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Key Points:

- Instream processes control the intra-annual pattern of N export
- The net effect of instream processes on annual N export may not be irrelevant
- High N load accelerates instream N cycling, leading to constant N pattern

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Effects of lateral nitrate flux and instream processes on dissolved inorganic nitrogen export in a forested catchment: A model sensitivity analysis

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Abstract The importance of terrestrial and aquatic ecosystems in controlling nitrogen dynamics in streams is a key interest of ecologists studying dissolved inorganic nitrogen (DIN) export from watersheds. In this study, we coupled a stream model with a terrestrial ecohydrological model and conducted a global sensitivity analysis to evaluate the relative importance of both ecosystems to nitrogen export. We constructed two scenarios (“normal” and high nitrate loads) to explore conditions under which terrestrial (lateral nitrate flux) or aquatic ecosystems (instream nutrient processes) may be more important in controlling DIN export. In a forest catchment, although the forest ecosystem controls the nitrogen load to streams, sensitivity results suggested that most nitrogen output from the terrestrial ecosystem was taken up by instream microbial immobilization associated with benthic detritus and retained in detritus. Later the immobilized nitrogen was remineralized as DIN. Therefore, the intra-annual pattern of DIN concentration in the stream was low in fall and became high in spring. Not only was instream microbial immobilization saturated with the high nitrogen load scenario, but also the net effect of immobilization and mineralization on DIN export was minimized because nitrogen cycling between organic and inorganic forms was accelerated. Overall, our linked terrestrial-aquatic model simulations demonstrated that stream process could significantly affect the amount and timing of watershed nitrogen export when nitrogen export from the terrestrial system is low. However, when nitrogen export from the terrestrial system is high, the effect of stream processes is minimal.

1. Introduction

Nutrient input from terrestrial ecosystems and instream processes may play important roles in modifying nutrient concentrations in streams [Bernhardt *et al.*, 2005; Sudduth *et al.*, 2013]. Many studies support the idea that terrestrial processes and hillslope hydrology have a dominant control on watershed-scale nutrient export [e.g., Bormann and Likens, 1967; Vitousek and Reiners, 1975; McGroddy *et al.*, 2008; Brookshire *et al.*, 2009]. In contrast, recent studies have shown that instream processes may also play a major role in controlling nutrient balance and export [e.g., Peterson *et al.*, 2001; Bernhardt *et al.*, 2005; Webster *et al.*, 2009]. One interesting question is under what conditions terrestrial and/or aquatic ecosystem processes control nutrient export from forested watershed systems.

There are three major components in a forest ecosystem controlling nutrient exports. First, trees take up bioavailable nutrients and incorporate them into biomass. Second, evapotranspiration by plants controls water runoff and stream discharge, resulting in a typical seasonal hydrologic pattern in forested catchments with high base flow in winter and low in summer. Third, a portion of plant biomass is converted to litter and soil organic matter, which can have significant effects on nutrient dynamics. Litter and soil organic matter decomposition immobilizes and mineralizes nutrients in the soil column, initially competing for nutrients with plants but then making nutrients available to plants. About 94–99% of nitrogen deposition is retained by undisturbed forest ecosystems in the southern Appalachian Mountains [Knoepp *et al.*, 2008], where most nitrogen is stored in plant biomass, litter, and soil organic matter [Rodin and Bazilevich, 1967; Swank and Waide, 1980; Cole and Rapp, 1981]. Excessive dissolved inorganic and organic nitrogen leach from the forest

floor [Currie and Aber, 1997] and are exported via surface and groundwater flows. Hillslope hydrology, hence, plays a critical role in transporting nitrogen from terrestrial to stream ecosystems [Creed and Band, 1998a, 1998b; Oldham et al., 2013; Adams et al., 2014] and controlling nitrogen concentrations in export [Thompson et al., 2011].

Nutrients are retained, transformed, and removed by instream aquatic biogeochemical processes, including: biological uptake, mineralization, nitrification, denitrification, physical absorption, and water loss to groundwater. In this study, we focused on microbial nutrient immobilization and mineralization associated with leaf decomposition (we refer to these as instream retention processes), two critical instream nutrient processes that may substantially modify stream nutrient concentrations in headwater streams within forested catchments. Immobilization refers to an accumulation of nutrients in litter, and mineralization refers to degradation of organic matter converting a fraction of organic matter bound nutrients into biologically available nutrients [Aber and Melillo, 1982; Berg and McLaugherty, 2003]. Investigation of the importance of instream retention processes can be traced back to Kaushik and Hynes [1971] and Hynes [1960]. Although nutrient immobilization has been a major focus of studies on nutrient dynamics in streams, we have less understanding of how mineralization influences instream nutrients because quantification of mineralization has been limited to whole-stream tracer studies [Beever and Burns, 1980; Jennings, 1995] or animal excretion experiments [Vanni, 2002; Hood et al., 2005; McIntyre et al., 2008]. Webster et al. [2009] illustrated and emphasized the importance of both nutrient immobilization and mineralization in modifying nutrient concentrations in streams.

The objectives of this study were (1) to explore the effects of terrestrial (lateral nitrate flux) and aquatic (instream nutrient processes) ecosystems on dissolved inorganic nitrogen (nitrate and ammonium; DIN) export from forested headwater catchments through a terrestrial-aquatic modeling framework; and (2) to evaluate the relative importance of terrestrial and aquatic ecosystems in contributing to nitrogen export by a series of global sensitivity analyses [Sobol, 2001; Nossent et al., 2011; Glen and Isaacs, 2012] with different levels of lateral nitrate flux from terrestrial to stream ecosystems.

2. Methods

2.1. Study Site

Small mountain headwater streams within forested catchments, such as those typical in the southern Appalachian Mountains, are characterized by heavy shade [Webster et al., 1997], low instream primary production [Bernot et al., 2010], and high allochthonous input of coarse organic matter [Webster et al., 1999]. Hugh White Creek (HWC) is a small stream at the Coweeta Hydrologic Laboratory, North Carolina, USA, located within the southern Appalachian Mountains (Figure 1). HWC drains a 61 ha undisturbed forested catchment (Watershed 14). Phosphorus and nitrogen dynamics [e.g., Golladay and Webster, 1988; Webster et al., 1991; Mulholland et al., 1997; Crenshaw et al., 2002; Brookshire et al., 2005; Valett et al., 2008; Brookshire et al., 2010; Cheever et al., 2012] and leaf decomposition [e.g., Benfield et al., 1991, 2001; Hagen et al., 2006; Webster et al., 2009; Cheever et al., 2012] in this stream have been extensively studied. The dominant canopy tree species are oaks and mixed hardwoods including *Quercus* spp. (oaks), *Carya* spp. (hickories), *Nyssa sylvatica* (black gum), and *Liriodendron tulipifera* (yellow poplar). Soils are relatively uniform, described as sandy loam inceptisols and ultisols typically of colluvial origin [Hales et al., 2009]. Coweeta has a mild and humid climate [Swift et al., 1988], and average annual precipitation for the study watershed is about 1880 mm. Rainfall occurs fairly evenly throughout the year, only 2–10% of which occurs as snow [Laseter et al., 2012]. Annual litterfall to the channel averages about 327 g ash-free-dry-mass m^{-2} (AFDM) [Webster et al., 2001]. Springs and groundwater that drain into HWC have low nutrient concentrations. About 5 $\mu\text{gNO}_3\text{-N L}^{-1}$ is found in hillslope soil water near streams and in spring seeps [Golladay et al., 1992]. Average nutrient concentrations in stream water are 25 $\mu\text{g NO}_3\text{-N L}^{-1}$ and 2 $\mu\text{gPO}_4\text{-P L}^{-1}$. Annual average nitrogen deposition is 1.0 g N $\text{m}^{-2} \text{yr}^{-1}$ [Knoepp et al., 2008].

