Biogeochemistry **57/58:** 199–237, 2002.

Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A.

SYBIL P. SEITZINGER[1*], RENÉE V. STYLES[1], ELIZABETH W. BOYER[2], RICHARD B. ALEXANDER[3], GILLES BILLEN[4], ROBERT W. HOWARTH[5], BERNHARD MAYER[6] & NICO VAN BREEMEN[7]

[1]*Rutgers University, Rutgers/NOAA CMER Program, Institute of Marine and Coastal Sciences, 71 Dudley Rd, New Brunswick, NJ 08901, USA;* [2]*State University of New York, College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210, USA;* [3]*U.S. Geological Survey, 413 National Center, 12201 Sunrise Valley Drive, Reston, VA 20192, USA;* [4]*UMR Sisyphe, Université Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France;* [5]*Department Ecology & Environmental Biology, Corson Hall, Cornell University, Ithaca, NY 14853, USA;* [6]*University of Calgary, Departments of Physics and Astronomy and Geology and Geophysics, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4;* [7]*Laboratory of Soil Science and Geology and Wageningen Institute for Environment and Climate Research, Wageningen University, P.O. Box 37, 6700 AA Wageningen, the Netherlands (*author for correspondence, e-mail: sybil@imcs.rutgers.edu)*

Key words: budgets, denitrification, model, nitrogen, rivers, watersheds

Abstract. A regression model (RivR-N) was developed that predicts the proportion of N removed from streams and reservoirs as an inverse function of the water displacement time of the water body (ratio of water body depth to water time of travel). When applied to 16 drainage networks in the eastern U.S., the RivR-N model predicted that 37% to 76% of N input to these rivers is removed during transport through the river networks. Approximately half of that is removed in 1st through 4th order streams which account for 90% of the total stream length. The other half is removed in 5th order and higher rivers which account for only about 10% of the total stream length. Most N removed in these higher orders is predicted to originate from watershed loading to small and intermediate sized streams. The proportion of N removed from all streams in the watersheds (37–76%) is considerably higher than the proportion of N input to an individual reach that is removed in that reach (generally <20%) because of the cumulative effect of continued nitrogen removal along the entire flow path in downstream reaches. This generally has not been recognized in previous studies, but is critical to an evaluation of the total amount of N removed within a river network. At the river network scale, reservoirs were predicted to have a minimal effect on N removal. A fairly modest decrease (<10 percentage points) in the N removed at the river network scale was predicted when a third of the direct watershed loading was to the two highest orders compared to a uniform loading.

Introduction

Human activities have markedly increased nitrogen (N) inputs to watersheds (Vitousek et al. 1997). A portion of this N enters river networks, degrading river water quality and increasing nutrient input and subsequent eutrophication of coastal marine ecosystems (National Academy of Sciences 2000). However, rivers do not act as "inert pipelines", transporting N from the land to the coastal zone. Processes such as denitrification, organic matter burial in sediments, sediment sorption, and plant and microbial uptake can remove N from the river network, and thus affect the amount of N that is transported by rivers to coastal ecosystems (Billen et al. 1991).

A number of studies have examined factors controlling N retention and/or denitrification rates in rivers including nitrate concentration, sediment properties, flow rate, and land use (e.g., Robinson et al. 1979; Cooke & White 1987; Christensen & Sørensen 1988; Jansson et al. 1994; Howarth et al. 1996; Mulholland et al. 2000; Peterson et al. 2001). In general studies have addressed N removal in short sections of a river, but give no direct information about the amounts of N removed throughout the complex network of rivers draining a watershed. A river network approach is needed for a watershed-wide quantification of the proportion of the N input that is removed during riverine transport. Such an approach, used in some recent watershed mass-balance studies (Smith et al. 1997; Alexander et al. 2000), is also needed to understand how the amount of N transported to the watershed outlet is affected by such factors as number and size of reservoirs in the network, location of N inputs within the network relative to the river mouth, size of watershed, and network configuration.

In this paper we: (1) use published data to develop a predictive model relating the physical and hydraulic properties of rivers and lakes to the proportion of the N input that is removed in these water bodies, (2) apply that model in sixteen drainage networks in the eastern U.S. to estimate riverine N removal, and (3) explore the effect of various watershed and river properties on N removal in the drainage network including size of watershed, presence of reservoirs and their location in the river network, distribution of N input to the river network within the watershed, and the scale of the river network data.

Model

Model development

Estimates of nitrogen removal in streams and rivers (expressed as a proportion of the external input) were obtained from published data. The studies were conducted in river reaches that ranged from first order headwater rivers to the tidal freshwater portion of major rivers (Table 1 plus Swank & Caskey 1982; Billen et al. 1985; Jacobs & Gilliam 1985; Cook & White 1987; Chesterikoff et al. 1992; Mulholland 1992; Jansson et al. 1994; Sjodin et al. 1997 and others). Land use in the watersheds included agricultural, urban, forested and mixed. No studies were found in which N removal was measured throughout an entire river network. Rather, measurements were usually made in only a short section, or reach, of a river (e.g., first order rivers, tidal freshwater portion of a river) which had fairly uniform characteristics (e.g., depth, water residence time, N loading, etc.). Combining the results of studies from sites with a wide range of characteristics is desirable to develop relationships between N removal and river characteristics that are widely applicable both within a drainage network and across different watersheds.

N removal in the river studies was quantified using one of two basic approaches: (1) mass balance calculations based on N concentration and water discharge measurements at an upstream and downstream location, or (2) denitrification measurements on sediment cores. There are many variations on the two approaches, and depending on the approach a slightly different set of N removal mechanisms may be captured. In some mass balance studies, calculations were based on nitrate or dissolved inorganic N (DIN = nitrate, nitrite plus ammonia) only; in others total N was used. Measurements of denitrification in sediment cores included a range of techniques. N removal in hyporheic zones, as well as uptake by benthic biota and burial in sediment generally would be captured in mass balance studies but not in denitrification measurements using core incubations of surface sediments. Some studies were conducted during a portion of the year, others over one or more annual cycles; whenever possible, we used annual studies. Generally, N input from upstream as well as direct watershed input (groundwater, point and non-point sources) for the study reach were used to compare with N removal within the study reach; however, in some cases only upstream N input was reported. We included the results from studies using all approaches in the model development, at the same time recognizing the limitations and uncertainties imposed by this approach. In the following, we use the term "N removal" to indicate all N removal/retention processes. However, denitrification, the only permanent N removal process in rivers, is expected to be the dominant loss process reflected in the literature measurements. Uptake by

Table 1. Studies used to develop model equation for estimating proportion of N input to a river reach that is removed as a function of depth/TOT

River	Watershed land use	Strahler order	Stream study length (km)	Depth (m)	Time of Travel (TOT) (hr)	Depth/TOT (m y^{-1})	%N removed	Period of study	Approach	Reference
Delaware (tidal freshwater), USA	Urban, Agriculture		120	6.8	967	62	20 (DIN)	Aug. 1984	Denitrification in cores	Seitzinger 1988a,b flow from Cole et al. 1993
Duffin Creek, ON, Canada	50% Agriculture 20% Forest 20% Abandoned farmland	6	26	0.35	16	190	6 (TN)[a,b]	May–Oct. 1973–75; Nov.–March 1978	Mass balance and denitrification in cores	Hill 1979, 1981, 1983
Gelbaek, Denmark	Agriculture	1	1	0.40	1.4	2500	1 (NO_3)[a]	Spring 1993–Summer 1994	Denitrification in cores	Christensen & Sorensen 1988; Christensen et al. 1990
Neversink, NY, USA	Forest	1 3	0.6 1.0	0.2 0.5	0.8 1.4	2190 3130	11(NO_3)[c] 12(NO_3)[c]	April, June, July, Sept. 1992	Mass balance	Burns 1998

Table 1. Continued

River	Watershed land use	Strahler order	Stream study length (km)	Depth (m)	Time of Travel (TOT) (hr)	Depth/TOT ($m\ y^{-1}$)	%N removed	Period of study	Approach	Reference
Potomac (tidal freshwater), USA	Urban, Forest			5.0	3264	13	35 (TN)	Sept. 1985	Denitrification in cores	Seitzinger 1988a, 1991
Purukohukohu, New Zealand	Pasture Forest	1 1	0.08 0.08	0.03 0.03	1.0 1.3	270 200	$14(NO_3)^b$ $17(NO_3)^b$	Aug., Nov. 1982; June 1983	Mass balance	Cooper & Cooke 1984
River Dorn Oxfordshire, England	Agriculture		35	0.5	65	67	$15(NO_3)^d$	June 1985	Denitrification in cores	Cooke & White 1987
Swifts Brook, ON, Canada	Forest, Unused pasture	1	2	0.11	19	51	$20(TN)^{a,b}$	1975-1976	Mass balance	Robinson et al. 1979; Kaushik & Robinson 1976

[a] Annual estimate.
[b] Removal attributed to denitrification.
[c] Average % N removal over 4 sampling periods. Includes removal due to both biological uptake and denitrification.
[d] Under summer, baseflow conditions.

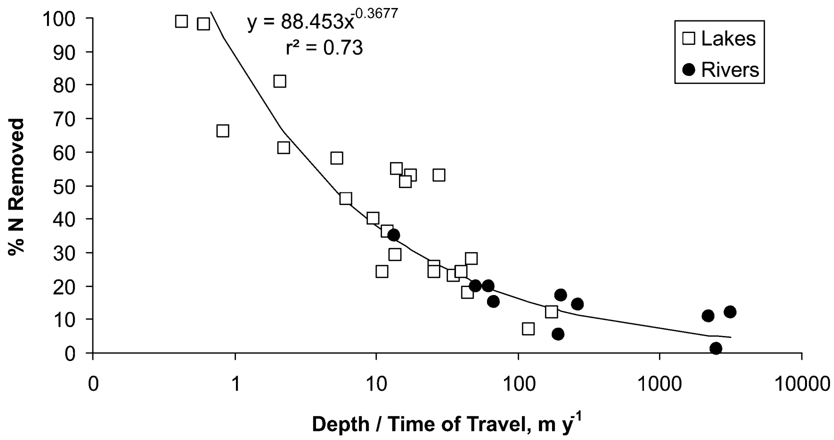


Figure 1. Empirical relationship between % N removed in a study area and depth divided by time of travel (water residence time for lakes) based on studies in river reaches and in lakes. Data sources and details for rivers are in Table 1. Data sources for lakes include: Garnier et al. 1999; Kelley et al. 1987; Andersen 1977; Calderoni et al. 1978; Ayers 1970 cited by Schelske 1975; Dillon and Molot 1990. All lake studies were conducted over at least a 1-year period.

biota and to some extent sedimentation only temporarily retain nitrogen, and generally would not be expected to influence the mean estimates of loss from mass balance studies of annual conditions. The studies used to develop the model do not include N removal in aquifers or wetlands in a watershed.

There is a wide range (1 to 80%) in the efficiency with which N is removed in river reaches (Table 1 plus Swank & Caskey 1982; Billen et al. 1985; Jacobs & Gilliam 1985; Cook & White 1987; Chesterikoff et al. 1992; Mulholland 1992; Jansson et al. 1994; Sjodin et al. 1997, others). Relationships between N removal and the following variables were examined: river order, river discharge, land use, N-loading, water residence time, and water displacement (ratio of water depth to water residence time). Nitrogen removal (R; expressed as a percentage of N input) was best described (i.e., based on r^2) as an inverse relation with water displacement according to:

$$R = 74.61 \left(\frac{D}{T}\right)^{-0.344} \tag{1}$$

(r^2 = 0.43; n = 10) where depth (D) is in meters and time of travel (T) is in years. Time of travel was calculated from length of study reach divided by velocity.

