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Nitrogen deposition and lake nitrogen concentrations: a regional analysis of terrestrial controls and aquatic linkages

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Abstract. Loading of nutrients from terrestrial ecosystems strongly influences the productivity and biogeochemistry of aquatic ecosystems. Human activities can supplement and even dominate nutrient loading to many lakes, particularly in agricultural and urbanized settings. For lakes in more remote regions such as the Adirondack Mountains of New York, N deposition represents the primary potential anthropogenic nutrient source. We combined a spatial model of N deposition with data on lake-N concentrations and spatial data on watershed configuration to identify the sources of watershed N loading for over 250 lakes in the Adirondacks. The analysis indicates that while wetlands are stronger sources of N loading per unit area than forests in the absence of inorganic N deposition, wetlands retain essentially all N deposition, while forests retained ~87% of N deposition. Since forests cover close to 90% of the watersheds, upland forests are, on average, the single largest source of N loading to Adirondack lakes. Direct deposition of N to the lake surface accounted for as large a fraction of loading as that from wetlands in the watersheds. We found no evidence that presence of wetlands along flowpaths to lakes reduced loading from upland forests. Moreover, there was no evidence that net loading to lakes declined with increasing distance of a source area to the lake. Lake N-concentrations thus primarily reflect N-loading from forests in concert with loss rates determined by water residence time and within-lake processes.

Key words: Adirondack Mountains; hydrologic processing; lake nitrogen concentration; nitrogen deposition; nutrient loss along flowpaths; spatially explicit models; watershed nutrient loading.

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Introduction

Loading of nutrients from terrestrial ecosystems strongly influences the productivity and biogeochemistry of aquatic ecosystems. Land conversion to agricultural and urban uses typically leads to increases in phosphorus and nitrogen loading causing eutrophication (Carpenter et al. 1998, Gemesi et al. 2011). For areas that have not undergone agricultural or urban development, watershed properties such as slope, size, soils, and vegetation are key influences on nutrient export (D'Arcy and Carignan 1997, Prepas et al. 2001, Campbell et al. 2004). In addition, the spatial configuration of landscape cover (forests and wetlands) affects the processing, loss and retention of nutrients along flow paths, modifying nutrient transport within and export from watersheds (e.g., Zhang 2011). Large areas of the northeastern United States are dominated by forests with little agriculture and minimal urbanization. The region also experiences high rates of nitrogen deposition due to regional air pollution with a deposition gradient (higher to lower) along a southwest to northeast axis (Driscoll et al. 2003). As a result of N-deposition, elevated nitrate concentrations are observed in some lakes in the region, especially at the western end of this gradient including the Adirondacks Mountains of New York (Sullivan et al. 1997, Momen et al. 1999).

These observations raise the general question of how the interaction of nitrogen deposition and watershed processing influences nitrogen export and nitrogen concentrations in aquatic systems. The Adirondack region, which is our focus in this paper, provides an interesting case because the landscape is a mixture of forests and wetlands with minimal human development. The region is rich in lakes with diverse morphometry, hydrology, chemistry and surrounding watersheds. In addition to the geographical gradient noted above, N deposition varies with vegetation type, elevation and aspect (Weathers et al. 2000, 2006). Hence, Adirondack watersheds experience a wide range of N deposition. Watershed coverage also varies in terms of the relative area of land in forests versus wetlands as well as in the relative spatial configuration of forests and wetlands within watersheds (Roy et al. 1997).