2.2. Development of the Terrestrial-Aquatic Integrated Model

Our model representation of a forested catchment consisted of two major components, a forest ecosystem and an aquatic ecosystem (presented as a stream network; Figure 1). We derived the stream network from a 10 m resolution elevation map (USGS National Elevation Data set) via geographic information system (GIS) software (GRASS GIS version 6.4). We used a surface flow generation threshold of 2.5 ha to approximate the

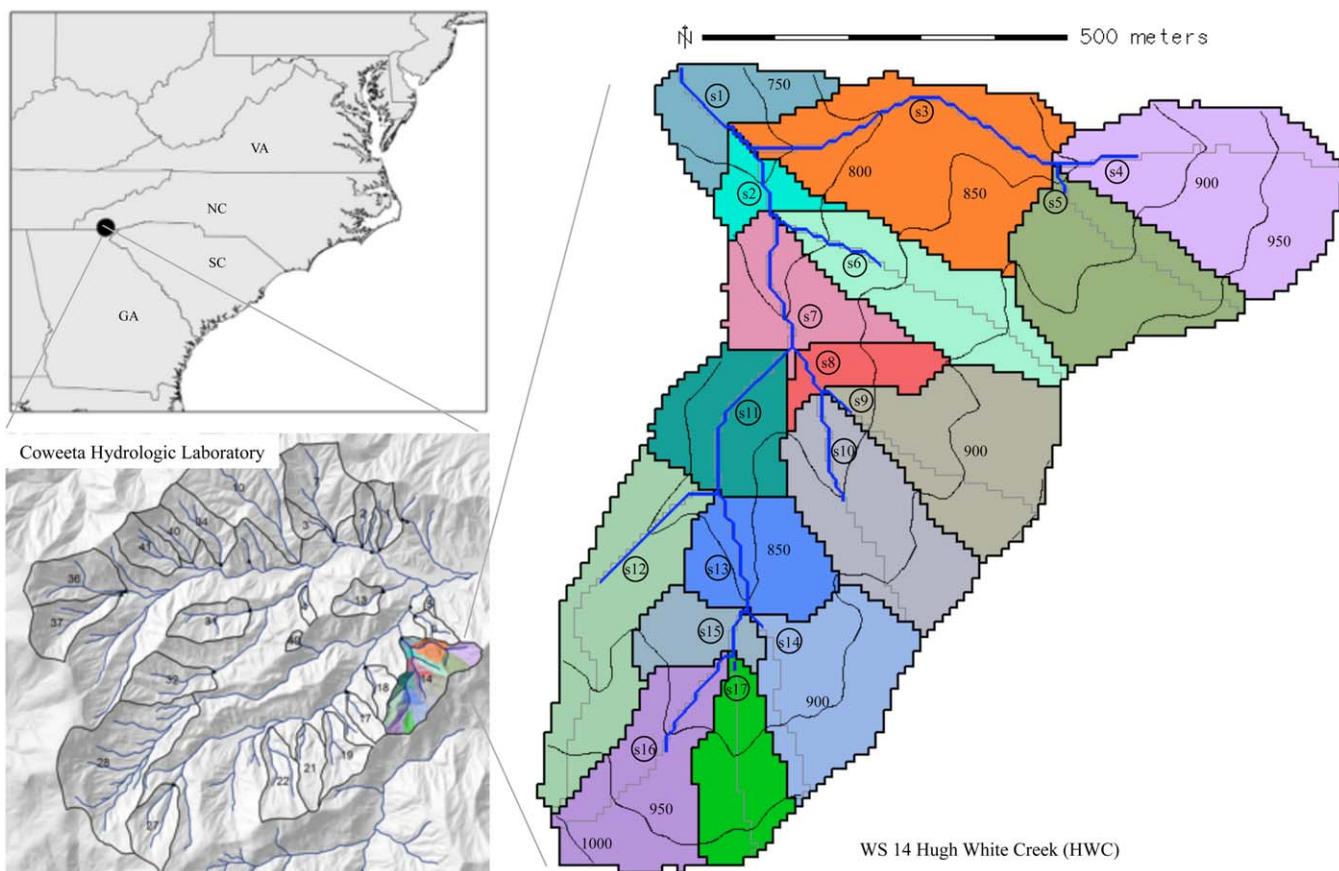


Figure 1. The study site, Watershed 14 and Hugh White Creek. Subcatchments are labeled with circled codes and colored differently. The stream network was broken down to stream segments, which correspond to each subcatchment. Thin black lines are contours to show elevations in the watershed.

location of flow initiation in the study watershed. The watershed boundary and stream networks were generated assuming the single flow direction along the steepest gradient of neighboring pixels, usually called a D-8 method [O'Callaghan and Mark, 1984; Band, 1986]. This method was quite effective in this steep mountainous terrain, therefore generated streams and segments matched well with the observed stream networks. A least-cost search algorithm [Kinner et al., 2005] with D-8 assumption was used in the GIS software to determine the watershed and stream network. The derived stream network was composed of 17 stream segments, each of which had a single channel with corresponding hillslopes on each side (Figure 1).

2.2.1. Terrestrial Model

To estimate lateral nitrate flux, we used the Regional Hydro-Ecologic Simulation System [RHESys, Tague and Band, 2004; Figure 2], a terrestrial ecohydrological model simulating forest biogeochemical cycles coupled with hillslope-scale hydrologic behavior. The nitrogen processes in the model were largely based on the BIOME-BGC model [Running and Coughlan, 1988; Running and Hunt, 1993; Kimball et al., 1997; Thornton et al., 2002] for vegetation and the CENTURY_{NGAS} model [Parton et al., 1996] for soil biogeochemistry. The model assumed different C:N ratios for each vegetation compartment (leaf, litter, fine root, live wood, and dead wood) and soil organic pool [Tague and Band, 2004]. These ratios were fixed in the model simulation. At the end of each daily time step, all soil/litter pools calculated the potential immobilization and decomposition rates based on the soil water and temperature modification functions. If nitrogen availability could not meet the sum of potential immobilization and plant uptake, these two demands competed for available soil mineral nitrogen, and available nitrogen would be proportionally allocated based on their original demands [Tague and Band, 2004]. Plants were also allowed to access translocated nitrogen pools from leaf and live vegetation parts for remaining demands for nitrogen. Available nitrogen also included atmospheric deposition, fertilization, and symbiotic/asymbiotic fixation. Detailed explanations of the

