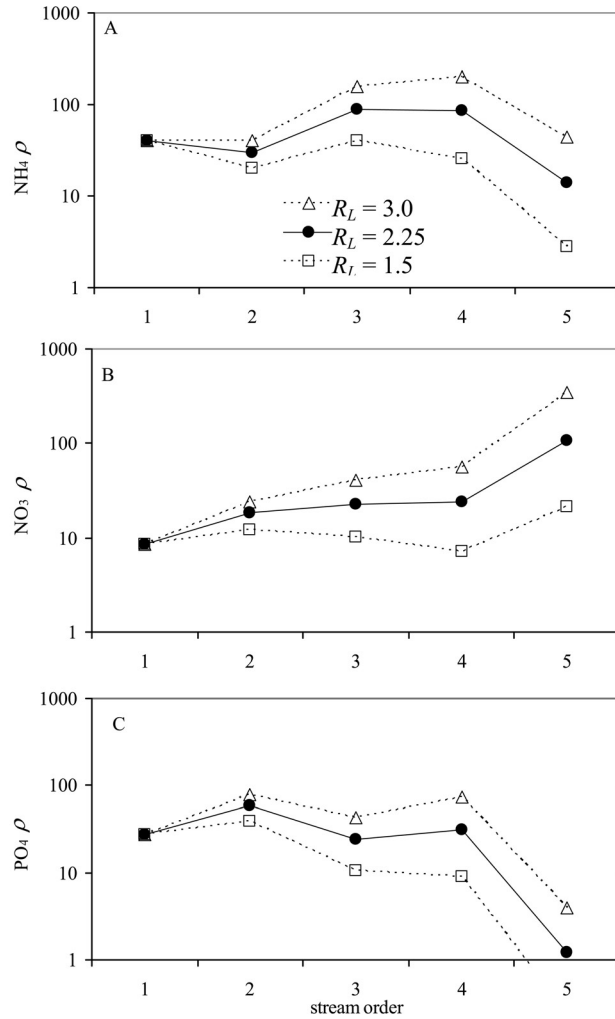
flowpaths of water and solutes between terrestrial and fluvial ecosystems [Fisher et al., 2004].

[34] Despite these advances in our understanding of hydrologic flowpaths at the reach scale, there is a gap in our understanding of how these processes are integrated between reaches, and consequently how nutrient spiraling functions throughout an entire stream network. In essence, the stream network encompasses a longitudinal gradient of the ecosystem, spanning from headwater streams to large rivers. Longitudinal patterns in the physical characteristics of the stream affect the trophic structure along the stream network [Minshall et al., 1983], and various conceptual models have been developed to describe this variability (e.g., the river continuum concept [Vannote et al., 1980]). Given the longitudinal gradients in community structure and energy flow along a stream network, we might also expect to find spatial patterns in nutrient spiraling along the river continuum.

[35] While variability of ecosystem processes along river continua is well established, fewer have considered how ecosystem processes are affected by the branching pattern characteristic of river networks. Integrating longitudinal patterns along the river continuum with branching patterns of channel networks requires consideration of the spatial configuration of the stream network, which is generally ignored in stream biogeochemistry [Fisher et al., 2004].

[36] Early observations of stream networks led to the development of scaling relationships for channel length, number of channels, and catchment area for each stream order in a network [Horton, 1945; Schumm, 1956]. Although more sophisticated techniques of drainage network analysis are now commonly used (e.g., the probabilistic-topologic approach, [Smart, 1968; Shreve, 1966]) these scaling relationships have been tested and upheld in





**Figure 3.** Number of (a)  $\text{NH}_4$ , (b)  $\text{NO}_3$ , and (c)  $\text{PO}_4$  spirals undergone within stream orders 1–5 determined using equation (4) and summary values of  $S_w$ .