A separate model fit that combined data from the 10 river observations with data from 23 lakes and reservoirs (see Figure 1 for data sources) was found to have similar coefficients as the model using only the river data (eq. 1):

$$R = 88.45\left(\frac{D}{T}\right)^{-0.3677} \tag{2}$$

(r^2 = 0.73) where T (in years) reflects the water residence time for lakes and reservoirs and the water time of travel for rivers (Figure 1). Therefore, equation (2), based on the combined data provides a generally consistent description of nitrogen loss in streams, reservoirs and lakes. A relationship which is applicable to both river reaches and reservoirs within a river is useful in evaluating N removal in a river network. This model is similar to the theoretical relationship for river reaches, lakes and reservoirs presented in Howarth et al. (1996) and Billen et al. (1998), which was based on the extension of a lake mass-balance model of nitrate removal quantifying the effects of benthic denitrification in oxic well-mixed shallow lakes (Kelly et al. 1987).

A log-linear form of the model (eq. 2) was used to estimate the model parameters by applying a natural log transformation to both the response and explanatory variables. The estimates of %N loss were not adjusted to correct for the log retransformation bias associated with the application of a log-linear model (Duan 1983). The river N removal studies which contained information on depth and time of travel and which, therefore, formed the basis of the final model are listed in Table 1. The range of stream sizes covered by the relation gives reasonable coverage of the stream sizes of interest in the northeastern U.S. watersheds. Most of the studies are for small streams, although the Potomac and Delaware extend the coverage to higher order streams relevant to the larger northeastern U.S. streams. An examination of the residuals of this model shows that there is relatively constant variance over the range of the data and that they are approximately normally distributed. The data (and residuals) do display greater scatter for larger values of the ratio (generally above 100 which includes many of the river observations), suggesting greater model uncertainty in this range.

The model in equation (2) empirically quantifies the fraction of nitrogen removed as a function of the rate of water displacement in streams, reservoirs/lakes (the ratio of depth to water travel time represents the height of the water column that is annually displaced from the water body). This hydraulic property provides a measure of the time for dissolved and particulate N to react with the benthic sediments. Variations in water contact time may occur as a result of the natural properties of streams related to channel size (i.e., water depth, velocity) as well as attributes intrinsic to the measurements of a particular study (i.e., reach length, velocity during study period). These characteristics may influence the removal of nitrogen from the water column by or to the benthic sediment, by such processes as denitrification, uptake by biota, and particulate settling (Wollheim et al. 2001). For example, increases in water residence times in streams and reservoirs/lakes generally increase particulate settling as well as increase the amount of nitrate (per unit volume of water) that can diffuse into the sediments, leading to the removal of a larger fraction of nitrogen. This model is consistent with a relationship between the fraction of N input that is removed and water residence time in estuaries (Nixon et al. 1996). It is also consistent with the notion that the fraction of nitrogen removed per unit of water travel time (i.e., first-order rate of nitrogen loss) varies inversely with stream channel depth (Smith et al. 1997; Alexander et al. 2000); this could reflect the smaller volume of water that is processed by a unit area of benthic sediment in shallow streams (Peterson et al. 2001).

Model application

Most of the river studies used to develop equation 2 were conducted over fairly short reaches of a river (i.e., sections of rivers with relatively uniform time of travel and depth). This has important implications when using this equation to estimate N retention throughout an entire river network. The equation must be applied to the individual reaches of the river network, with exports from a reach routed downstream to subsequent reaches for processing.

N removal in river networks was calculated for sixteen watersheds in the eastern U.S. between Maine and Virginia (Figure 2; Table 2). The most downstream reach of each watershed coincided with the location of a USGS station with a high density of water quality data (Boyer et al. this volume); thus the most downstream reach of each watershed area was not necessarily at the fall line or coast. The study watersheds varied considerably in physiographic and hydrographic characteristics such as watershed area, total river length and discharge (Table 2). A complete description of the watersheds is presented in Boyer et al. (this volume) and van Breemen et al. (this volume). We applied equation 2 using EPA-USGS reach network files for the sixteen watersheds. Subsets of the sixteen watersheds were chosen for more detailed analysis of the model output.

Base case scenario

The river network configuration was based on the enhanced EPA-USGS Reach File Version 1 (RF1; Alexander et al. 1999), which we supplemented with the higher resolution EPA-USGS National Hydrography Dataset – NHD (as described below). RF1 is a spatial data file that contains 60,000 major river and stream reaches in the conterminous U.S. and has been used in predictive

Table 2. Characteristics of the sixteen watershed river networks, and base case ($RF1_m$ + NHD') and reduced scale (RF1 only) model predictions of proportion of N inputs to the river network that are removed by in-river processes

Watershed[1]	Watershed area[2] km^2	Discharge[2] $m^3\ s^{-1}$	River export[2] kg TN $km^{-2}\ y^{-1}$	Number of reservoirs	RF1 total reach length km	NHD total reach length km	Number of reaches	% N input removed $RF1_m$ + NHD' Base case	% N input removed RF1 only Reduced scale
Penobscot	20,109	375	317	22	4,344	19,798	5,917	68	59
Kennebec	13,994	251	333	14	2,716	12,182	3,651	63	52
Androscoggin	8,451	171	404	8	1,076	5,737	1,938	52	44
Saco	3,349	71	389	5	644	2,896	880	47	33
Merrimack	12,005	224	499	13	1,070	12,784	3,509	61	38
Charles	475	9	644	0	78	626	205	37	15
Blackstone	1,115	23	1,140	0	108	1,148	317	53	22
Connecticut	25,019	509	538	18	4,748	23,173	7,380	66	55
Upper Hudson	11,942	236	502	5	2,213	8,420	2,384	58	50
Mohawk	8,935	155	795	6	1,677	8,471	2,704	60	47
Delaware	17,560	304	961	13	2,612	14,228	5,011	60	48
Schuylkill	4,903	76	1,755	2	550	3,625	966	52	31
Susquehanna	70,189	1,084	977	21	9,612	69,248	17,499	76	63
Potomac	29,940	312	897	3	5,089	25,105	8,624	68	60
Rappahannock	4,134	47	470	0	844	3,041	806	57	42
James	16,206	209	314	3	3,322	15,375	4,885	72	61

[1]see Figure 1 for watershed delineations.
[2]From Boyer et al. (2002).

Figure 2. Delineation of the 16 watershed regions used in the current analysis. Black filled circles denote watershed outlets at the following locations: Penobscot River at Eddington, ME; Kennebec River at North Sidney, ME; Androscoggin River near Auburn, ME; Saco River at Cornish, ME; Merrimack River below Concord River at Lowell, MA; Charles River at Dover, MA; Blackstone River at Manville, RI; Connecticut River at Thompsonville, CT; Hudson River above lock 1 near Waterford, NY; Mohawk River at Cohoes NY; Delaware River at Trenton, NJ; Schuylkill River at Philadelphia, PA; Susquehanna River at Conowingo, MD; Potomac River near Washington, DC Lower Falls Pump Station; Rappahannock River near Fredericksburg, VA; James River at Cartersville, VA. (From Boyer et al. 2002)

water quality models of stream nutrient transport (Smith et al. 1997; Alexander et al. 2000). RF1 is approximately the resolution of the "blue-line" drainages that show up on a USGS 1:500,000 scale map. Reach characteristics used from the RF1 file included reach length, Strahler river order, reach time of travel (TOT), reach watershed area, reach mean flow, reservoir time of travel, and reach and reservoir node identification. Mean depth of each reach was calculated from mean flow (Q) based on the following relationship (Alexander et al. 2000):

$$D = 26.12Q^{-0.3966} \tag{3}$$

where reach depth is in meters and flow is in m^3 sec^{-1} ($r^2 = 0.83$). This relationship was based on stream morphology and hydraulic data for 112 rivers in the U.S. (Leopold & Maddock 1953). Mean reservoir depth was computed as the ratio of the normal capacity to surface area (Ruddy & Hitt 1990). The reach network configuration and flow paths were constructed based on the node identifiers.

The effect of map scale on defining existing rivers in a watershed is well known. A more comprehensive representation of the river network in each watershed (EPA-USGS National Hydrography Dataset – NHD – see <http://nhd.usgs.gov>) was used to supplement the information in RF1. NHD is a newly-released reach file available in beta form, and depicts approximately the resolution of the "blue-line" drainages that show up on a USGS 1:100,000 scale map (7.5 degree quadrangle). A comparison of the drainage density for these two map scales is shown for the Saco watershed (Figure 3A, B). The relatively coarse scale of RF1 generally does not capture true 1st, 2nd and 3rd order rivers. While NHD gives much better information on total length and reach lengths of rivers in each watershed, it does not contain information on the flow, depth and TOT of stream reaches and reservoirs. Therefore, for the additional river lengths not contained in RF1 (termed NHD'; calculated as NHD total reach lengths minus RF1 total reach lengths), reach depth and TOT were estimated using established relationships between hydraulic and physiographic factors which were tailored to each watershed based on the characteristics documented in RF1 (see Appendix for detailed description).

The total watershed area did not change when the NHD' reaches were added to the RF1 file. However, obviously, the total length of the river reaches did increase. Therefore, the direct watershed area to RF1 reaches was reapportioned to account for the stream lengths added with the inclusion of NHD'. The direct watershed area was uniformly apportioned per meter of stream length (RF1+NHD') throughout the watershed. We refer to this modified RF1 file in which the direct watershed area to RF1 reaches has been adjusted as $RF1_m$.

There were very few reaches in RF1 for the two smallest watersheds, the Blackstone and Charles. Therefore, there was increased uncertainty in extrapolating depth and TOT for NHD' reaches (Appendix) in those two watersheds. As such, our model estimates of N removal in those two watersheds are likely to be less certain than for the other watersheds in this analysis.

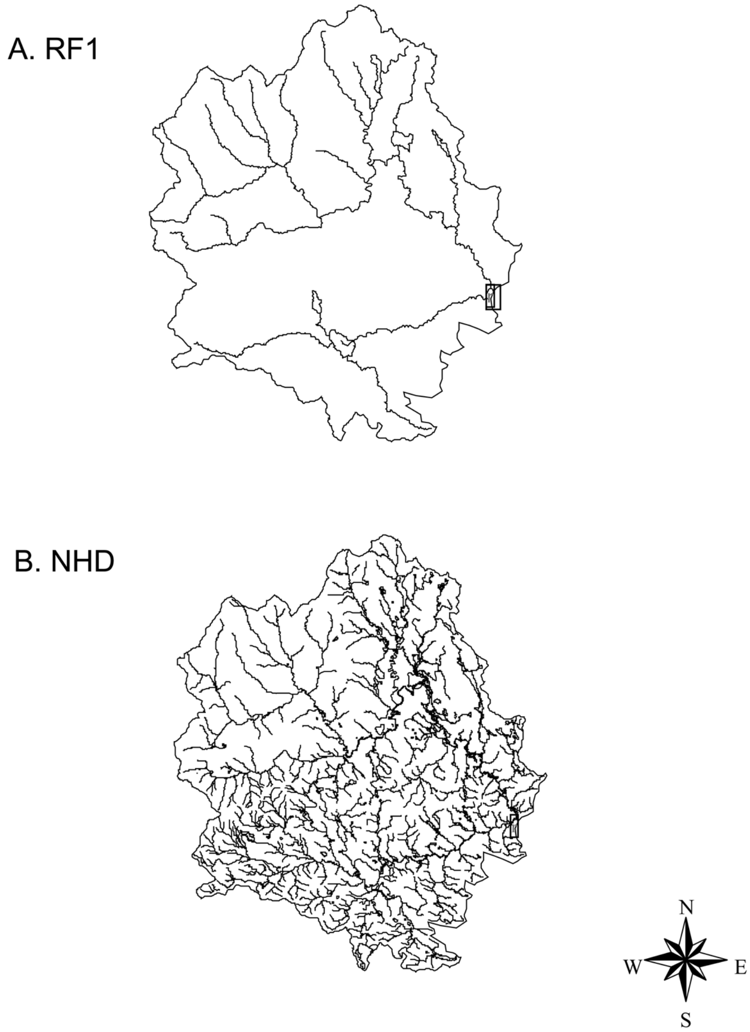


Figure 3. Map of river reach network in the Saco basin as defined by: (A) RF1 and (B) NHD. The scale of the reach networks used in the base case scenario for the RivR-N model is approximately that shown in (B), while the reduced scale scenario used only RF1 files.