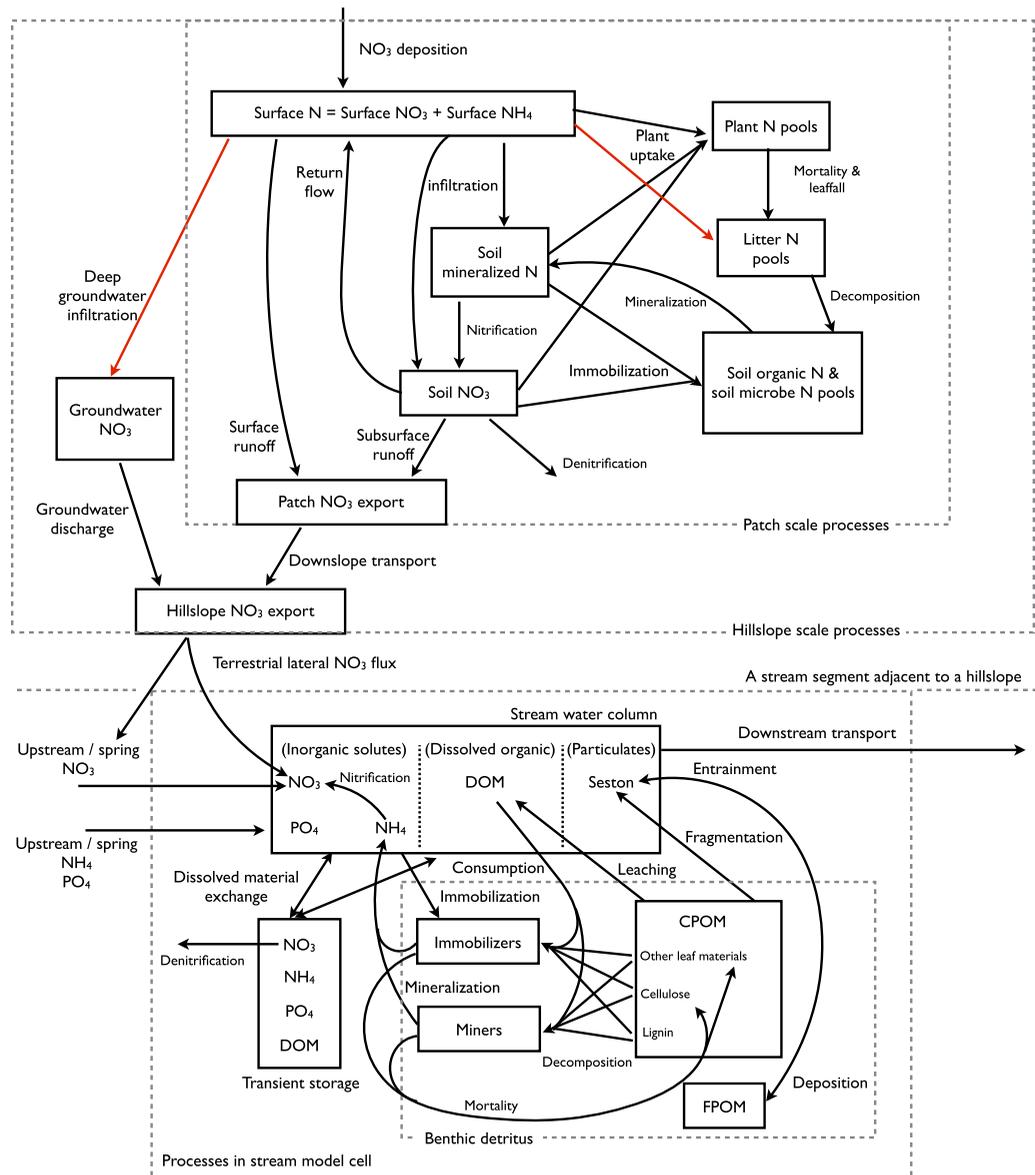


Figure 2. A conceptual diagram of the terrestrial-aquatic integrated model. In this diagram, we mainly focused on the nitrogen pathways and compartments in the model. The red arrows indicate the modified or added processes in the RHESSys model. The terrestrial-aquatic integrated model is a spatially nested hierarchical representation of a forested catchment. The terrestrial ecosystem is a collection of hillslopes (a subcatchment has two hillslopes, i.e., left and right sides of a stream segment), and a hillslope is a collection of patches, in which biological processes were modeled. Outputs from patches were aggregated in a hillslope. A stream segment consists of stream cells, in which biological processes were modeled. Output from hillslopes was distributed into stream cells in each corresponding stream segment.

nitrogen cycle of the model are available [Thornton, 1998; Tague and Band, 2004]. We incorporated soil data (USDA SSURGO Database), forest cover [National Land Cover Database, 2001], leaf area index (LAI) [Hwang et al., 2009], elevation (USGS National Elevation Data set), and roads (Macon County street map) to parameterize RHESSys. Climate data and Hugh White Creek discharge records were available at the base station on the valley bottom and at the catchment outlet gage through Coweeta Hydrologic Laboratory, USDA Forest Services.

2.2.2. Stream Model

The stream model was programmed in an object oriented and parallel process architecture (JAVA v7). The stream network composed of stream segments that were derived using elevation data in GIS (GRASS) (see above). In GIS, we estimated the longitudinal patterns of width, depth, (mean annual) discharge, and

Table 1. Equations for Channel Bankfull Width, Depth, and Instream Coarse Benthic Organic Matter Annual Input^a

Equations	References
Channel bankfull width (m) = $1.97 A^{0.44}$ if $A \geq 10$	<i>Faustini et al.</i> [2009]
Channel bankfull width (m) = $2.328 A^{0.266}$ if $A < 10$	<i>Leigh</i> [2010]
Channel depth (m) = $0.0305 A^{0.507}$	<i>Webster</i> [2007]
CBOM annual input ($\text{mg C m}^{-2} \text{ yr}^{-1}$) = $184382 e^{(-0.0021 * A)}$	<i>Webster</i> [2007]

^aA = drainage area (km^2).

detritus input. Channel morphology, discharge, and detritus input were calculated based on drainage area (Table 1). Using channel morphology and annual mean discharge, we approximated flow velocity in the stream network. Stream segments were constructed based on the above GIS information. Each stream segment was composed of stream cells. The size of each stream cell was determined by a 3 min travel distance, average width within the travel distance, and average

depth within the travel distance. The 3 min travel distance was calculated by time integration based on the velocity pattern. A 3 min time interval was chosen for numerical stability.

Each stream cell consisted of three model compartments: stream water column, transient storage, and benthic detritus (leaf litter and microbes) (Figure 2). In the model, we assumed the stream water column and benthic detritus were aerobic while water in transient storage was less aerobic and where anaerobic processes were likely to occur. Solute export, particulates, and discharge from upstream cells were transported to downstream cells. If a segment was a headwater segment (first order segment; directly drains from a spring), we split the water and nitrogen inputs into spring and lateral inflow based on the proportion of the drainage area at the origin of this segment relative to the total drainage area of the segment. If a segment was a downstream segment (second-order or higher-order stream segments), the water and nitrogen inputs were treated as lateral inputs.