diverse landscapes. The average length of streams of each order ( $L_i$ ) can be estimated as

$$L_i = R_L \times L_{i-1}, \quad (1)$$

where  $R_L$  is the stream length ratio observed throughout the watershed [Horton, 1945]. Next, the number of streams of each order ( $N_i$ ) in a stream network can be estimated as

$$N_i = R_B \times N_{i-1}, \quad (2)$$

where  $R_B$  is the average bifurcation ratio of the stream network [Horton, 1945]. Finally, the drainage area ( $D_i$ ) of each stream order can be calculated as

$$D_i = R_A \times D_{i-1}. \quad (3)$$

These equations, referred to as the laws of drainage network composition, have values of  $R_L$ ,  $R_B$ , and  $R_A$  that consistently range from 1.5–3, 3–5, and 3–6, respectively [Knighton, 1998]. These laws of stream length and number can be integrated with the summary data from the current

study to estimate the recycling and uptake of N and P within a stream network.

### 5.1. Recycling of Nutrients Through a Stream Network

[37] The number of times an atom of N or P is spiraled between the water column and benthos along a stream is a function of the stream's length and the nutrient atom's spiraling length. Spiraling length is composed mainly of the  $S_w$  [Newbold *et al.*, 1981], and  $S_w$  will be used here as an approximation of the total spiraling length. The number of spirals ( $\rho$ ) occurring along a stream of a particular order,  $i$ , is calculated as

$$\rho = \frac{L_i}{S_w}, \quad (4)$$

where  $L_i$  is the length of channel for the stream order  $i$  ( $\rho$  is identical to the recycling ratio calculated for lakes and streams by Essington and Carpenter [2000]).

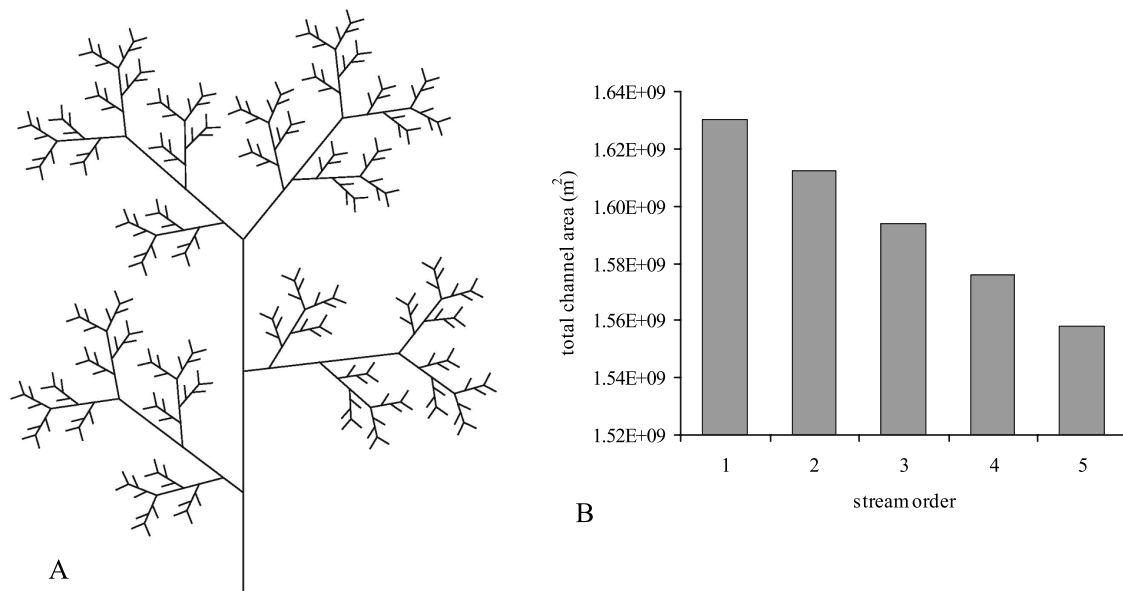
[38] Here we consider nutrient spiraling within a hypothetical drainage basin with a first-order stream length of 1.61 km (the average length of first-order streams in the United States as summarized by Leopold *et al.* [1964]). In this example, the  $\rho$  of first-order streams is thus equal to:  $1.61 \div S_w$  of first-order streams. Using the median  $S_w$  for second-order streams and combining equations (1) and (4), the  $\rho$  of second-order streams is equal to

$$\rho = \frac{R_L \times 1.61}{S_w}. \quad (5)$$

Calculation of  $\rho$  for a higher order stream simply requires substitution of the length of the next lowest stream order for 1.61 in equation (5).