Adirondack lake N concentrations reflect the variable processing and loading of nitrogen from watersheds ("indirect inputs"), as well as direct deposition of N from the atmosphere ("direct inputs") to the lake surface, plus within-lake processing and losses. Atmospherically deposited nitrogen occurs mainly as nitrate, ammonium, and organic nitrogen (Driscoll et al. 2003). In the terrestrial portion of the watershed reactive forms of N are taken up by terrestrial plants and microorganisms and mostly retained in soils and plant biomass (Aber et al. 2003, Lovett and Goodale 2011). N exported to lakes is mainly in the form of dissolved organic nitrogen, although nitrate can also be an important component of export especially during snowmelt (McHale et al. 2000, Mitchell et al. 2001, Ito et al. 2005). In terms of inputs to lakes, different watershed cover types (e.g., forests versus wetlands) export different quantities of N (Ito et al. 2005). Direct N deposition to the surfaces of lakes may also be an important input especially for lakes in areas of high deposition (Sullivan et al. 1997). Hydrological losses from lakes have a strong influence on nitrogen in lakes with short water residence times (Ito et al. 2005). Sedimentation and denitrification are the other losses that influence lake N, but these rates are poorly known for Adirondack lakes (Ito et al. 2005).

In this study we test whether spatial variation in N deposition along with variation in the spatial configuration of land cover types within watersheds influences nitrogen loading and concentrations in lakes. We also evaluate the significance of direct N deposition to lakes relative to watershed loading. We sampled the chemistry of lakes in 252 watersheds in the Adirondack Park of New York (USA) and compiled detailed land and wetlands cover data as well as lake morphometric and hydrological data. We estimated N deposition across the region using a spatial model that incorporates the influence of elevation and land cover. We then developed and parameterized a spatially explicit, mass-balance watershed-scale model of lake total nitrogen (TN) concentrations following the general approach used in Canham et al. (2004). The model allowed us to estimate the retention of N deposition and total export from different cover types within the watersheds. We also examined whether N loading from source areas varies with distance from lakes, and as a function of the presence of wetlands along flowpaths. Finally, we considered the relative importance of hydrological losses due to flushing relative to within-lake N losses, and how these vary with lake morphometry.

Methods

Study site

The Adirondack Park of New York is a mixture of public and private lands covering 2.4 million ha. There are approximately 2750 lakes with area

>0.2 ha within the Park (Kretser et al. 1989). Much of the land in the Park (40%) is owned by the State of New York and protected from development. An equally large portion of the region is privately owned and managed for commercial forestry. Very little of the Park is developed. Forests dominate the landscape (>80% of land cover) and include areas of old growth as well as more extensive areas of second growth forest. Wetlands occupy approximately 10% of the Park and include a diversity of habitats and plant communities. There is little current agriculture and most of the landscape was never converted to agriculture. Urban areas including small towns and villages are scattered throughout the Park, but development is limited, especially outside municipal boundaries. Lakes, rivers, and streams are abundant but cover <10% of the landscape.

In the 1980s the Adirondack Lake Survey Corporation (ALSC) sampled a large number of lakes to assess acidification (Kretser et al. 1989). We selected a subset of these lakes for this study because of the availability of ALSC data on lake morphometry (lake volume and mean depth). We used these data along with estimates of runoff (Primack et al. 2000) to calculate flushing rates for the lakes. Watershed delineation and land cover data are described below.

N deposition

The Adirondack region of New York experiences elevated N-deposition due to power plant, automobile and other pollutant sources. Deposition varies geographically: high altitude and western-facing slopes are hot spots of elevated deposition, and local areas may have N-deposition 20-fold above background rates (Weathers et al. 2000, 2006, Weathers and Ponette-Gonzalez 2011).

We generated a map of estimated total (wet + dry) inorganic (nitrate and ammonium) nitrogen deposition across the region using the methods of Weathers et al. (2006), and Thomas et al. (2010).

Wet deposition.—Average annual (based on 2000–2004 data) wet inorganic nitrogen (NO_3-N and NH_4-N) deposition for the Adirondack region, and subsequently to each watershed, was calculated as the product of estimated average annual precipitation from PRISM (http://www.prism.oregonstate.edu/), based on 30 year normals (1970–2000) and kriged NO_3-N and NH_4-N chemistry from National Atmospheric Deposition Program site locations from the northeastern US (http://nadp.sws.uiuc.edu/).