Solutes and dissolved organic matter (DOM) were exchanged between water column and transient storage. Particulates in the water column were either deposited to the benthic area or entrained from the benthic area. Bioavailable phosphorus and ammonium inputs to the stream were based on previously estimated values [Webster et al., 2009]. DOM and seston in the model were generated during instream detritus breakdown. Biological processes in the model included detritus breakdown, immobilization, mineralization, nitrification, and denitrification. In the model, benthic detritus was broken down by two mechanisms, fragmentation via current forces and macroinvertebrate consumption and by decomposition driven by microbial processes. We included two microbial groups in the model, immobilizers and miners. Immobilizers use detritus and DOM as their primary carbon and nutrient sources. When nutrients obtained from detritus and DOM are insufficient for the microbial demand for growth, immobilizers can additionally take up dissolved inorganic nutrients in the water column. Miners grow more slowly [Moorhead and Sinsabaugh, 2006] and rely on detritus and DOM for both their carbon and nutrients. Nitrification occurred in the water column, and denitrification occurred in transient storage. We assumed the same detritus stoichiometry (C:N and C:P) and substrate quality (i.e., % labile, % cellulose, and % lignin) for all detritus initially in the model. Microbial specific growth, microbial respiration, and nitrification were adjusted according to observed water temperature [Webster et al., 2001] based on a Q_{10} equation [Webster et al., 2015]. Daily water temperature varied from 2°C in winter to 18°C in summer. Denitrification rate was a function of nitrate concentration [Mulholland et al., 2008] in transient storage. Details of the decomposition model development and equations were described by Lin and Webster [2014].

2.3. Model Calibration

We performed a step-wise calibration procedure for the terrestrial-aquatic integrated model. We first calibrated the hydrology component in the RHESSys model and initialized the calibrated RHESSys model to stabilize the forest ecosystem, and we then calibrated nutrient process rates in the stream model. Only the nitrate and water runoff output from the RHESSys model were incorporated into our stream model. Other nutrient inputs (e.g., phosphorus) to the steam model were treated as constants.

2.3.1. RHESSys Hydrology Calibration

RHESSys “hydrological” parameters included scalars that adjusted the numerical values of soil-specific parameters. To calibrate those “hydrological” scalars, we used the observed daily average discharge in HWC from September 2000 to September 2002 with one and half-year buffering the beginning of simulation. The

model was calibrated with six key hydrological parameters: the decay rate of saturated hydraulic conductivity with depth (m; both vertical and lateral dimensions), the saturated hydraulic conductivity at the soil surface (K_{sat_0} ; both vertical and lateral), and two conceptual groundwater parameters (gw_1 and gw_2). Monte Carlo simulation was implemented four thousand times from uniform distributions within each prescribed parameter range. We used the Nash-Sutcliffe efficiency of daily log streamflow data as an objective function to identify an optimal parameter set for two reasons. First, the concentration-discharge relationship and cumulative distribution function of total DIN exports in HWC showed that a large proportion of DIN exports occurred under low to moderate flow levels [Shields *et al.*, 2008]. Second, larger uncertainty is expected in simulating high flows due to strong orographic precipitation patterns in the study site [Swift *et al.*, 1988]. We used nongrowth mode in RHESSys with explicit routing in this calibration procedure. In nongrowth mode, the annual growth of plant biomass was zero, and the plant phenological changes were simulated. Initial plant biomass was estimated from the remotely sensing derived LAI map [Hwang *et al.*, 2009].

2.3.2. RHESSys Biological Initialization and Modification

With calibrated hydrological parameters, we ran the model for 500 years in growth mode with explicit routing to initialize the model. In growth mode, RHESSys initially had very little plant biomass and 8–10 kg m⁻² soil carbon. Plant growth, leaf litter, and soil organic matter decomposition and the corresponding nitrogen processes were simulated. This initialization procedure was performed to ensure that carbon and nitrogen model compartments in the forest ecosystem were stabilized.

The estimated nitrate export from the stabilized RHESSys model was 0.33 g N m⁻² yr⁻¹, which was 10 times higher than the measured nitrate export in Coweeta streams in terms of magnitude (0.014 g N m⁻² yr⁻¹ to 0.06 g N m⁻² yr⁻¹) [Knoepp *et al.*, 2008]. We, hence, made three step-by-step structural and parametric adjustments to the nitrogen cycling models in RHESSys. The goal of adjustments was to lower the nitrate export to a level similar to the observed magnitude and to better represent the study watershed.

The first adjustment was to allow leaf litter microbes to take up nutrients on the soil surface. The original RHESSys model assumes that all the litter groups are able to access only the subsurface DIN. This assumption implies that all the actively decaying litter materials (including the fresh litter materials) are in the subsurface layer. However, most fresh litter materials are on the soil surface and they are actively decaying and acquiring nitrogen from the surrounding environment. With our adjustment, estimated nitrate export was reduced by 3–4 times (0.11 g N m⁻² yr⁻¹), although its magnitude was still high compared to the observed values. The second adjustment was to modify the decay rates to the literature values for Coweeta. The default decay rates in the original RHESSys model are very high compared to the decay rates measured at Coweeta [Reynolds and Hunter, 2001]. As a result of the first two adjustments, nitrate export in RHESSys was decreased to 0.033 g N m⁻² yr⁻¹. The third adjustment was to reduce the nitrogen surface-to-groundwater infiltration rate in the original RHESSys model (by 98% in our simulations). The hydrology-driven nitrogen vertical transport in the original RHESSys model may have forced nitrogen to directly deposit to the groundwater pool rather than to vertically move through soil layers where microbes and plants can utilize the nitrogen. With these three adjustments, the estimated nitrate export was decreased to 0.019 g N m⁻² yr⁻¹, which was similar to the observed values in Coweeta streams.

2.3.3. Stream Model Calibration

To calibrate the stream model, we took (modified) RHESSys simulated nitrate as an input to the stream model and fitted the stream model predicted time series of detritus standing stock and nitrate and ammonium concentrations to the observed data. The model was calibrated with three parameters: microbial specific growth rates for immobilizers and miners and nitrification rate. Monte Carlo simulation was implemented four thousand times from uniform distributions within each prescribed parameter range. We used the likelihood probability (i.e., the probability of observed data supporting the proposed parameter set) of detritus standing stock and nitrogen (nitrate and ammonium) concentrations as an objective function to identify an optimal parameter set [Casella and Berger [2002]. The parameter set that maximized the likelihood was considered to be optimal and was used in model simulation. After calibration, the nitrification rate was 0.0017 s⁻¹ and the microbial-specific growth for immobilizers and miners were 0.030 h⁻¹ and 0.0099 h⁻¹ at 25°C.

2.4. Global Sensitivity Analysis

2.4.1. Scenarios

We conducted a global sensitivity analysis under two scenarios with different levels of lateral nitrate flux to the stream from the terrestrial ecosystem. Changing the level of lateral nitrate flux was achieved by scaling

Table 2. Model Parameter Values for Initializing the Stream Model and Ranges of Model Parameter Values for Sobol Sequence Randomization Used in the Global Sensitivity Analysis

Parameters	Initial Value	Min Value	Max Value	References
Detritus mass C:N	93.5	34	95	Cross et al. [2005]
Detritus mass C:P	490.1	490	1830	Cross et al. [2005]
Detritus cellulose %	20.3	10	40	Berg and McLaugherty [2003]
Detritus lignin %	16.3	8	30	Berg and McLaugherty [2003]
Immobilizer mass C:N	7.2	2.4	10	Cross et al. [2005]
Immobilizer mass C:P	188.1	18	385	Cross et al. [2005]
Miner mass C:N	4.7	2.4	10	Cross et al. [2005]
Miner mass C:P	20.2	18	385	Cross et al. [2005]

the annual pattern of lateral nitrate flux estimated by RHESSys with a scalar rather than by changing hydrological and biological parameters within RHESSys. The latter approach would require us to rerun RHESSys for 500 years to restabilize the RHESSys forest ecosystem for each parameter change, which would be impractical given the large number of parameter values to test in our sensitivity analyses.