[39] The median of the  $S_w$  values for each nutrient (Table 2) were used in conjunction with equation 5 to calculate  $\rho$  within a theoretical stream network (Figure 3). Three values were used for  $R_L$  spanning the range of values commonly found in watersheds [Knighton, 1998]. Choice of a different first-order stream length than the one here (1.61 km) would subsequently affect  $\rho$  values for the other stream orders, though the relative pattern would remain the same between stream orders. Therefore we emphasize the patterns in  $\rho$  between stream orders and nutrients, not the absolute value of  $\rho$  because it may vary dramatically between diverse watersheds.

[40] The  $\rho$  values in Figure 3 demonstrate how many times an atom of N or P is recycled during transport through each stream order along a single river continuum (i.e., not considering networking). For all nutrients, streams with a gradual increase in channel length throughout the watershed (represented by  $R_L = 1.5$ ) show less recycling than along a river continuum with rapidly increasing channel length (represented by  $R_L = 3.0$ ). In general, Figure 3 suggests that  $\text{NH}_4$  recycling peaked in stream orders 3 and 4. Nitrate recycling increased with stream order, but was nearly always less than  $\text{NH}_4$   $\rho$ . In general, recycling of N intensified as channel size increased, with biological sequestration offsetting the effect of increased discharge and subsequent downstream transport. Phosphate recycling peaked in second-order streams, and  $\rho$  in third- and fourth-order streams was roughly equivalent to  $\rho$  in first-order streams. Recycling of  $\text{PO}_4$  occurred less



**Figure 4.** (a) Planform schematic of the fifth-order stream network used to calculate cumulative uptake,  $G$ , and (b) the total channel area in each stream order of the network.

rapidly in higher order streams (third to fifth), indicating a more direct coupling between  $\text{PO}_4$  loading to headwater streams and their downstream ecosystems.

[41] Calculation of the recycling ratio,  $\rho$ , enhanced our understanding of spatial trends in  $S_w$  throughout a river continuum, and indicated differences in N and P spiraling. While there is a clear increase in  $S_w$  with stream order due to increased advection, this did not necessarily mean that higher order streams were less capable of retaining nutrients in the larger context of a stream network. The recycling analyzed here involves remineralization of organic N and P back into the water column in a dissolved inorganic form. Biotic sequestration and the associated turnover time delays the downstream transport of nutrients, thus slowing the movement of N and P between terrestrial and aquatic, estuarine, or marine ecosystems downstream.

## 5.2. Nutrient Uptake in Stream Networks

[42] The analysis of recycling ratio,  $\rho$ , considered streams as they have traditionally been treated: as a single-thread river continuum [e.g., *Vannote et al.*, 1980]. In reality, streams are branching networks, and so we next present a different perspective on stream network-scale nutrient spiraling based on  $U$ , with explicit consideration of variability in networking patterns.

[43] The nutrient spiraling metric  $U$  summarized from the literature in the current study can be used to calculate the cumulative flux of nutrients from the water column into the benthos at the stream network scale. For this exercise we constructed a hypothetical fifth-order watershed. Cumulative nutrient uptake ( $G$ , mass time<sup>-1</sup>) within all streams of each stream order ( $i$ ) was calculated as

$$G_i = L_i \times W_{b(i)} \times N_i \times U_i, \quad (6)$$

where  $L$  was the channel length for a particular order,  $W_b$  was channel width, and  $N$  was the number of channels of stream order  $i$ . We used the 25th, 50th, and 75th percentile

of the  $\text{NH}_4$ ,  $\text{NO}_3$ , and  $\text{PO}_4$   $U$  values summarized previously for each stream order (Table 2). Channel length was fixed at 1.6 km for first-order streams, and adjusted using  $R_L = 2.25$  for subsequent stream orders (Figure 4). Number of streams of each order was adjusted using  $R_B = 4$  (Figure 4). Drainage area of first-order streams ( $3.2 \text{ km}^2$ ) was estimated using an empirical formula based on stream length [*Hack*, 1957], and drainage area of second- through fifth-order streams was scaled using equation (3) with  $R_A = 4.5$ . Bankfull channel width ( $W_b$ ) was calculated as