Dry deposition.—Dry inorganic N deposition (HNO_3-N, particulate NO_3-N and NH_4-N) across the Adirondack region was calculated as the product of air concentrations, based on the average of 2000–2004 CASTNET air chemistry data from sites in the northeastern US, and deposition velocities based on vegetation cover, following the Clean Air Status and Trends Network (CASTNet) protocols (http://www.epa.gov/castnet/). The dry deposition velocities generated from the CASTNet data were specific to forest types (coniferous and deciduous) and leaf-off (dormant) and leaf-on (growing) seasons, where the growing season was May 16 to October 15, and the rest of the year was classified as dormant. Watershed landcover was determined as described below. High-elevation wet + dry + cloud deposition for areas >650 m was modeled as a function of elevation after the methods of Weathers et al. (2006). We note that only a few of the study lakes were located in watersheds with significant high elevation area within them (Fig. 1). For each watershed, average total annual inorganic N deposition was calculated. Hydrography data layers were used to estimate (wet only) direct deposition to lake surfaces.

Lake sampling

We sampled lakes in three separate years (2000, 2006, and 2007) to obtain a large sample of total nitrogen measurements for Adirondack lakes. A subset of lakes was sampled in two of the three years to help constrain estimates of interannual variation in nutrient loading and lake N concentrations. At each lake a mid-summer surface water sample was collected into a clean container. Samples were acidified to a pH of 2 with the addition of 300 μL of 2 N H_2SO_4 and stored for subsequent analysis. Total nitrogen (TN) was measured on unfiltered samples that were oxidized in persulfate, autoclaved, and run on an auto-analyzer. The 2000 survey was conducted from June through early September by accessing lakes near roads or via hikes. In 2006 and 2007 we sampled lakes from late June to

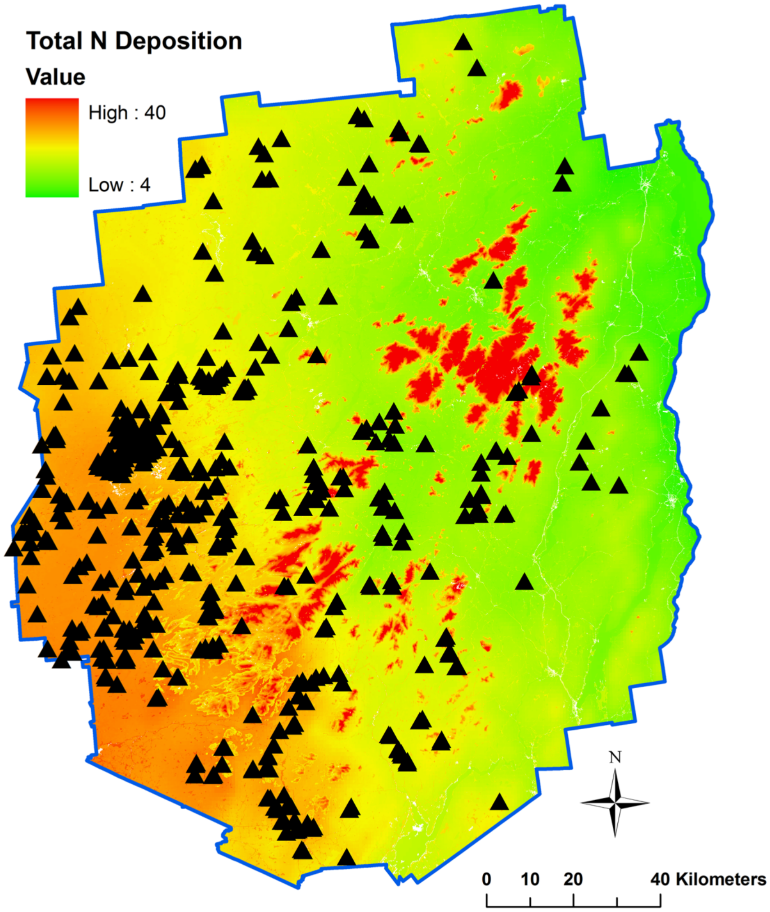

Fig. 1. Predicted total (wet + dry) inorganic N deposition (kg ha^{-1} yr^{-1}) for the Adirondack Park. Locations of the sampled lakes are indicated by triangle symbols.

early August using a float plane with sufficient power to land and take off from even very small lakes (ca. 2–4 ha). The plane substantially increased our ability to access remote lakes. We obtained additional lake samples in 2007 from a survey conducted in mid-summer by the New York State Department of Environmental Conservation. In total, the surveys provided 343 observations of TN from 252 unique watersheds. The survey lakes do not represent a random sample of available lakes for logistical reasons (e.g., not all lakes were suitable for landing a plane) and because permission to access lakes was not always available. Nonetheless, the sampled lakes encompass a wide range of watershed sizes, land cover conditions, and N-deposition.