In the first scenario (“normal” nitrate load), we used a scalar with a mean of one (selected from the range 0–2 based on Sobol sequence randomization; see below) so that the average nitrate flux to the stream was $0.019 \text{ g N m}^{-2} \text{ yr}^{-1}$. In the second (high nitrate load) scenario, we increased the scalar to have a mean of five (randomly selected from the range 0–10), which increased the mean lateral nitrate load up to five times of that in the first scenario. Sensitivity results were organized by fall (September–November), winter (December–February), spring (March–May), and calendar year (January–December).

2.4.2. Rationale

Unlike traditional sensitivity, global sensitivity analyzes the relative influence of a single or a set of model parameters on model output by varying all other parameters simultaneously while keeping the single or the set of model parameters unchanged [Glen and Isaacs, 2012]. We preferred this approach because ecological processes are often nonlinear, multivariable-dependent, and interactive. In global sensitivity analysis, sensitivity of model output to a model parameter (or a set of model parameters) can be expressed in two ways, direct effect and total effect [Sobol, 1996; Sobol and Levitan, 1999]. We used the Glen and Isaacs [2012] method to calculate the direct effect and total effect. The direct effect of a model parameter (or a group of model parameters) refers to the correlation (Pearson correlation coefficient) between outputs from two model runs in which the target parameters are the same in both model runs while all other parameters are different [Sobol, 1996; Sobol and Levitan, 1999; Glen and Isaacs, 2012]. The total effect of a model parameter (or a set of model parameters) is the sum of the main effect and all other interacting effects [Glen and Isaacs, 2012]. We defined interactive effect as the difference between total and direct effect. Model parameters were sampled by the low-discrepancy randomization method [Sobol, 1990, 2001] within each prescribed parameter range based on previous freshwater and decomposition studies [Berg and McLaugherty, 2003; Cross et al., 2005] (Table 2). This randomization method generated a series of points within a 9-dimensional space (we had nine parameters in our global sensitivity analysis). We then projected these 9-dimension coordinates into the parameter space.

In this study, the importance of the terrestrial ecosystem to DIN export (kg N month^{-1}) was evaluated by the direct effect of the scalar used to manipulate lateral nitrate flux. The importance of the aquatic ecosystem to nitrogen export (kg N month^{-1}) was evaluated by the direct effect of a group of model parameters (detritus C:N, C:P, cellulose %, lignin %, immobilizer C:N, C:P, and miner C:N, C:P) in the stream model. Detritus quality, e.g., C:N and lignin content, is well-known to affect detritus decay rate [Howarth and Fisher, 1976; Melillo et al., 1984; Taylor et al., 1989; Gessner and Chauvet, 1994; Manzoni et al., 2008] and could change the timing and magnitude of immobilization and mineralization.

3. Results

3.1. RHESSys Estimated Discharge

The hydrological component of RHESSys was calibrated in nongrowth mode using (NSE = 0.67; Figure 3a) and the observed daily average discharge in the study watershed from September 2000 to September 2002. After RHESSys initialization, we further verified the simulated stream flow of the stabilized RHESSys

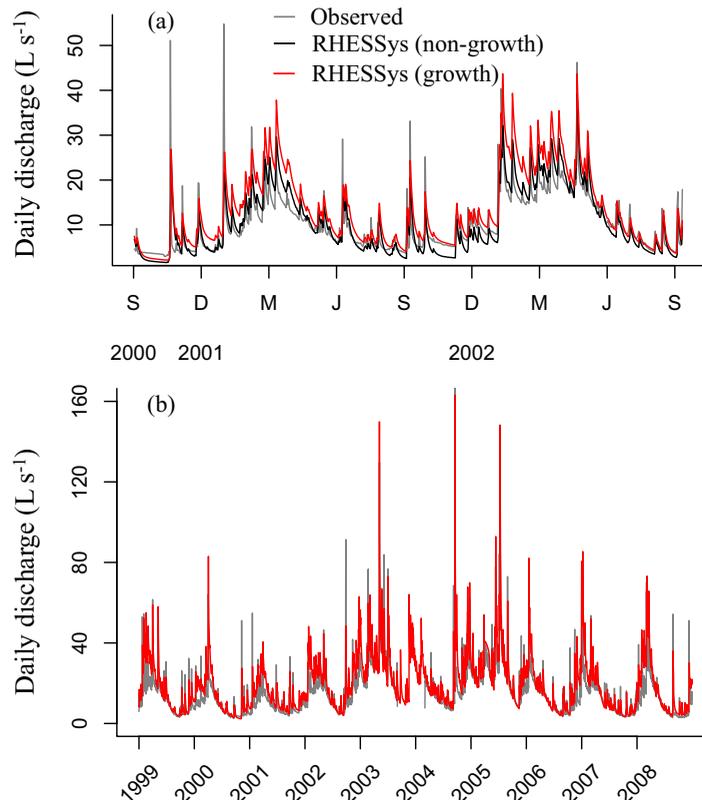


Figure 3. Discharge patterns estimated by the RHESSys model. (a) Observed discharge (gray) in HWC from September 2000 to September 2002 (hydrological calibration period), as well as RHESSys estimated discharge in non-growth and growth modes after calibration (detail description in text). (b) Observed discharge (gray) in HWC from January 1999 to December 2008 (hydrological validation period), as well as the simulated daily discharge in growth mode after biogeochemical calibration.

the observed concentrations in terms of magnitude. In terms of pattern, the modified pattern had higher nitrate concentrations in fall and lower concentrations in summer. Compared to the original pattern, the modified pattern was still high in fall but its magnitude was much lower. Instead of rising in the early spring until fall in the original pattern, the modified pattern appeared relatively flat and decreased in early spring until summer and rose in late summery until fall.

3.3. Effects of the Aquatic Ecosystem on Nitrate Export

The effects of the aquatic ecosystem on nitrogen export were indicated by the difference between the catchment nitrogen pattern that was estimated from the terrestrial-aquatic integrated model and the pattern that was estimated from the modified RHESSys model (middle plot in Figure 4). Lateral nitrate was taken up by instream processes in fall and winter. Stream water nitrate also increased in spring because of mineralization. Stream ammonium was generated by instream processes (red line in the bottom plot in Figure 4).

3.4. Relative Importance of Terrestrial and Aquatic Ecosystem to DIN Export

In the “normal” nitrate load scenario, the terrestrial ecosystem (i.e., the amount of lateral nitrate input to streams) influenced the seasonal and annual DIN exports less than the aquatic ecosystem, and the influence of the terrestrial ecosystem increased from fall to spring (direct effect, Figure 5). The interactive effect also showed a seasonal pattern, increasing from fall to spring. In the high nitrate load scenario, the influence of terrestrial ecosystem to both seasonal and annual DIN exports became higher than that of the aquatic ecosystem (direct effect, Figure 5). The interactive effects became higher than the direct effect of either

model from January 1999 through December 2008. The discharge pattern from the stabilized RHESSys model captured the seasonal trend of observed daily average discharge (Figure 3b; NSE = 0.57). Based on RHESSys estimates, (deep) groundwater contributed 14% of the annual discharge.