The proportion of N loading to the river that was removed in the river network was calculated for each watershed using the $RF1_m$ + NHD' network configuration. N entered each reach from direct watershed loading and from N exported from the adjacent upstream reach (Figure 4). Direct watershed loading refers to all N inputs to the river from the direct watershed area for a reach and would include groundwater, point and non-point source inputs. Whole-watershed N inputs and N inputs to the rivers were estimated by Boyer

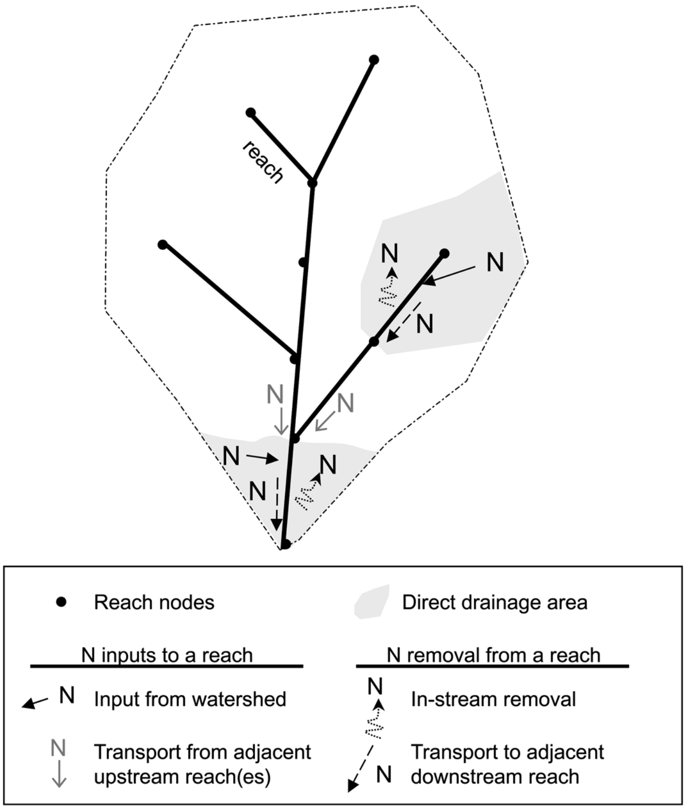


Figure 4. Simplified schematic of a river network. The network was assembled using reach node identifiers. N enters a reach from the direct drainage area for that reach plus transport from the adjacent upstream reach or reaches. N is removed from a reach by both in-stream processes (e.g., denitrification, burial, biotic uptake) and transport to the adjacent downstream reach. The direct drainage area and the N input/output detail are shown for 2 reaches.

et al. (2002) and van Breemen et al. (2002). However, the final estimates were not available when the final RivR-N model runs were conducted; in addition, those estimates did not maintain information in the spatial distribution of N inputs within a watershed. Therefore, in the RivR-N model base case scenario, land use throughout a watershed was assumed uniform, with direct watershed N loading to a reach (kg N per km^2 of direct watershed per year) uniform throughout the watershed. We choose 100 kg N per km^2 of direct watershed per year as a loading rate, which is similar to, although on the low end, of N loading to surface waters from forested areas (summarized in Howarth et al. 1996). The model calculates the proportion of the N input that is removed, which does not vary as a function of the rate of N loading; therefore, the model can be run without knowing the exact N loading rate to the river. To summarize, the base case scenario used the combined $RF1_m$ + NHD' network configuration and a uniform direct watershed N loading.

Alternate scenarios

Additional model runs were conducted to explore the following: (1) effect of reservoirs on N removal, (2) scale of river network, and (3) distribution of N loading to the river within the watershed. The amount of N removed in reservoirs was examined by removing reservoirs from each watershed file and substituting the pre-reservoir TOT and depth information for those reaches (also available in RF1). The effects of using only the lower resolution RF1 network files were examined by calculating the proportion of N removed using only the RF1 network files; we refer to this scenario as the reduced scale scenario. The effect of a non-uniform distribution of N loading within the watershed on N removal in the river network was examined by allocating a third of the total N loading in a watershed to reaches of the two highest orders.

Statistical analysis of model uncertainty

Statistical uncertainties in model coefficients and predictions were quantified using bootstrapping techniques (Efron 1982). Estimation of coefficient errors was based on a resampling with replacement from the original set of lake and stream observations (sample size = 45) and fitting of separate regression models to the resampled data for a total of 200 iterations. Confidence intervals were developed from the resulting statistical distributions for the model coefficients. Errors in model predictions of the proportion of nitrogen removed for each of the sixteen watersheds included uncertainties in both the model coefficients and the observed data (i.e., regression residuals). Contributions from the latter term were based on a random sampling of the model residuals associated with each of the bootstrap regressions. For each of the 200 iterations (i.e., bootstrap regression), a model residual was randomly assigned to each reach or reservoir prediction of the proportion of nitrogen removed. The resulting proportion was applied to the reach or reservoir mass flux, which was added to the cumulative mass of stored or denitrified nitrogen for each watershed. The residual error contributed only to the estimates of the quantities of nitrogen removed from individual reaches or reservoirs, and was not applied to the nitrogen mass transported to downstream segments. Errors in equation (2) are assumed to be multiplicative because of the log-linear form of the model. Inclusion of the regression residual errors serves to correct for the log retransformation bias associated with the application of a log-linear model. The uncertainty estimates were only computed for losses in the RF1 streams and reservoirs (reduced scale scenario).

Results and discussion

Base case results

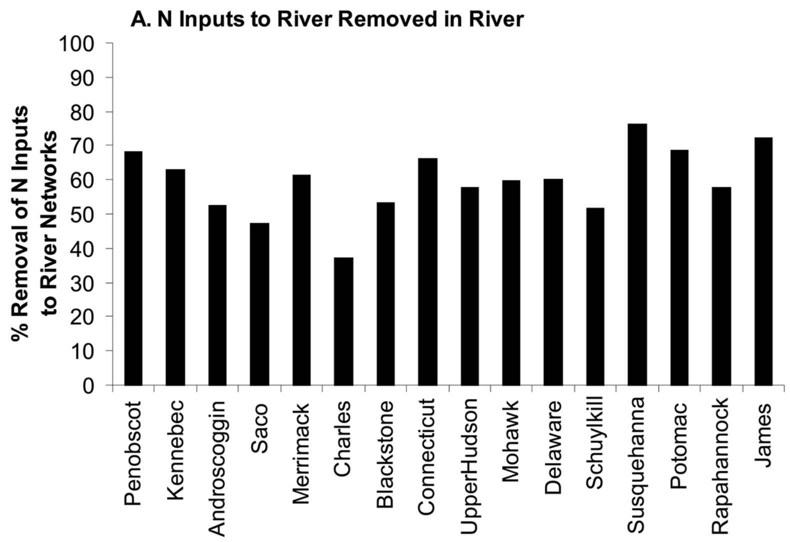
N removal at the river network scale

A substantial proportion of the N input to rivers is removed during transport through the river network according to the model (hereafter referred to as the RivR-N model; **Riv**er **R**emoval of **N**itrogen). Between 37% and 76% of the N inputs were removed in the16 river networks for the $RF1_m$ + NHD' scenario (Figure 5A; Table 2); on average 60% (+/– 10%; S.D.) of the N inputs were removed. The smallest proportion removed was in the Charles and the largest proportion removed was in the Susquehanna. The proportion removed at the river network scale is considerably higher than the proportion of N input to an individual reach that is removed in that reach (reach-specific removal). Each river network in our suite of 16 watersheds consists of between ~200 and ~17,500 reaches (Table 2) with reach lengths ranging from less than 1 km to approximately 100 km in length. Approximately 85–90% of the reaches have depth/TOT characteristics and consequently reach-specific N removals (based on an analysis of the 5 scenario watersheds) within the range of literature values for river reaches that were used to develop the empirical model equation (1% to 35%; Table 1; Figure 1). At the river network scale the proportion of total N input that is removed is considerably larger than for an individual reach because of the cumulative effect of continued nitrogen removal along the entire flow path in downstream reaches (Figure 4). This has not generally been recognized in previous studies, but is critical to an evaluation of the total amount of N removed within a river network.

The amount of N removed in the respective river networks is not only a substantial portion of the total N input to the rivers (Figure 5A), but also a substantial portion of the total N input to these 16 watersheds (Figure 5B). The RivR-N model predicts the proportion of N input to a river network that is removed within the river. It does not require knowing the amount of N input to the river, which is difficult to quantify given the multiple sources and pathways of N inputs throughout a river network. However, both the amount of N removed in a river network ($totN_{rem}$) and the input of N to a river network (N_{input}) can be estimated by combining the RivR-N model estimate of the proportion of N input to a river network that is removed ($fractionN_{rem}$) (Figure 5A) with the river export of N at the mouth of the defined watershed (N_{export}) as follows:

$$N_{input} = N_{export}/(1 - fractionN_{rem}) \tag{4}$$

$$totN_{rem} = N_{input} * fractionN_{rem} \tag{5}$$



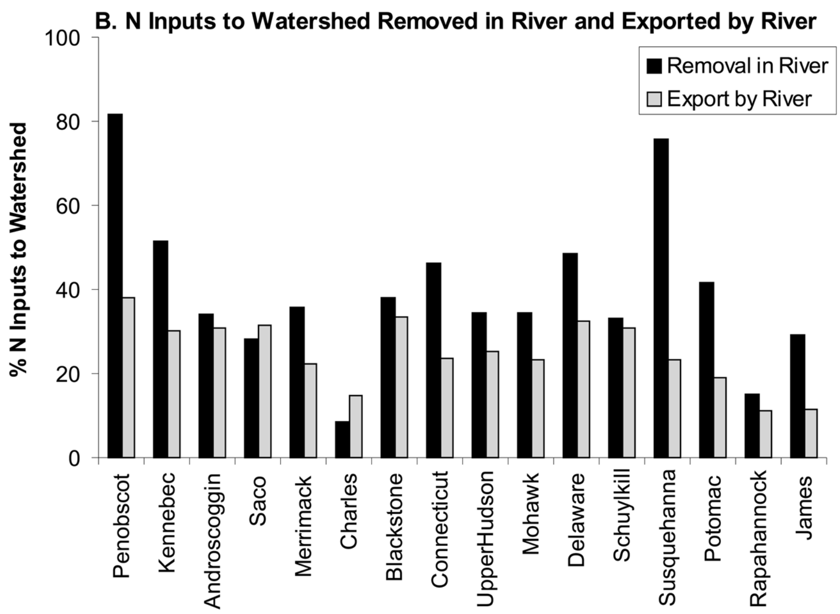


Figure 5. (A) Model-predicted proportion of N input to the river networks that is removed by in-river processes, and (B) proportion of N input to the watershed that is removed by in-river processes and river export for the 16 river networks (shown in Figure 2) for the $RF1_m$ + NHD' scenario (base case).