A spatially explicit watershed analysis of lake N concentration

The analysis was designed to predict average mid-summer concentrations within individual lakes. Our approach was based on the principles of mass-balance, in which variation in lake total nitrogen (TN) concentration is a balance between total inputs to the lake, primarily from the surrounding watershed, and net losses, primarily as a result of in-lake degradation and output in lake discharge (Canham et al. 2004, 2009, Maranger et al. 2006). Inputs to the lake are assumed to be independent of in-lake concentration, while losses are assumed to be proportional to in-lake concentration. These assumptions result in a predicted steady-state concentration [TN] (in μg L^{-1}) defined by:

$$[\mathrm{TN}] = \frac{\text{inputs}}{\text{volume}\ (k + \text{flushing rate})} \quad (1)$$

where volume is lake volume, k is an estimated in-lake loss term (yr^{-1}), and flushing rate (yr^{-1}) is the lake flushing rate (Canham et al. 2004).

Losses of N are conceptually separated into (1) lake discharge and (2) within-lake losses. Loss via lake discharge is estimated from flushing rates based on data on runoff from within the immediate watershed, lake morphometry, and discharge from upstream lakes. Within-lake losses of N occur primarily as denitrification and sedimentation. Regardless of the specific processes involved, we combine their effects into a single decay constant:

$$\text{Within lake losses} = k \times \text{volume} \times [\mathrm{TN}] \quad (2a)$$

where TN is total N concentration in the lake. We also tested a variant of the model in which the in-lake decay coefficient (k) was an exponential function of lake mean depth:

$$k = k' \exp^{-\gamma \times \text{depth}}. \quad (2b)$$

Our analysis examined four major inputs of N to Adirondack lakes: (1) atmospheric deposition to the surface of the lake, (2) N carried via inflowing stream water and groundwater from wetlands, upland vegetation, and developed areas within the immediate watershed, (3) input via streams that carry N exported from upstream lakes and their associated watersheds, and (4) inputs from residential development within the immediate watershed. While there can be within-lake input of N from processes such as N fixation, we tested models that included a term that estimated an average within-lake production proportional to lake surface area, but the estimated average input was effectively zero so we dropped the term from subsequent models. Thus total input is a function of four sources,

$$\begin{aligned}\text{Inputs} = {} & \text{Lake surface N deposition} \\ & + \text{watershed inputs} + \text{upstream inputs} \\ & + \text{residential inputs}.\end{aligned} \quad (3)$$

N deposition to the surface of the lake ($\mathrm{kg\ yr^{-1}}$) was calculated from our spatially explicit estimates of total wet inorganic N deposition (described above). Watershed inputs were estimated using the spatially explicit analysis developed by Canham et al. (2004). Specifically, each watershed was subdivided into a grid of source areas of fixed size (10 × 10 m), in which each source area is classified as a discrete cover type based on vegetation. Inputs to the lake originating from a given grid cell move along flow paths that include both overland and groundwater flow, until they reach surface water (either the lake shore or streams feeding into the lakes). Our analysis does not discriminate between overland vs. groundwater flowpath segments, but instead lumps this as "ground" flow, as distinct from "stream" flowpath segments. The total lake input from these n source areas is then estimated as:

$$\text{Watershed input} = \sum_{i=1}^{n} \text{Export}_c e^{-\alpha_c D_i} \quad (4)$$

where Export_c is the export (in kg) of the ith grid cell (0.01 ha) of a given cover type c within the immediate watershed, and α_c is an estimated cover-type specific parameter that determines loss of that export as a function of distance D_i along the flowpath to the lake. We tested models using total flowpath distance to the lake or alternatively, the distance to the nearest connecting surface water (i.e., streams).