3.2. Effects of the Terrestrial Ecosystem on Nitrate Export

The 3 year averaged daily nitrate concentrations estimated by the original RHESSys model (black line in the top plot in Figure 4; original pattern) were different from the observed concentrations (open circles in the top plot in Figure 4) in both magnitude and seasonal patterns. The estimated nitrate concentrations were high in fall and low in winter and early spring.

The nitrate concentrations estimated by the modified RHESSys model (black line in the middle plot in Figure 4; modified pattern) was similar to

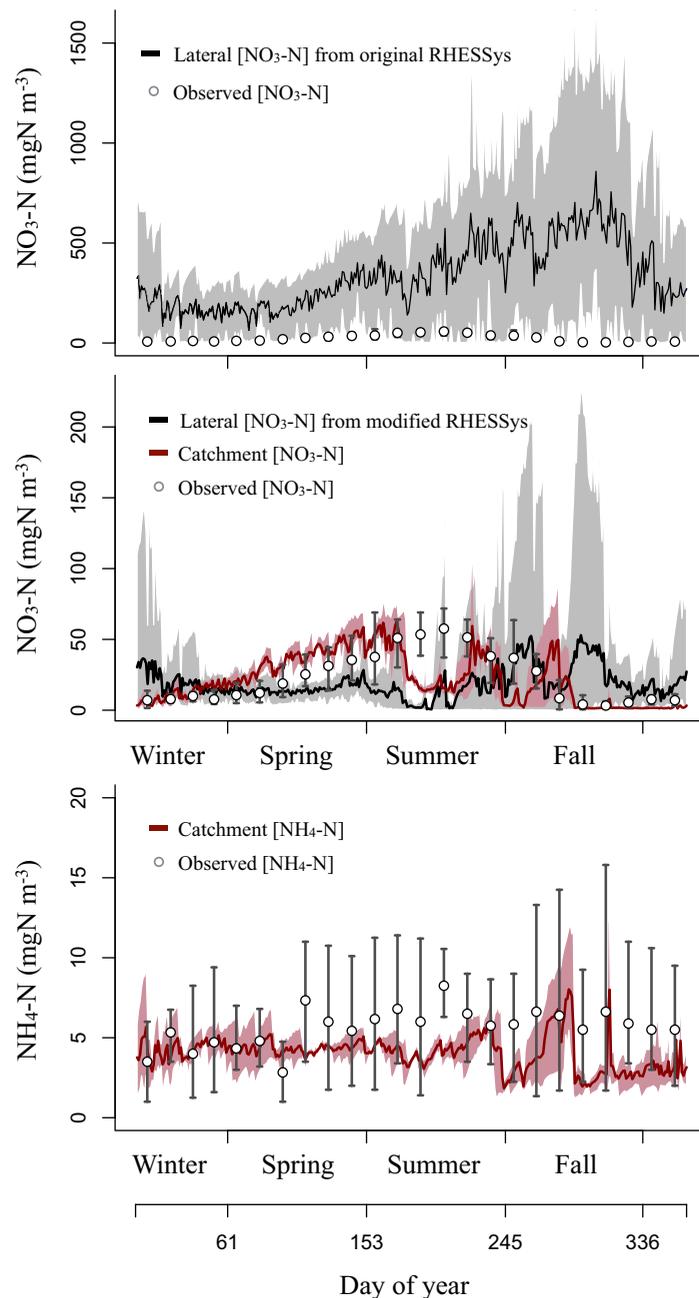


Figure 4. Patterns of nitrate concentrations in lateral input and catchment output. Lines are daily averages of simulated nitrate concentration over 10 years (1999–2008). Shaded areas are the 95% percentiles of the daily nitrate concentrations. Lateral nitrate concentrations were simulated by the original (top) and the modified RHESSys model (middle). Catchment nitrate and ammonium concentrations were estimated by the terrestrial-aquatic integrated model (red lines in the middle and bottom plots). Circles are averages of biweekly measurements of nitrate and ammonium concentrations in HWC from 2005 to 2008. Error bars on circles are standard deviations of nitrogen concentration in the biweekly interval based on the 3 years of data.

topography in the model can reduce the accuracy of soil moisture prediction, especially when the topography and soil moisture in the riparian areas are misrepresented in the model [Tague and Band, 2004; Duncan et al., 2013]. In our study, the original RHESSys model with 10 m spatial resolution predicted that 3.7% of the deposited nitrogen was denitrified in Watershed 14. RHESSys denitrification may increase if we were to use finer spatial resolution (e.g., 1 m or submeter) especially around the riparian area in the model or by

ecosystem in all three seasons with a slight increase from fall to spring. Within the annual time frame, the interactive effect was always higher than the direct effect of either ecosystem under both scenarios.

4. Discussion

4.1. Modeling Nitrogen Dynamics in Forest Terrestrial Ecosystem

The original RHESSys model predicted very high nitrate export from the forest ecosystem (Figure 4). There are two ways we could reduce this simulation of high nitrate export. The first way would be to boost denitrification in riparian areas. Some studies have suggested that high nitrate export could be the result of low denitrification in the model [Tague and Band, 2004; Duncan et al., 2013] due to insufficient spatial resolution of modeled soil water and carbon. Riparian areas have been recognized as potential hot spots for denitrification in which converging shallow and deep groundwater deliver nitrogen and carbon and provide suitable conditions for denitrification [McClain et al., 2003]. Through model simulations with the high-resolution LiDAR-derived topography, Duncan et al. [2013] estimated that more than 99% of total terrestrial denitrification occurred in stream riparian margins and that terrestrial denitrification could be as much as 27% of the atmospheric nitrogen deposition. Terrestrial denitrification is strongly controlled by soil moisture [Heinen, 2006]. A coarse spatial resolution of