We estimated $totN_{rem}$ by the river using N_{export} for each river network calculated from USGS monitoring data by Boyer et al. (2002) and $fractionN_{rem}$ from the RivR-N model output (Figure 5A). We then estimated the proportion of total watershed inputs that were removed by the river (Figure 5B) by comparing this value to total N inputs to these watersheds from atmospheric deposition (wet and dry NOy), fertilizer use, N_2-fixation in forests and agriculture, and net import of food and feed (Boyer et al. 2002; van Breemen et al. 2002).

On average about half (48% +/– 19) of the total N inputs to these watersheds was removed within the river, based on the $RF1_m$ + NHD' scenario (base case). There was considerable variation among rivers with approximately 10% (Charles River) to 80% (Penobscot River) of the total known N inputs to the watershed removed within the associated river network (Figure 5B). On average, N export by the rivers was equal to 25% (+/– 8) of the total N inputs to the watersheds (Boyer et al. 2002). The combined removal of N by in-river processes (RivR-N model estimates) plus river export accounts for an average of 65% (+/– 24) of the total N input to the watershed.

There are numerous processes within the watershed that remove N, in addition to river export and denitrification. Comprehensive N budgets were developed for these sixteen watersheds by van Breemen et al. (2002) that included all known input terms (noted above; as developed by Boyer et al. 2002) and N removal and storage terms (soil denitrification in forests, agriculture and urban land; forest harvest; storage in wood and soils; waste volatilisation; river N export; denitrification in rivers). Overall, the three largest sinks for N were denitrification in soils and rivers and river export. On average, there was considerable agreement between the estimated watershed total N inputs and total N storage and losses (van Breemen et al. 2002). However, there are considerable uncertainties in a number of budget components, including denitrification in soils and in rivers, and the watershed N balance depends to a considerable extent on the choice of values used for these terms, as they discuss. Uncertainties in the river denitrification term, as estimated by the RivR-N model, are discussed in more detail below (Model Uncertainty).

Calculation of N removal in a river network with the RivR-N model requires detailed reach scale information on depth, time of travel, and river network configuration. Comparison of the model-estimated N removal at the river network scale (Figure 5A) with more readily available river network scale parameters suggests that both watershed area and total length of all reaches in a watershed are reasonably good predictors of the proportion of N input to rivers that is removed in the river network of a watershed, under

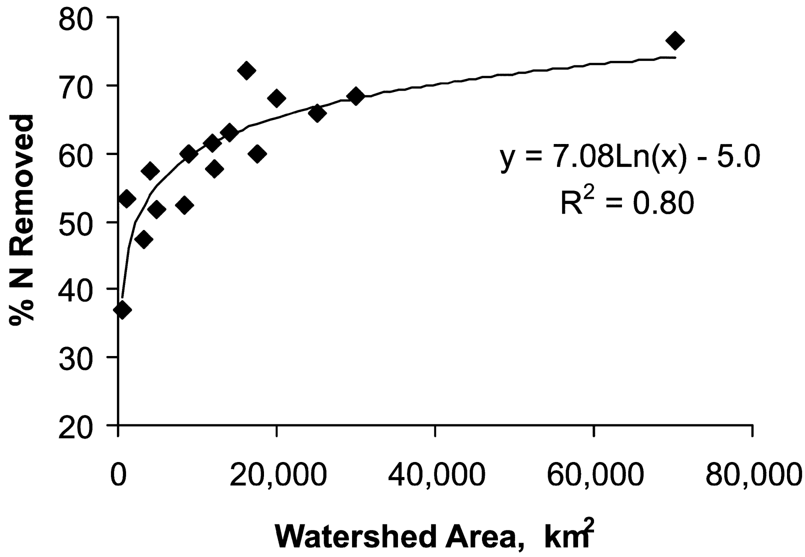


Figure 6. Relationship between watershed area and the proportion (as a percentage) of N input to the river network that is removed by in-river processes according to the RivR-N model ($RF1_m$ + NHD' scenario, base case).

the base case scenario (constant N loading per unit area of watershed). The RivR-N model predicted proportion of N removed is related to the log of the watershed area ($r^2 = 0.80$) (Figure 6) or log of the total length of all reaches ($r^2 = 0.84$; %N Removed = 7.5∗Ln(total reach length, m) – 59). These relationships may provide approaches for estimating N removal in watersheds where detailed river network information is not available, at least in watersheds with hydrological and physiographic characteristics similar to the watersheds used in this study.

N removal patterns within the river networks

There are a number of perspectives from which to examine the pattern of N removal within a river network. N removal varies as a function of stream size, both at the reach scale and at the river network scale. Reaches within a river network range from small, shallow headwater streams to wider, deeper reaches of rivers. There are a number of methods to classify stream systems. In the Strahler channel-ordering system, a first order stream has no tributaries; where two 1st order channels join, a stream of 2nd order is formed, and so on (Strahler 1952 modified from Horton 1945). Strahler order is identified for each reach in the RF1 file, and therefore, provides one perspective from which to examine the contribution of different stream sizes to N removal in the16 river networks.

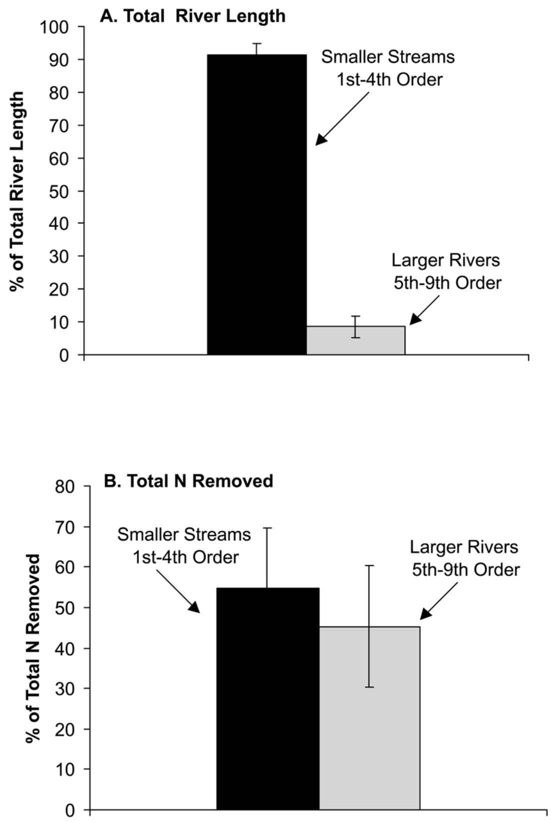


Figure 7. Proportion of: (A) total river length, and (B) model predicted percent of total N removed in the river network, for small to intermediate (1st through 4th order) and larger (5th order and greater) streams/rivers ($RF1_m$ + NHD' scenario). Average ± S.D. for the 16 study watersheds.

The vast majority of the total stream length in a river network is in relatively small streams (Leopold & Maddock 1953). In the16 study watersheds, reaches identified as 1st through 4th order account for an average of 91% (+/– 3%) of the total stream length in the river network, while reaches that are 5th order and greater account for only 9% (+/– 3%) of the total stream length (Figure 7A). There is considerable variation among reaches within a stream order in reach-specific N removal (proportion of N input to a reach that is removed in that reach). However, overall, the model suggests that reach-specific N removal generally decreases with increasing stream order, as illustrated by the Penobscot, Connecticut and Kennebec rivers (Figure 8A). In these three rivers, approximately 20–25% of the N input to first order reaches is removed within the reach, while in 7th and 8th order reaches only about

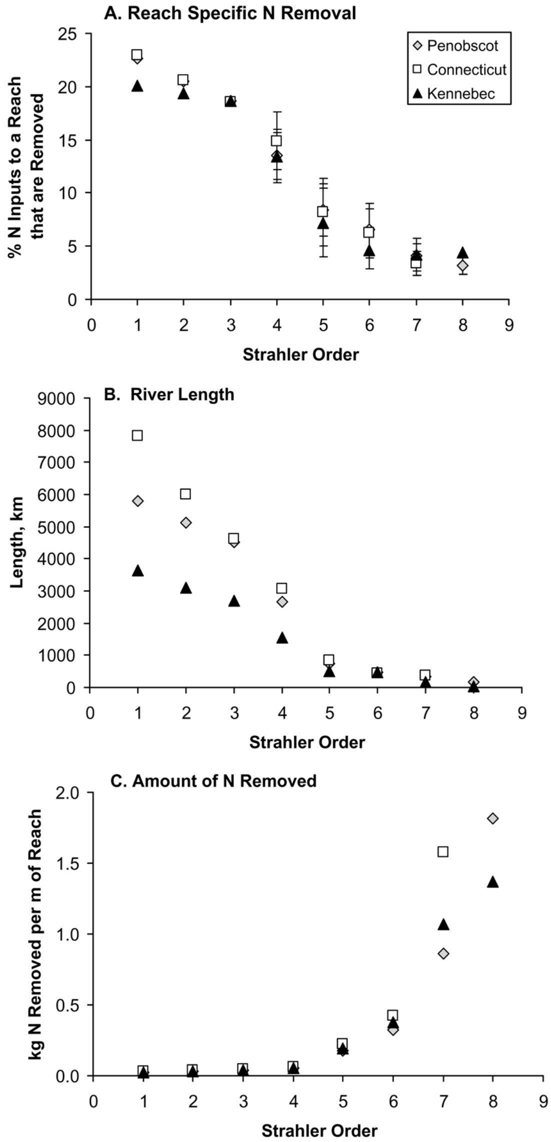


Figure 8. Relationship to Strahler order for the: (A) proportion of N input to a reach that is removed within that reach (average ± S.D.), (B) amount (km) of the total river length in a watershed, and (C) average amount of N (kg) removed per meter of stream/river for the $RF1_m$ + NHD' scenario with uniform direct watershed N loading to river (100 kg N km^{-2} watershed y^{-1}). Results for the Penobscot, Connecticut and Kennebec river networks are shown.

5% of the N input (direct watershed input plus input from upstream reaches) are removed within the reach. This general pattern is similar across the 16 watersheds and is related to the depth/TOT characteristics which, on average, increase with increasing channel size. Both the water depth and velocity increase with increasing channel size. However, depth increases relatively faster than velocity, resulting in an increase in the ratio of depth to time of travel, and thus a decrease in the model predicted proportion of N input that is removed in the reach.

The contribution of streams of different sizes (i.e., orders) to the total N removed in a river network depends on a number of factors related to stream size according to the RivR-N model. These factors include the: (1) contribution of streams of different sizes to total river length, (2) depth and time of travel characteristics of streams of various sizes, and (3) magnitude of N input to streams of different sizes (from both upstream reaches and direct watershed input). The contribution of each stream order to total stream length in a river network decreases with increasing stream order (Figure 8B). In addition, reach-specific N removal is greatest in smaller streams (Figure 8A). However, the model suggests that the total mass of nitrogen removed per meter of stream length increases with increasing stream order (Figure 8C). The reason for this seemingly contradictory pattern is the effect of stream morphology on N inputs and losses, specifically the dendritic pattern displayed in stream channels. Higher order streams and rivers have many more interconnected segments arranged in a linear series that extend over long distances as compared to the more parallel, and hydrologically independent, arrangement of segments that is reflected in lower order streams (see Figures 3, 4). This, in combination with N export from upstream lower order streams, leads to a greater cumulative effect on the absolute quantities of nitrogen that are input and removed in the individual reaches of higher ordered streams. Therefore, while a smaller proportion of N entering a reach is removed in higher order reaches, larger amounts (mass) of N are input in these reaches resulting in a larger amount of N removed per meter of stream length in higher order reaches (Figure 8C). At the river network scale this results in approximately half (45 +/– 15%) of the total N being removed in streams of 5th order and higher, and half (55 +/– 15%) in 1st through 4th order streams, according for the RivR-N model (Figure 7B). Thus, the larger river channels as well as small to intermediate streams are important in total N removal at the river network scale, although the larger channels account for only ∼10% of the total length of river channels.