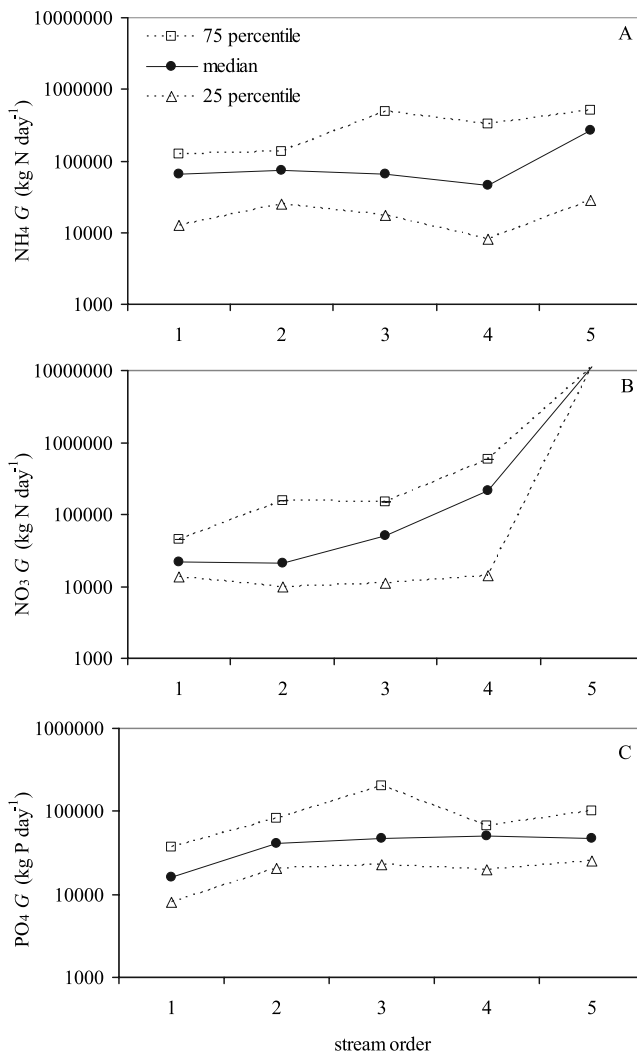
$$W_b = B \times Q^x, \quad (7)$$

where  $B$  and  $x$  are empirically derived values set equal to 3.93 and 0.5, respectively [*Leopold et al.*, 1964; *Knighton*, 1998]. Bankfull discharge was calculated as

$$Q = E \times D^y, \quad (8)$$

where  $E$  and  $y$  are empirically-derived values set equal to 0.42 and 0.75, respectively [*Leopold et al.*, 1964; *Knighton*, 1998]. The total channel area of each stream order is given in Figure 4. The coefficient and exponents for equations (7) and (8) vary owing to climate and underlying geology, but can be easily adapted on the basis of regional observations. While different sets of these parameters would influence the results of equation (6), the difference in values would not affect the relative change in  $G$  between stream orders. Consequently, we emphasize the relative changes in  $G$  between stream orders and nutrients rather than the absolute values.

[44] Figure 5 presents  $G$  calculated from the summary statistics of  $U$  compiled in the current study and applied to the hypothetical fifth-order watershed. Given the median value of  $\text{NH}_4$   $U$ ,  $\text{NH}_4$   $G$  decreases slightly between first- and fourth-order streams, peaking in fifth-order streams. Nitrate  $G$  increased within increasing stream order when the median  $U$  value is used in equation (6), rising most



**Figure 5.** Cumulative uptake flux ( $G$ ) of (a)  $\text{NH}_4$ , (b)  $\text{NO}_3$ , and (c)  $\text{PO}_4$  in first- to fifth-order streams of a hypothetical watershed calculated using equation (6) and the 25th, 50th, and 75th percentile values of  $U$  from the database. Only 1 value was available for  $\text{NO}_3$   $U$  in fifth-order streams and therefore Figure 5b is not scaled to include this data point.

dramatically between second- and fourth-order streams (we disregard the data for fifth-order streams because it is based on a single data point). Phosphate  $G$  increases substantially between first- and second-order streams, and then rises gradually through fifth order. Higher-order streams are thus equally as important in  $\text{PO}_4$  uptake as are headwater streams. The  $\text{NO}_3$  and  $\text{PO}_4$  data suggest that larger, higher-order rivers are of more significance to watershed-scale nutrient uptake than headwater streams.