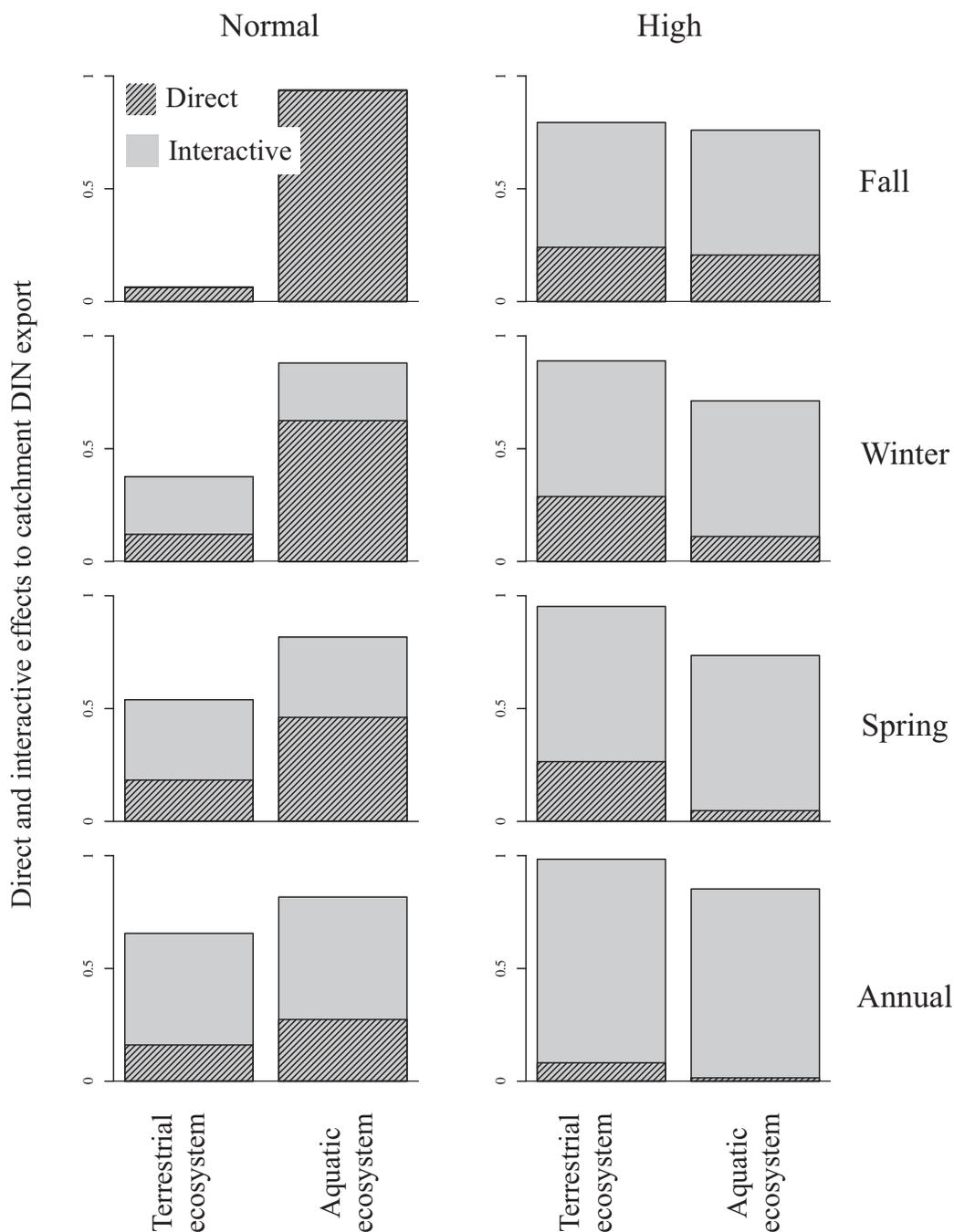


Figure 5. Direct and interactive effects of terrestrial and aquatic ecosystems on dissolved inorganic nitrogen export (ammonium and nitrate). Direct effects are represented by the shaded bars, and interactive effects are represented by the gray bars. Sensitivity analyses were run in two scenarios: normal (left column, average $0.019 \text{ g N m}^{-2} \text{ yr}^{-1}$) and high (right column, average $0.095 \text{ g N m}^{-2} \text{ yr}^{-1}$) nitrogen loads. Sensitivity results were organized seasonally and annually: fall (September–November), winter (December–February), spring (March–May), and calendar year (January–December).

incorporating subgrid variance in soil moisture conditions and integrating nitrogen cycling over the distribution of moisture conditions [Tague and Band, 2004].

The second way to reduce the high nitrate export from the forest terrestrial ecosystem is to increase nitrogen retention in soil organic matter, as we did in this study. Many studies have shown that a large proportion of fertilizer nitrogen or atmospheric deposited nitrogen is retained in the litter and soil (as much as 70%) and plant short-term biomass (20%, e.g., leaves and fine roots) [Nadelhoffer et al., 1999; Templer et al.,

2012; *Schrumpf et al.*, 2014]. With the model structural changes and litter decay rate adjustments, the modified model simulated (1) higher nitrogen content in plant biomass and leaf litter; (2) higher leaf litter accumulation; and (3) higher soil organic matter accumulation, compared to the original RHESSys.

Although both approaches can reduce annual nitrate export from the terrestrial ecosystem, the intra-annual nitrate pattern generated from these two approaches could be different. The reduced nitrate export derived by boosting denitrification may be closely related to seasonal hydrological dynamics, whereas the reduced nitrate export obtained by increasing retention in soil organic matter may be more biological related. We recommend validating these two approaches through comprehensive field experiments. For example, stream water chemistry has been monitored in many forest reference sites to study forest ecosystem export. In addition to stream water chemistry, we need to better understand the riparian interface where nutrients are delivered to streams from terrestrial ecosystems [*Sudduth et al.*, 2013]. For that, we would need to sample soil solution chemistry in cross-sectional transects from hillslopes to streams.

4.2. Influences of Instream Processes on DIN Export

Model results (Figure 4) and sensitivity results (Figure 5) support the conclusion that small streams in forested catchments can alter the timing, magnitude, and form (e.g., organic, nitrate, or ammonium) of nitrogen export [*Peterson et al.*, 2001; *Bernhardt et al.*, 2005; *Webster et al.*, 2015]. The influence of instream processes on nitrate export was represented by the difference between the terrestrial output concentrations and catchment output concentrations in fall, winter, and early spring (i.e., the difference between the black line and the pattern formed by circles in Figure 4). Previous studies attempted to relate instream nitrogen uptake to instream biological processes through laboratory manipulations and statistical relationships between nutrient uptake and instream respiration [*Mulholland et al.*, 1985; *Webster et al.*, 2003; *Gibson and O'Reilly*, 2012]. In this study, we further supported this biology-driven instream uptake argument and showed that instream nitrogen uptake could be the result of net immobilization associated with detritus decomposition. Coupling RHESSys and the stream model provided more accurate predictions of observed nitrate concentrations at the watershed outlet, especially in fall and winter (red line in Figure 4). Although nitrate in stream water could be denitrified, measurement of instream denitrification in HWC has shown very low rates [*Mulholland et al.*, 2008], and so we used a low denitrification rate in the model.

In our global sensitivity analyses, the direct effect of the terrestrial ecosystem on DIN export can be interpreted as DIN directly transported to the catchment outlet without instream processing. The direct effect of the aquatic ecosystem on DIN export can be interpreted as DIN cycled by immobilization and mineralization (instream retention processes) and that these two processes were further controlled by the initial benthic detritus quality. The interactive effect can be interpreted as nitrogen cycling between organic and inorganic forms. Nitrogen immobilization in the stream model was a function of benthic detritus quality, microbial stoichiometry, and available dissolved inorganic nitrogen [*Lin and Webster*, 2014]. Benthic detritus quality and microbial stoichiometry are important in controlling instream retention processes, and instream retention determines how much of terrestrially exported nitrogen is in the dissolved inorganic form or transformed to organic form. In our model, once nitrate from the terrestrial ecosystem entered the stream, it could be immobilized and become a part of microbial biomass and detritus in the organic nitrogen form. The organic nitrogen then remained in that form until it was mineralized and returned back to DIN. DIN immobilization increased the quality of detritus for consumers and microbes and affected the timing and magnitude of detritus mineralization [*Lin and Webster*, 2014].