The RivR-N model output was used to explore how much of the river N input from the watershed to streams of various sizes is removed before reaching the watershed outlet. A detailed examination of results from the

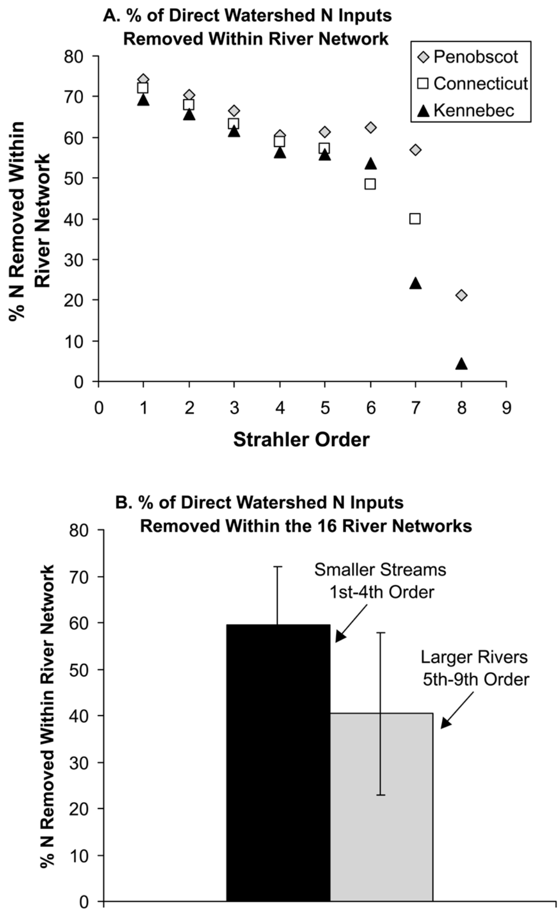


Figure 9. Model predicted percent of direct watershed input to a particular Strahler order that is removed within the river network for (A) the Penobscot, Connecticut and Kennebec river networks and (B) all 16 river networks (average ± S.D.). For example, (A) approximately 60% of the direct watershed N input to 4th order streams is removed within streams of order four and greater.

Penobscot, Connecticut and Kennebec river networks suggests that about 60 to 70% of the direct watershed N input to 1st through 5th order rivers is removed within the river network (Figure 9A). Conversely, 30 to 40% of that N input is exported by the river to the watershed outlet. In rivers of 6th order and higher a decreasing proportion of the direct watershed N input is removed within the river network, which reflects the decreased in-river processing time as well as lower reach-specific removal in higher order rivers (Figure 8A). In the 16 river networks, an average of 60% (±13) of the river

N inputs from the watershed areas draining 1st through 4th order streams is removed before reaching the watershed outlet, according to the RivR-N model (Figure 9B). A more variable and smaller proportion (40% ± 18) of the N entering larger river channels (≥5th order) from the surrounding watershed is removed within the river network. These results are consistent with the SPARROW (Spatially-Referenced Regression On Watershed attributes) model analysis of the Mississippi River basin and demonstrate the importance of distance traveled through the river network for efficient removal of N (Alexander et al. 2000). SPARROW is a statistical watershed model (see Smith et al. 1997) that provides empirical estimates of nitrogen loss in streams and rivers.

Finally, the RivR-N model output was used to explore where N is removed that originates from watershed areas draining 1st, 2nd, etc. order streams. Direct watershed N loading to 1st order streams is removed throughout the river network, with a significant amount removed even in the highest order rivers, as illustrated by the Penobscot river results (black bars, Figure 10). The largest amount of the direct watershed N loading to 1st order streams is removed within the 1st order streams compared to any other single downstream order. Similarly, 2nd order streams remove more of the direct watershed N loading to 2nd order streams than is removed in any single downstream order, although all downstream orders contribute to additional removal. The same is true of direct watershed N loading to all orders. Examination of the total N removed by river order shows that, in general, the highest order rivers remove more N than any other single lower order (Figure 10), although they account for only a small percentage of the total river length (Figure 7A and 8B). Furthermore, most of the N removed in these highest orders originates from the smaller (1st through 4th) order rivers under the base case scenario of uniform direct watershed N loading.

Scenario results

Effect of reservoirs

The effect of human modification of river hydrology on nutrient transport is the subject of considerable interest (Garnier et al. 2000; Vörösmarty et al. 1997). Reservoirs are one such modification. The model equation (eq. 2) for predicting reach-specific N removal was based on both river and lake studies and thus was considered applicable to reservoirs. We used the RivR-N model to explore the potential effect of reservoirs on N removal at the network scale. The number of reservoirs in each of the study watersheds ranged from 0 (Blackstone and Charles) to over 20 (Susquehanna and Penobscot) (Table 2).

At the river network scale, the effect of reservoirs on N removal was minimal. Removing all reservoirs from a watershed river network and substi-

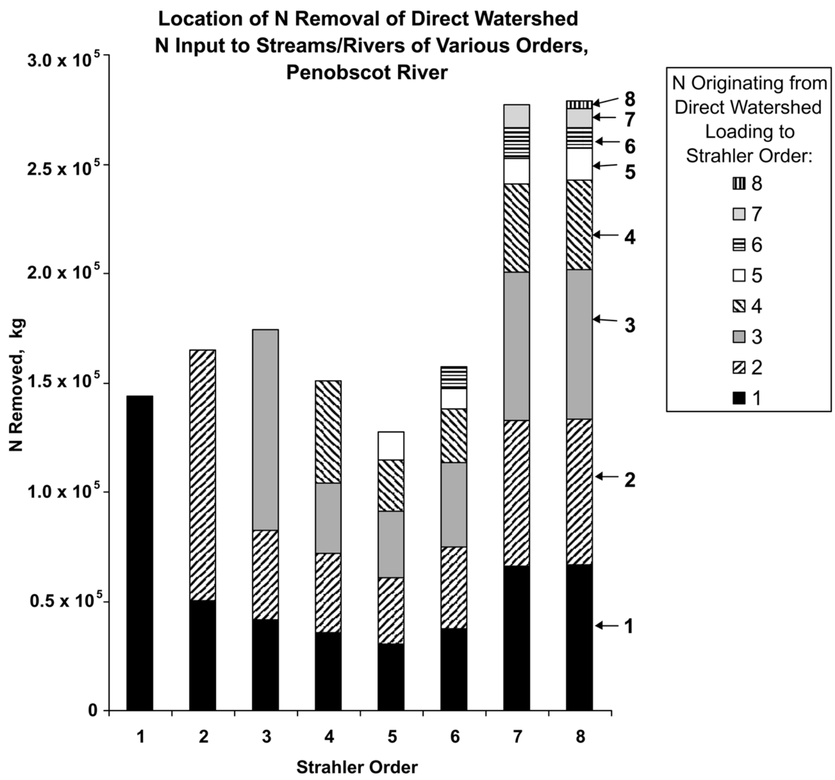


Figure 10. The location of N removal of direct watershed N input to streams/rivers of various Strahler orders for the Penobscot river network according to the RivR-N model. For example, the total amount of N removed in each Strahler order that originates from direct watershed N loading to 1st order reaches is represented by the black portion of the bars. The amount of N removed (kg) is determined using the RF1 + NHD' scenario with uniform direct watershed N loading (100 kg N km^{-2} watershed y^{-1}).

tuting pre-reservoir depth and TOT information for those reaches had little effect on the proportion of N removed (Figure 11A). The difference in the proportion of N removed with and without reservoirs was less than 2 percentage points, and in some cases removal of all reservoirs slightly increased N removal.

Examination of individual reservoirs on N removal provides insight into why the total contribution of reservoirs within the river network of a watershed is often predicted to be small by the RivR-N model. While reservoirs increase both depth and water residence time in a section of river, it is the ratio of these two characteristics that determines the proportion of N removed according to the model (eq. 2). The proportion of N input to a reservoir that is removed can be greater, less than, or essentially the same as the propor-

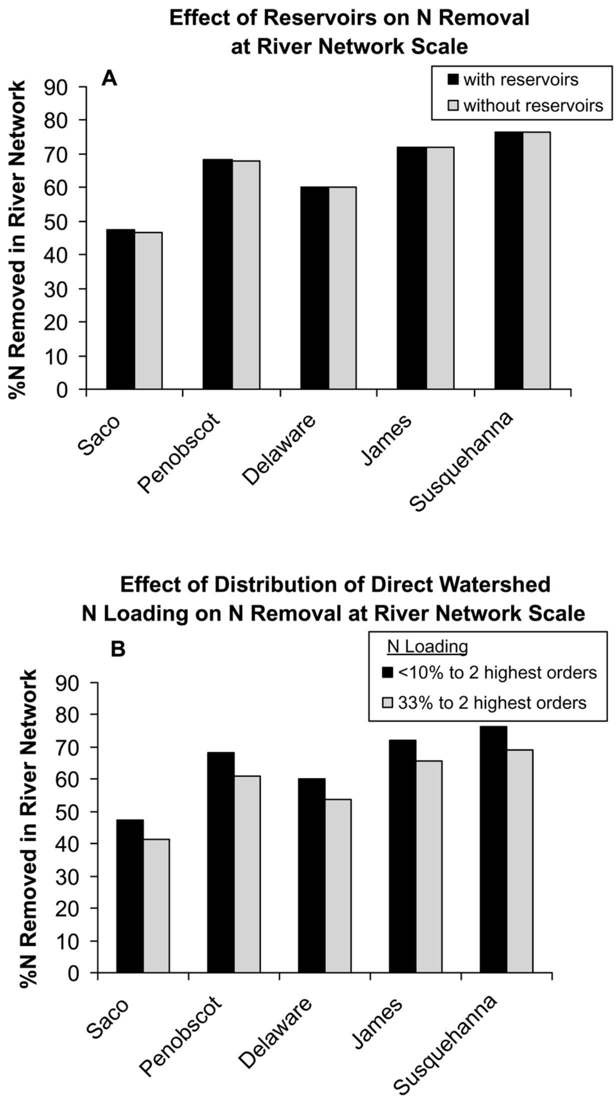


Figure 11. River network scale comparison of the proportion (as a percentage) of N input that is removed: (A) with reservoirs (base case) and without reservoirs, and (B) with $\leq$ 10% and 33% of the total direct watershed N load entering rivers of the 2 highest orders.

tion of N input removed in that river section under pre-reservoir depth and TOT (Figure 12). For example, the depth (8.9 m) and TOT (1.06 years) for Schoodic Lake (designated #1078 in the RF1 file) in the Penobscot basin results in a considerably higher (40.5%) proportion of N input to the reservoir that is removed compared to the pre-reservoir removal (14%) which had a