[45] The trends in  $\rho$  and  $G$  represent slightly different perspectives on the longitudinal trends in nutrient spiraling through a stream network. The  $\rho$  values highlight the interaction between nutrient spiraling and ever-increasing channel lengths through a stream network. Increased channel length compensates for higher flow velocity and depth along the longitudinal river continuum, thereby allowing more recycling of inorganic N (at least up through fourth-

order streams). The  $G$  values indicate that the relative mass of nutrients processed at each stream order along the downstream gradient decreases slightly ( $\text{NH}_4$ ) or may increase ( $\text{NO}_3$  and  $\text{PO}_4$ ).

[46] Our results are similar to those of *Wollheim et al.* [2006], who found that the proportion of nutrient removal in each stream order increased when uptake remained constant along the stream network. Their model was based on  $V_f$  whereas ours was based on  $U$  and predicted mass of removal instead of the fraction of nutrient removed. However, this pattern is sensitive to variation in channel width scaling, and highlights the need for further investigation of how stream network characteristics influence nutrient spiraling. The simple scaling methods we used for stream length, number of streams, catchment area, and resulting width of the stream are a simplistic approach to modeling stream networks. Further research is needed to investigate how different styles of drainage networks, such as dendritic and pinnate, would affect the mass flux of nutrients to the stream ecosystems. The laws of drainage networks used here perform well for dendritic watersheds, as these watersheds display the most self-similar patterns over a broad scale and number of stream orders. Other types of watersheds, such as those with pinnate drainages, may not be as consistent. This work would provide important information on spatial patterns in nutrient spiraling across broad physiographic areas, but will be hindered by the paucity of nutrient spiraling data in larger rivers (fourth order and greater).

## 6. Conclusions

[47] Much attention has been given to the importance of headwater streams in nutrient spiraling research [*Alexander et al.*, 2000; *Peterson et al.*, 2001], and indeed much of our knowledge of stream ecosystems is biased toward first- and second-order streams (Figure 1). However, the network scaling data shown here suggests an equally important role for larger rivers downstream in nutrient spiraling. Several patterns in nutrient spiraling were evident from the broad array of streams synthesized in this study. Phosphorus (as  $\text{PO}_4$ ) recycling and uptake was relatively constant as it was transported downstream within a stream network, indicating that headwater streams are not necessarily the most important regions of  $\text{PO}_4$  spiraling. Nitrogen (as  $\text{NO}_3$ ) was recycled more intensively as it was transported to higher order streams where mass flux was greater. Likewise,  $\text{NH}_4$ -N is recycled more in mid-order streams while maintaining a nearly constant rate of uptake across stream orders. Altogether these data suggest that larger streams appear to play an equally important role in buffering downstream ecosystems (lakes, estuaries, and oceans) from nutrient pollution as do headwater streams when considered within the context of the stream network.

[48] Application of nutrient spiraling theory and data to watershed-scale processes requires more research in larger (>third order) rivers. It is critical that future research address the ecological connectivity of these small streams with their lower end-members (rivers, lakes, and estuaries). The network-scale analysis provided here is intended to stimulate consideration for how to integrate the nutrient spiraling model with other longitudinally-based models of fluvial



systems. Knowledge of how nutrients spiral within stream networks, not just a stream, will be especially valuable to aquatic research in downstream environments where prediction of nutrient delivery is so obscured by in-stream processes.

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- M. W. Doyle, Department of Geography, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA.
- S. H. Ensign, Curriculum in Ecology, University of North Carolina at Chapel Hill, 3431 Arendell Street, Morehead City, NC 28557, USA. (ensign@email.unc.edu)