Sensitivity results suggested that catchment DIN export was not solely controlled by either terrestrial ecosystem or aquatic ecosystem. Additionally, the relative influences of both ecosystems on DIN export varied seasonally ("normal" nitrate load scenario in Figure 5). This seasonal variation in the relative influences of these two ecosystems was closely related to the instream retention processes. In fall, most DIN exported by the terrestrial ecosystem was immobilized and only a small amount of DIN was directly exported from the catchment. Mineralization was much less than immobilization at this time of year (net immobilization period), and immobilization was strongly controlled by the initial quality of benthic detritus, which led to no interactive effect and a high direct effect of the aquatic ecosystem. In winter, immobilization was still greater than mineralization, but winter immobilization was less than in fall because detritus had been enriched by fall immobilization [*Webster et al.*, 2009; *Lin and Webster*, 2014]. This reduced instream immobilization was also indicated by a slight increase in the direct effect of the terrestrial ecosystem (Figure 5

“normal” scenario). Mineralization became greater at the same time, as indicated by the increasing interactive effect. Organic nitrogen that was previously immobilized became DIN again, producing a greater interactive effect. Initial detritus quality still strongly controlled the instream retention processes. In spring, mineralization became as much as or greater than immobilization (net mineralization period). Less immobilization allowed more DIN to be directly exported from the catchment (reflected in an increase in the direct effect of the terrestrial ecosystem in Figure 5 “normal” scenario). Greater mineralization produced a greater interactive effect. The influence of initial detritus quality on the instream retention processes remained strong. This result was consistent with the findings from leaf detritus decomposition studies showing that initial detritus quality is an important factor controlling immobilization and mineralization in both terrestrial and aquatic ecosystems [Manzoni *et al.*, 2008; Webster *et al.*, 2009].

Because detritus decomposition is more rapid in streams than leaf litter decomposition in terrestrial ecosystems, net immobilization and net mineralization phases occur within a year. Therefore, much of immobilized nitrogen is again mineralized, reducing the effect of instream processes on annual nitrogen export. Our sensitivity results, however, suggested that instream retention processes still play an important role in annual DIN export (“normal” scenario in Figure 5). Even at an annual time scale, terrestrial DIN was not directly transported to the catchment outlet without being processed by instream biota. Although some immobilized DIN was remineralized, the amount of DIN was less than originally immobilized because of export of DON and PON. Benthic detritus was continuously broken down by physical flow and animal consumption [Mulholland *et al.*, 2000; Tank *et al.*, 2000; Ashkenas *et al.*, 2004]. This fragmented organic matter contained immobilized DIN that was then exported as particulate nitrogen [Hall *et al.*, 1998]. Additionally, instream processes could increase DIN export by mineralizing original leaf nitrogen. Besides instream immobilization and mineralization, denitrification, which was not included in our sensitivity analyses, could have a significant effect on seasonal and annual nitrogen export. For example, Bernhardt *et al.* [2005] found that an increase in instream denitrification led to a decline in long-term annual nitrogen export. Based on our model estimates, about 11.9 kgNO₃-N flowed into streams from the terrestrial ecosystem annually, and 11.3 kgN was exported as DIN through the aquatic ecosystem annually. Nitrogen input and output in the aquatic ecosystem seems balanced. However, our model further revealed that about 69% of the annual DIN export originated from the terrestrial DIN, and the rest of 31% originated from the original leaf nitrogen. In an annual nitrogen budget, about 30.4% and 65% of the terrestrial DIN was denitrified and exported as DIN, respectively. About 4.6% of terrestrial DIN was converted to organic nitrogen in the benthic detritus annually, in which 50% of that organic nitrogen was exported as particulate nitrogen.

In this modeling exercise, we found that the integrated model of terrestrial and in-stream processes underestimated summer nitrate concentrations in the catchment export (red line in summer in Figure 4). That may be explained by two factors. First, the current stream model only captured the nutrient dynamics related to coarse benthic detritus decomposition and did not include other biological processes associated with fine particulate and dissolved organic matter. Through decomposition and physical breakdown, coarse benthic detritus can become fine particulate organic matter, which can be transported by high flows [Petersen and Cummins, 1974]. This fine particulate organic matter can be mineralized during summer when the flow is also low. Besides fine particulate organic matter, dissolved organic matter in the hyporheic zone or from the terrestrial lateral input can be abundant and potentially influence nitrogen dynamics. A great amount of dissolved organic nitrogen can be mineralized in summer [Brookshire *et al.*, 2005]. More research on how fine particulate and dissolved organic matter affect nutrient spiraling is needed. Second, hydrological connectivity between the channel and its riparian hillslopes can become higher during storms. Nitrogen stored in riparian areas can be transported to streams during high flows [Vidon and Hill, 2004; Vidon *et al.*, 2010]. This dynamic hydrological connectivity is not well captured by the coarse resolution of topography in our current model.

High nitrogen load decreases the ability of streams to retain and remove nitrogen [Dodds and Welch, 2000; Bernot and Dodds, 2005; O'Brien *et al.*, 2007; Mulholland *et al.*, 2008]. Because nitrogen concentration has a saturation effect on biological nitrogen uptake [Dodds *et al.*, 2002; Mulholland *et al.*, 2002; Payn *et al.*, 2005], biological processing rates reach their maximum and the excess DIN is directly exported from the catchment without being processed by instream biota when nitrogen concentration is high. Our sensitivity results illustrate this saturation effect (i.e., the direct effect of the terrestrial ecosystem on nitrogen export was high from fall to spring in Figure 5). More importantly, our sensitivity analyses revealed that, in

additional to increasing biological processing rates, high nitrogen concentration accelerated the transition from net immobilization to net mineralization and accelerated nitrogen cycling between organic and inorganic forms, as indicated by the high interactive effect in fall, winter, and spring in the high nitrogen load scenario (Figure 5). Immobilized nitrogen was mineralized quickly rather than being retained as a part of detritus until net mineralization occurred in late winter. Consequently, the net effect of immobilization and mineralization was minimized at any given time within a year. Therefore, at high nutrient concentrations, instream retention processes may be inefficient in affecting nitrogen concentration in stream water, perhaps leading to the flat longitudinal pattern of nitrogen concentration observed in some streams [Brookshire *et al.*, 2009].

In a natural system, high nitrogen load to streams is usually the consequence of some forest disturbances. For example, stream nitrate concentration substantially increased after forest logging and after conversion from hardwoods to white pine or grass [Swank, 1988; Webster *et al.*, 1992]. At the same time, the instream environment may also have changed in response to the forest changes. For example, stream water temperature rises due to the canopy opening [Webster *et al.*, 1992], and sedimentation in streams increases due to erosion and high runoff [Swank *et al.*, 1988; Swift, 1988; Webster *et al.*, 1992]. These environmental changes accompanying increased nitrogen loading were not incorporated in our model. Therefore, our sensitivity analysis may be limited to scenarios with relatively low nitrogen load and may not be able to fully assess nutrient dynamics under high nitrogen load scenarios.

5. Conclusions

1. In our simulations, instream biological processes, e.g., immobilization and mineralization, not only modified the magnitude and timing of interannual nitrogen export but also affected annual nitrogen export by mineralizing detritus nitrogen to DIN and transforming DIN to fine particulate organic matter.
2. Our model also demonstrated that high nitrogen load can increase instream biological processing rates and accelerate the transition of benthic detritus decomposition from net immobilization to net mineralization, which reduces the net effect of instream biological processes on nitrogen in stream water and potentially leads to a constant downstream pattern of nitrogen concentration.

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