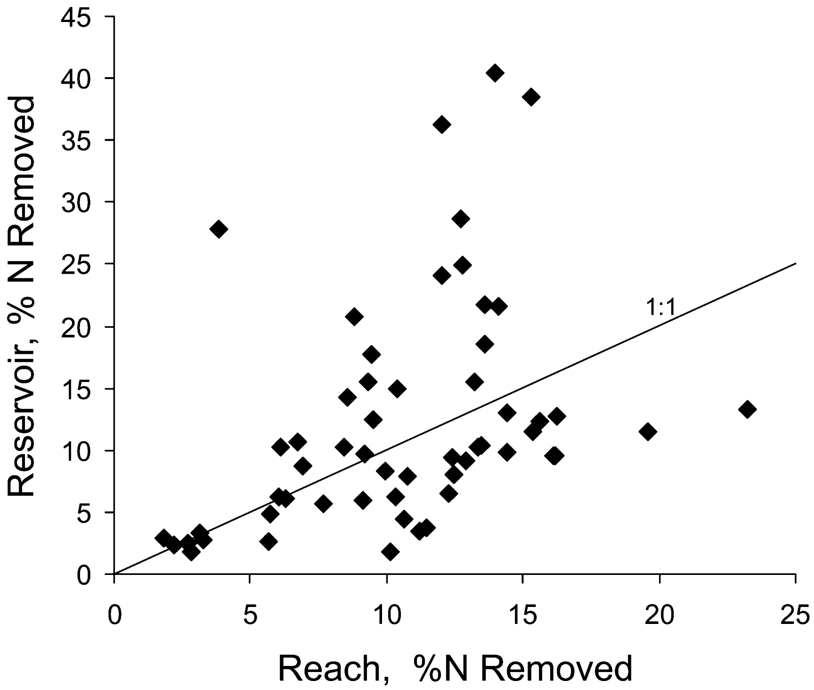


Figure 12. Reach scale comparison of the proportion (as a percentage) of N input that is removed in a reservoir and in the same reach under pre-reservoir depth and time of travel characteristics, according to the RivR-N model.

depth of 0.23 m and a TOT of 0.0015 y. In contrast, the Toronto reservoir (designated #1683 in the RF1 file) in the Delaware basin with a depth of 89.6 m and TOT of 0.42 y yielded a 12.4% removal of N input to the reservoir, which is slightly less than the proportion of N input that was removed in the reach (15.6%) before the reservoir (0.34 m depth; 0.003 y TOT), according to the RivR-N model.

The position of a reservoir within the river network, in addition to the ratio of the depth to the TOT of water in the reservoir, is also important in determining the contribution of a reservoir to N removal at the river network scale. For example, a reservoir with optimal depth and TOT (shallow with long residence time) placed near the outlet of a watershed would be relatively more effective at reducing N export by a river than the same reservoir placed in the upper reaches of a watershed where relatively less of the total N loading would pass through the reservoir. To explore this, we artificially replaced a 4th order and a 7th order reach of the Delaware with a theoretical reservoir with a depth of 16 m, a 1 y TOT, and a model predicted N removal of 32% of the N input to the reservoir. These were the characteristics of reservoir #1070 (Rangeley Lake; RF1 file) in the Androscoggin watershed; the proportion of N input to this reservoir that is removed is one of the highest in the 5 scenario watersheds. Placement of this reservoir in a 4th order reach (0.42 m depth, 0.00318 y TOT) of the Delaware river network increased the N removal within that reach from 14.7% to 32% of the N input to that reach. However, at the river network scale the N removal increased by only 0.1 percentage points (from 60.0% to 60.1%). Placement of this reservoir in the most downstream reach (depth 2.7 m, TOT of 0.00099 y) of the Delaware river network where it is a 7th order river increased the N removal within that reach from 4.8% to 32% of the input to the reach. The total N removal in the Delaware river network increased from 60% to 70%. The discharge of the Delaware River at this location (365 m^3 s^{-1}) would necessitate a very large reservoir (719 km^2) to maintain the theoretical reservoir depth and TOT. However, the exercise illustrates the relatively small additional N removal that a reservoir even with "optimal" depth, TOT and location is predicted to have in a watershed under the base case scenario with uniform N loading from the direct watershed.

Scale of river network information

Two reach files with different scales were combined to apply the RivR-N removal model to the study watersheds in the base case scenario (as detailed above in Model application: Base case scenario). RF1 and NHD depict approximately the resolution of the "blue-line" drainages that show up on USGS 1:500,000 and 1:100,000 scale maps, respectively (Figure 3A, B). The effect of the spatial scale of the reach network file used to estimate N removal in a watershed was examined by comparing the RivR-N model output for the base case (approximately the scale of NHD) with the reduced scale (RF1 data only). The reduced scale scenario eliminated all 1st, 2nd, 3rd and in some cases 4th order rivers in the base case scenario. The total watershed area and total watershed direct N loading was the same as in the base case, however, the watershed area draining directly into a specific reach in RF1 was greater than under the base case scenario, because of the greatly reduced total reach length in a watershed. Direct watershed area for each reach in RF1 was available in the RF1 file. The predicted proportion of N removed in a river network in the reduced scale scenario was less than with the higher resolution base case (Table 2). This was expected given the greatly reduced total reach length, and thus reduced cumulative N removal, in the RF1 only scenario. However, the decrease in the proportion of N removed under the reduced scale scenario averaged only 14 percentage points less than the higher resolution base case (S.D. +/– 7; range ~8 to 31 percentage points), although the total reach length was approximately 80% less. The somewhat smaller than expected difference in the predicted N removal between the $RF1_m$ + NHD' and RF1 scenario is due to the larger direct watershed area for reaches in RF1 in the RF1 scenario compared to those same reaches in the $RF1_m$ + NHD' scenario. This resulted in a larger N input to the RF1 reaches (and thus larger N removal) in the RF1 scenario compared to the $RF1_m$ + NHD' scenario. This effect is also illustrated by comparison of Figure 7B which shows that in the $RF1_m$ + NHD' scenario approximately 50% of the total N was removed in 1^{st} through 4^{th} order streams (Figure 7B) which are primarily the NHD' reaches, with the finding that the difference in N removed in the RF1 scenario was only 14 percentage points, on average, less than in the $RF1_m$ + NHD' scenario.

Distribution of N loading within the watershed

The varying distribution of source inputs across the landscape in a watershed is expected to affect the N removed in a river network (Alexander et al. 2000). Total N loadings and N inputs to the rivers for the 16 study watersheds were estimated using GIS land-use distributions coupled with N loading information that was developed for specific land uses (Boyer et al. 2002; van Breemen et al. 2002). However, the geographic distribution of N loading within each watershed was not maintained in those budgets. So, as a first approximation of the effect of varying degrees of source inputs across the landscape on N removal in rivers, we explored several theoretical patterns of the N distribution. In the base case scenario, N loading to the rivers per unit area of watershed (referred to as direct watershed N loading) was held constant (100 kg N per km^2 per year). Such a scenario could be considered to represent a uniform distribution of land use in a watershed, such as a completely forested watershed. Uniform land use is not generally the case today, given the mosaic of human development/alteration in watersheds, including agriculture and urban land uses.

It is not uncommon for major cities to be located at the base of a watershed, on the higher order river segments, resulting in a high N input from wastewater treatment facilities, urban runoff, etc. near the base of a watershed. To explore the effect of the distribution of N loading (land use) in a watershed on the amount of N removed during river transport, we allocated a third of the total direct watershed N loading to reaches of the two highest orders (these were generally between 6th and 9th orders); lower order reaches received the remaining N at a constant rate. The total direct watershed N loading to the river network remained the same as in the base case scenario. The five test watersheds were used for this scenario run.

In the base case, approximately 90% of the total direct watershed N loading entered 1st through 4th order reaches. This was the combined result of 1st through 4th order reaches generally accounting for ∼90% of the total

Table 3. Regression estimates for nitrogen loss model. CI = Confidence interval

Model parameters	Parametric coefficient	Bootstrap coefficient	Lower 90% CI	Upper 90% CI	Standard deviation
Intercept	88.45	90.19	74.85	110.06	14.5
Ratio of depth to water residence time	0.3677	–0.3722	–0.2930	–0.4665	0.064
R-squared	0.73				
Mean square error (log units)	0.2403				

river length (Figure 7B), a constant drainage density (km^2/river length) in the watershed, and an assumed even N loading per unit area of watershed. The two highest orders account for a total of between 1% and 10% of the total river length, and, therefore, 1% to 10% of the total direct watershed N loading. Re-allocating a third of the direct watershed loading to the two highest orders resulted in a fairly modest decrease in the proportion of N removed in the river network: 6 to 7 percentage points (Figure 11B). These results are generally consistent with the findings of a SPARROW-based analysis of non-uniformities in the spatial distribution of sources in these watersheds and their effects on in-stream N loss (see Alexander et al. 2002). The decrease in the N removal compared to the base case is partly the result of a larger amount of N entering the higher order reaches which are subject to less additional removal in downstream reaches (shortened flow path to watershed outlet). In addition, these higher order reaches tend to have a lower proportion of reach-specific N removal than lower order reaches due to their depth and water residence time characteristics (Figure 8A).

Model uncertainty

There are several sources of model uncertainty, including: (1) statistical uncertainties in model coefficients and predictions, and (2) uncertainties in the river reach files (RF1 and NHD) used in the model application.

Statistical uncertainties in model coefficients (Table 3) and predictions (Table 4) were quantified using bootstrapping techniques (Efron 1982), as described above (Model application: Statistical analysis of model uncertainty). A number of factors contribute to the statistical uncertainties in the model coefficients (Table 3). These include the small number of river studies that were available for use in the development of the model equation, as well as uncertainties associated with each study in the determination, or our extra-

Table 4. Evaluations of equation 2 (RivR-N Model) for estimating N loss in river networks using only the RF1 data files (reduced scale scenario) for the 16 watersheds. Results from the SPARROW Model (Alexander et al. 2000) also using the RF1 data files are shown for comparison

Watershed	Equation 2 parametric[a]	Bootstrap % boot mean[b]	Bootstrap % w/model error[c]	Lower 90%[d]	Upper 90%[e]	SPARROW
Penoboscot	59	61	67	51	82	47
Kennebec	52	53	57	42	70	46
Androscoggin	44	47	51	37	64	40
Saco	33	35	38	27	49	35
Merrimack	38	45	50	35	63	34
Charles	15	15	15	7	24	30
Blackstone	22	24	26	16	35	31
Connecticut	55	60	66	49	80	47
Upper Hudson	50	48	52	39	65	45
Mohawk	47	51	55	39	69	40
Delaware	48	53	59	42	74	38
Schuylkill	31	30	33	22	42	28
Susquehanna	63	67	73	57	87	45
Potomac	60	59	64	49	78	59
Rappahannock	42	41	45	33	56	59
James	61	57	62	46	74	58
25th Percentile	37	40	43			35
Median	48	50	54			43
75th Percentile	56	58	62			47

[a]RF1 loss based on equation 2 %N = 88.45* Ratio**–0.3677 with parametric estimates.
[b]RF1 loss – based on bootstrap mean coefficients for equation 2 : %N = 90.19* Ratio**–0.3722.
[c]RF1 loss – based on bootstrap mean coefficients for equation 2 as above with model error (regression coefficients & residuals).
[d]Lower 90% confidence interval on bootstrap %N based on inclusion of model error.
[e]Upper 90% confidence interval on bootstrap %N based on inclusion of model error.

polation, of the proportion of TN removed on an annual basis in each of those studies. In addition, variables not currently included in the model, but which are important in controlling the proportion of TN removed in a river reach, would contribute to the uncertainty in the model coefficients. Future studies quantifying N removal in rivers are needed for independent comparison with the model predictions and to potentially improve the model equations.

Errors in model predictions of the proportion of nitrogen removed for each of the sixteen watersheds included uncertainties in both the model coefficients and the observed data (i.e., regression residuals). Errors in model predictions at the river network scale were computed utilizing the uncertainties associated with the regression residuals (see Model application: Statistical analysis of model uncertainty). These computations were only done for the reduced scale scenario for the RivR-N model. Therefore, they include errors in model predictions of N losses in the RF1 streams and reservoirs, but not losses in NHD' reaches. The prediction uncertainties for the 90% confidence interval in the proportion of nitrogen removed at the river network scale (Table 4) range from +/– 17 to +/– 32 percentage points with a median of +/– 28. For example, in the Delaware basin the 90% confidence interval on the mean nitrogen loss of 59% ranges from 42 to 74% or +/– 32 percentage points. Expressed as a proportion of the mean nitrogen loss in the river networks, the 90% confidence intervals range from 39 to 113 percent (median = 54 percent). The greatest uncertainty is generally displayed in the smallest watersheds, such as the Charles (113 percent) and Blackstone (73 percent), where the least amount of averaging of errors would be expected to occur.

The in-stream losses calculated for the sixteen eastern U.S. watersheds using the RivR-N model are very similar to those using the SPARROW model (see Alexander et al. 2000) (Table 4), based on a comparison of estimates for both models using the RF1 scale reaches (reduced scale scenario of RivR-N model) (see Alexander et al this volume for additional comparisons). SPARROW estimates of the rates of nitrogen loss decline rapidly with channel size from 0.45 per day of water travel time in small streams to 0.005 per day in large rivers (Alexander et al. 2000). The SPARROW estimates show general agreement with the pattern in the RivR-N model (Figure 8A) and with literature estimates of loss, including those for streams used in the calibration of the RivR-N model.

While the river reach files used in the model application are the most comprehensive available, they both have shortcomings. As previously noted, approximately 80% of the total channel length (true 1st, 2nd and 3rd order rivers) in a network are not contained in the RF1 files because of their lower spatial resolution. The higher resolution NHD files contain more accurate total length of reaches in the rivers in each watershed but do not contain information on the flow, depth and TOT of stream reaches. We estimated these parameters for NHD' for each watershed based on extrapolations using characteristics of the higher order RF1 reaches for the associated watershed (detailed in Appendix). The errors incurred by combining of NHD' and RF1 and with estimating reach characteristics for NHD' are not known. Within the next few years it will be possible to rerun the RivR-N model when the fully annotated NHD reach files are available (R. Pierce, U.S. Geological Survey, pers. comm. 2000).

Summary

Many coastal ecosystems are receiving increased N inputs due to anthropogenic N inputs to their watersheds. Management of nutrient inputs to coastal ecosystems requires not only knowing the sources and magnitude of N to their watersheds, but also knowing where and how much of that N is removed during its movement through the terrestrial and freshwater ecosystems. A substantial amount of nitrogen can be removed within the network of streams and rivers draining watersheds as shown by studies in a wide range of stream/river sizes and geographic locations. However, most studies have examined N removal in short sections of a river (reach), such as a first order stream or a larger channel of the river and the proportion of N removed at the river reach scale varies widely (1% to >80%) (e.g., Table 1; Swank & Caskey 1982; Chesterikoff et al. 1992; Jansson et al. 1994). Previous studies generally have not addressed how to scale-up those results to the whole river network, with the exception of Smith et al. (1997) and Alexander et al. (2000). The current analysis suggests that the water displacement of streams and reservoirs (ratio of depth to time of travel for a river reach) can explain a considerable amount of the variation in the reported N removal efficiencies. In order to evaluate the N removed in a river network, the relationship must be applied to reaches throughout a river network, and any N not removed in a reach must be routed to downstream reaches where it is subject to additional removal. As a result of this cumulative removal, the proportion of the N inputs to a river network are considerably larger than the proportion removed in any one reach or section of river, as shown by the RivR-N model developed in this study. Application of the RivR-N model to sixteen river networks in the eastern U.S. indicates that in-river processes significantly reduce N transport to coastal ecosystems. Between 37% and 76% of the total N input to these river networks was removed during transport. In the context of the total N inputs to these watersheds, in-river processes removed an average of 40% (± 19) of the inputs.

The relationship developed for the RivR-N model describing the proportion of N input that is removed in a river reach as an inverse function of "reaction time", in this case water displacement (depth/water time of travel), is consistent with findings across a wide range of aquatic ecosystems. This includes studies within an individual river reach where N removal decreased as flow increased (Jansson et al. 1994; Pind et al. 1997). It is also consistent with the watershed mass-balance model, SPARROW, in which the proportion of N removed decreases with increasing stream channel depth (Smith et al. 1997; Alexander et al. 2000), with a relationship developed for estuaries in which the proportion of N removed decreases with decreasing water residence time (Nixon et al. 1996), and with a relationship developed for shallow, well-mixed lakes in which the proportion of nitrate removed decreases with increasing nitrate concentration and the ratio of depth/water residence time (Kelly et al. 1987). Modifications to the RivR-N model would likely be necessary for rivers with characteristics widely different than those used to develop the model, such as rivers with extensive hyporheic flow (Sjodin et al. 1997). The model does not include processes in riparian areas where a substantial amount of N also can be removed (Peterjohn & Correll 1984; Lowrance et al. 1984; Billen & Garnier 1999).

Analysis of the RivR-N model output was used to explore where in the river network most of the N removal is occurring and what factors contribute to those patterns, based on the $RF1_m$ + NHD' scenario. Larger river channels generally have the lowest reach-specific N removal (proportion of total N input to a reach that is removed in that reach). However, per meter of stream, the greatest amount of N removed is in the larger river channels, because of the large amount of N passing through them due to export from upstream reaches. Approximately half of the N in the sixteen eastern U.S. river networks is removed in larger rivers ($\geq$5th order) and half in small to medium size streams ($\leq$4th order), although streams of $\geq$5th order account for only about 10% of the total stream length. In the 16 river networks, an average of 60% ($\pm$ 13) of the river N inputs from the direct watershed areas draining 1st through 4th order streams is removed before reaching the watershed outlet. A more variable and smaller proportion (40% $\pm$ 18) of the N entering larger river channels ($\geq$5th order) from the directly surrounding watershed is removed within the river network. Direct watershed N loading to, for example, 1st order streams is removed throughout the downstream river network, with a significant amount removed even in the highest order rivers. Most of the N removed in the highest orders originates from the smaller (1st through 4th) order rivers. The RivR-N model indicates that reservoirs account for a small proportion (less than 2 percentage points) of the total N removed throughout a river network, although within any one reach a reservoir can substantially increase or decrease N removal. Varying the distribution of N loading within the river network indicated that the N removal decreased by less than 10 percentage points when the direct watershed N input to the two highest orders increased from less than 10% to 33%. Clearly, N removal in river networks is important in determining the amount of N delivered from watersheds to coastal marine systems. Future field studies and annotation of high resolution river reach files will be important in improving our understanding of this important sink for N.

Appendix 1
Development of depth and TOT characteristics for NHD' reaches

The numbers of 1st, 2nd, 3rd, and in some cases 4th order rivers in NHD' in each watershed were estimated using the average length of 1st, 2nd, 3rd and 4th order rivers (1609 m, 3701 m, 8528 m, 19308 m, respectively) and a bifurcation ratio of approximately 3.5, both derived from many samples of basins in the U.S. (Leopold et al. 1964). Bifurcation ratios normally range between 2 and 4; the ratio varied between 2.6 and 3.7 in our analysis to accommodate the various NHD' lengths in the different watersheds while maintaining the length of nth order rivers constant.

Reach depths for NHD' were estimated as a function of reach discharge using eq. 3 (main text). Time of travel (TOT) for NHD' reaches was estimated from river length divided by velocity. Velocity is a power function of discharge (Leopold & Miller 1956). The relationship between velocity and discharge (Figure A1) for each watershed was calculated using RF1 data; the relationship varied within a watershed, depending on discharge. Therefore, only data from reaches with discharges less than 1–2 m^3/s were used to develop the relationship for NHD' velocities (which have low discharges). NHD' velocities were then used with NHD' reach lengths to calculate the time of travel for reaches in NHD'.

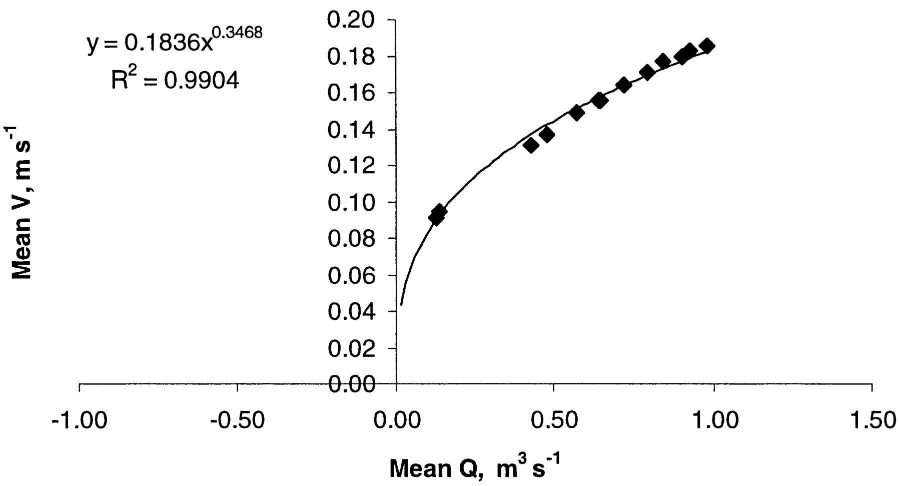


Figure A1. Graph of Q vs V for Delaware (all reaches with Q less than 1).

Discharge is needed in both equations 2 and 3 (main text). Within a basin, river order generally is related to the log of the discharge (Leopold & Miller 1956). There was a significant relationship between log of discharge and river order in RF1 (0.001 level of significance) for each of the study watersheds. Therefore, the relationship between river order and discharge in RF1 for each watershed was used to estimate the discharge of river orders in NHD' (i.e., 1st, 2nd, and 3rd order rivers) for each watershed (Figure A2). There are multiple rivers of nth order in a river network. Within RF1 often there are multiple contiguous reaches of the same order within a river. Only data for the most downstream reach within each river of order n were used to derive the relationship between river order and discharge.

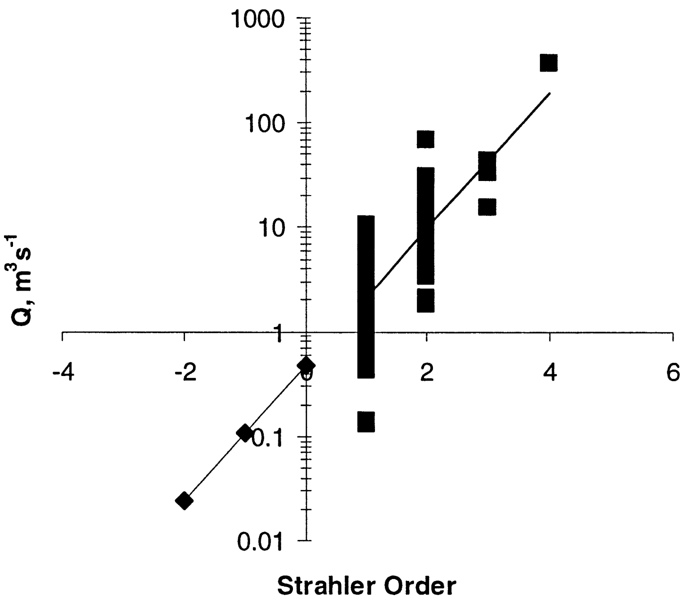


Figure A2. Example graph of Q vs Strahler order for Delaware [regression equation: Q = (0.651 ∗ Strahler #) – 0.318]. Predicted Q for NHD' Strahler orders (here denoted as 0, –1 and –2; in the $RF1_m$ + NHD' scenario all orders were renumbered such that in the current example the final orders would be 1 through 6).

NHD' reaches were connected to the RF1 network by assuming that half of all rivers of order n discharge to rivers of n+1 order (Leopold et al. 1964). The remaining rivers of order n were then connected to rivers of greater than n+1, equally per unit length of river.

Acknowledgements

This work was initiated as part of the NOAA Atmospheric Assessment Project and continued under the International SCOPE Nitrogen Project that received support from both the Mellon Foundation and from the National Center for Ecological Analysis and Synthesis. This work was supported, in part, by funding (to SPS) from NOAA NJ Sea Grant (NJSG # 99–427) and the NOAA Coastal Ocean Program. The views expressed herein are those of the authors and do not necessarily reflect the views of NOAA or any of its sub-agencies. We would like to thank Hilairy Hartnett and Tracy Wiegner for useful discussions during the development of this project and three anonymous reviewers of the manuscript who provided insightful comments.

References

Alexander RB, Johnes PJ, Boyer EA & Smith RA (2002) A comparison of methods for estimating the riverine export of nitrogen from large watersheds. Biogeochemistry 57/58: 295–339

Alexander RB, Brakebill JW, Brew RE, & Smith RA (1999) ERF1 – Enhanced River Reach File 1.2, U.S. Geological Survey Open-File Report 99–457. Reston, Virginia

Alexander RB, Smith RA & Schwarz GE (2000) Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403: 758–761

Andersen JM (1977) Rates of denitrification of undisturbed sediment for six lakes as a function of nitrate concentration, oxygen, and temperature. Arch. Hydrobiol. 80: 147–159

Ayers JC (1970) Lake Michigan environmental survey. University of Michigan, Great Lakes Research Division Special Report 49

Billen G, Lancelot C & Meybeck M (1991) N, P and Si retention along the aquatic continuum from land to ocean. In: Mantoura RFC, Martin JM & Wollast R (Eds) Ocean Margin Processes in Global Change (pp 19–44). Dahlem Workshop Reports, Wiley

Billen G, Somville M, De Becker E & Servais P (1985) A nitrogen budget of the Scheldt hydrographical basin. Netherlands Journal of Sea Research 19(3/4): 223–230

Billen G, Garnier J & Meybeck M (1998) Les sels nutritifs: l'ouverture des cycles. In: Meybeck, de Marsily & Fustec (Eds) "La Seine en son bassin: fonctionnement écologique l'un système fluvial anthropisé". Elsevier

Billen G & Garnier J (1999) Nitrogen transfers through the Seine drainage network: a budget based on the application of the "Riverstrahler" model. Hydrobiologia 410: 139–150

Boyer EW, Goodale CL, Jaworski NA & Howarth RW (2002) Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A. Biochemistry 57/58: 137–169

Burns DA (1998) Retention of NO_3^- in an upland stream environment: A mass balance approach. Biogeochemistry 40: 73–96

Calderoni A, Mosello R & Tartari G (1978) P, N and Si budget in Lago Mergozzo. Verh. Int. Verein. Limnol. 20: 1033–1037

Chesterikoff A, Garban B, Billen G & Poulin M (1992) Inorganic nitrogen dynamics in the River Seine downstream from Paris (France). Biogeochemistry 17: 147–164

Christensen PB, Nielsen LP, Sørensen J & Revsbech NP (1990) Denitrification in nitrate-rich streams: Diurnal and seasonal variation related to benthic oxygen metabolism. Limnology Oceanography 35(3): 640–651

Christensen PB & Sørensen J (1988) Denitrification in sediment of lowland streams: Regional and seasonal variation in Gelbaek and Rabis Baek, Denmark. FEMS Microbiology Ecology 53: 335–344

Cole JJ, Peierls BL, Caraco NF & Pace ML (1993) Nitrogen loading of rivers as a human-driven process. In: McDonnel MJ (Ed) Humans as Components of Ecosystems (pp 141–157). Springer-Verlag, New York

Cooke JG & White RE (1987) The effect of nitrate in stream water on the relationship between denitrification and nitrification in a stream-sediment microcosm. Freshwater Biology 18: 213–226

Cooper AB & Cooke JG (1984) Nitrate loss and transformation in 2 vegetated headwater streams. New Zealand Journal of Marine and Freshwater Research 18: 441–450

Dillon PJ & Molot LA (1990) The role of ammonium and nitrate retention in the acidification of lakes and forested catchment. Biogeochem. 11: 23–44

Duan N (1983) Smearing estimate: A nonparametric retransformation method. J. Am. Stat. Assoc. 78: 605–610

Efron B (1982) The jackknife, the bootstrap and other resampling plans, in CBMS-NSF Regional Conference Series in Applied Mathematics, Soc for Ind. And Appl. Math., Philadelphia, PA

Garnier J, Leporcq B, Sanchez N & Philippon X (1999) Biogeochemical mass-balances (C, N, P, Si) in three large reservoirs of the Seine Basin (France). Biogeochemistry 47: 119–146

Garnier J, Billen G, Sanchez N & Leporcq B (2000) Ecological functioning of the Marne reservoir (upper Seine basin, France). Regulated Rivers-Research & Management 16(1): 51–71

Hill AR (1979) Denitrification in the nitrogen budget of a river ecosystem. Nature 27: 291–292

Hill AR (1981) Nitrate-nitrogen flux and utilization in a stream ecosystem during low summer flows. Canadian Geographer 25: 225–239

Hill AR (1983) Nitrate-nitrogen mass balances for two Ontario Rivers. In: III Fontaine (Ed) Dynamics of Lotic Ecosystems (pp 457–477). Ann Arbor Sciences Publishers, Ann Arbor

Horton RE (1945) Erosional development of streams and their drainage basins. Geol. Soc. America Bull. 56: 275–370

Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K, Downing JA, Elmgren R, Caraco N, Jordan T, Berendse F, Freney J, Kudeyarov V, Murdoch P & Zhao-Liang Z (1996) Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry 35: 75–139

Jacobs TC & Gilliam JW (1985) Headwater stream losses of nitrogen from two coastal plain watersheds. J. Environ. Qual. 14(4): 467–472

Jansson M, Leonardson L & Fejes J (1994) Denitrification and Nitrogen Retention in a Farmland Stream in Southern Sweden. Ambio 23: 326–331

Kaushik NK & Robinson JB (1976) Preliminary observations on nitrogen transport during summer in a small spring-fed Ontario stream. Hydrobiologia 49(1): 59–63

Kelly CA, Rudd JWM, Hesslein RH, Schindler DW, Dillon PJ, Driscoll CT, Gherini SA & Hecky RE (1987) Prediction of biological acid neutralization in acid-sensitive lakes. Biogeochemistry 3: 129–140

Leopold & Maddock (1953) The hydraulic geometry of stream channels and some physiographic implications. Geological Survey Professional Paper #252, 57 pp, US Government Printing Office

Leopold LB & Miller JP (1956) Ephemeral streams – hydraulic factors and their relation to the drainage net. U.S. Geol. Survey Prof. Paper 282-A: 16–24

Leopold LB, Wolman MG & Miller JP (1964) The drainage basin as a geomorphic unit. In: Gilluly J & Woodford AO (Eds) Fluvial Processes in Geomorphology. San Francisco

Lowrance R, Todd R & Fail J (1984) Riparian forests as nutrient filters in agricultural watersheds. BioScience 34: 374–377

Mulholland PJ (1992) Regulation of nutrient concentrations in a temperate forest stream: Roles of upland, riparian, and instream processes. Limnology Oceanography 37(7): 1512–1526

Mulholland PJ, Tank JL, Sanzone DM, Wollheim WM, Peterson BJ, Webster JR & Meyer JL (2000) Nitrogen cycling in a forest stream determined by a ^{15}N tracer addition. Ecological Monographs 70: 471–493

National Academy of Sciences (2000) Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution. Committee on the Causes and Management of Eutrophication, Ocean Studies Board, Water Science and Technology Board, National Research Council, 428 pp

Nixon SW, Atkinson LP, Berounsky VM, Billen G, Boicourt WC, Boynton WR, Church TM, Ditoro DM, Elmgren R, Garber JH, Giblin AE, Jahnke RA, Owens NJP, Pilson MEQ & Seitzinger SP (1996) The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35: 141–180

Peterjohn WT and Correll DL (1984) Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65: 1466–1475

Peterson BJ, Wollheim WM, Mulholland PJ, Webster JR, Meyer JL, Tank JL, Marti E, Bowden WB, Valett HM, Hershey AE, McDowell WH, Dodds WK, Hamilton SK, Gregory S & Morrall DD (2001) Control of nitrogen export from watersheds by headwater streams. Science 292 (5514): 86–90

Pind A, Risgaard-Petersen N & Revsbech NP (1997) Denitrification and microphytobenthic NO_3^- consumption in a Danish lowland stream: Diurnal and seasonal variation. Aquatic Microbial Ecology 12: 275–284

Robinson JB, Whiteley HR, Stammers W, Kaushik NK & Sain P (1979) The fate of nitrate in small streams and its management implications. In: Lohr RC (Ed) Best Management Practices for Agriculture & Silviculture (pp 247–259). Ann Arbor Science Publications, Ann Arbor

Ruddy BC & Hitt KJ (1990) Summary of selected characteristics of large reservoirs in the United States and Puerto Rico 1988, U.S. Geological Survey Open File Report 90–163, Reston, Virginia

Schelske CL (1975) Silica and nitrate depletion as related to rate of eutrophication in lakes Michigan, Huron, and Superior. In: Hasler AD (Ed) Coupling of Land and Water Systems (pp. 277–298). Springer-Verlag, New York

Seitzinger SP (1988a) Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical importance. Limnology Oceanography 33: 702–724

Seitzinger SP (1988b) Benthic nutrient cycling and oxygen consumption in the Delaware Estuary. In: Majumdar SK (Ed) The Ecology and Restoration of the Delaware River Basin (pp 132–147). PA Acad. Sci.

Seitzinger SP (1991) The effect of pH on the release of phosphorus from Potomac Estuary sediments: Implications for blue-green algal blooms. Estuarine, Coastal and Shelf Science 33: 409–418

Sjodin AL, Lewis J & Saunders III (1997) Denitrification as a component of the nitrogen budget for a large plains river. Biogeochemistry 39: 327–342

Smith RA, Schwarz GE & Alexander RB (1997) Regional interpretation of water-quality monitoring data. Water Resources Research 33(12): 2781–2798

Strahler AN (1952) Hyposometric (area-altitude) analysis of erosional topography. Geol. Soc. America Bull. 63: 1117–1142

Swank WT & Caskey WH (1982) Nitrate depletion in a second-order mountain stream. J. Environ. Qual. 11(4): 581–584

Van Breemen N, Boyer EW, Goodale CL, Jaworski NA, Paustian K, Seitzinger SP, Lajtha K, Mayer B, van Dam D, Howarth RW, Nadelhoffer KJ, Eve M & Billen G (2002) Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A. Biogeochemistry 57/58: 267–293

Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW, Schlesinger WH & Tilman DG (1997) Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications 7: 737–750

Vörösmarty CJ, Sharma KP, Fekete BM, Copeland AH, Holden J, Marble J et Al. (1997) The storage and aging of continental runoff in large reservoir systems of the world. Ambio 26(4): 210–219

Wollheim WM, Peterson BJ, Deegan LA, Hobbie JE, Hooker B, Bowden WB, Edwardson KJ, Arscott DB, Hershey AE & Finlay J (2001) Influence of stream size on ammonium and suspended particulate nitrogen processing. Limnology and Oceanography 46(1): 1–13