The Export_c term is a function of the estimated N deposition to the grid cell. We tested both linear and sigmoidal (logistic) relationships between N deposition and N export, but a simple linear model was the most parsimonious:

$$\text{Export}_c = a_c + b_c \text{NDep} \quad (5)$$

where NDep is the calculated annual total wet plus dry inorganic N deposition ($\mathrm{kg\ ha^{-1}\ yr^{-1}}$) to the grid cell, and a_c and b_c are parameters estimated by the analysis. Note that a_c is the estimated N export from cover type c in the absence of N deposition, and $1 - b_c$ is an estimate of the retention of atmospheric N deposition by cover type c.

Eq. 4 embodies a simple additive model of non-point inputs in which each unit area of the watershed is a potential source, and the amount of N from each source area that reaches the lake is a declining function of the distance of the source area from the lake. In this simplest model, loss along a flow path that originated from an upslope source area does not depend on the nature of the cover type that the constituent has to pass through on its way to the lake. Given the potential importance of denitrification in wetlands and saturated soils (Gold et al. 2001), we tested variants of Eq. 4 in which there was an additional loss term that was a sigmoidal function of the distance of each flowpath (D_i) that passed through a grid cell with either of the wetland cover types, or a grid cell with a topographic index (TI) > 12.5, where TI is the log of the ratio of upslope contributing area to the tangent of the slope (Beven and Kirkby 1979). TI is frequently used to identify watershed areas prone to saturated soils. In the Adirondacks, TI values of 12.5 or greater generally correspond to portions of the wetlands that showed evidence of long-term inundation.

For lakes that are downstream from other lakes, the analysis is recursive and calculates the total discharge from the headwater lakes first, and then estimates the fraction of that amount that reaches the next downstream lake, and so on down the lake chain:

$$\text{Upstream input} = \sum_{j=1}^{m} \lambda \times \text{ULE}_j \qquad (6)$$

where ULE is the upstream lake export (in kg) from $j = 1, ..., m$ immediately upstream lakes, and λ is the average proportion of upstream lake export that is not lost through processing within a stream before it reaches the next downstream lake. As in our previous work (Canham et al. 2004, Maranger et al. 2006), we have assumed that λ is independent of stream length. Note that since the analysis is recursive, inputs from lakes located further up a lake chain are already taken into account when calculating the discharge from the immediately upstream lake.

Commercial development within the park is largely clustered within villages and hamlets that were already captured in the land cover data as "developed" areas, but residential development is typically embedded within one of the upland vegetation cover types. In order to test whether there was evidence of additional input of nitrogen to the lake as a function of the density of homes and their proximity to the lake, we used tax parcel records from the New York State Office of Real Property Services and from individual counties within the Park for the year 2007 to compile data on residential development in each of the 252 watersheds. We used the parcel centroid to approximate the distance from the residence to the lakeshore. We then incorporated a term in the model in which the estimated input from residential development was a negative exponential function of that distance (dist). The total residential input to the lake was thus estimated as:

$$\text{Residential inputs} = \sum_{i=1}^{r} R_t \exp^{-\beta_t \text{dist}_{it}} \qquad (7)$$

for $i = 1, ..., r$ residential parcels in the watershed of type t, and R_t andβ_t were estimated parameters. We tested models with 3 different classifications of property types: (1) all residences combined (seasonal and year-round, single and multi-family), (2) 3 different types: seasonal residences, single family residences, and multi-family residences, and (3) the 3 residence types plus additional categories for (a) "camps" and "resort complexes" and (b) golf courses and country clubs.

Year-to-year variability in mid-summer average lake chemistry is incorporated in the model through additional terms that account for effects of interannual variability in climate and hydrology on nutrient loading and lake discharge. Years with high runoff could alter lake chemistry because of higher inputs (changes to the numerator in Eq. 1) and/or higher flushing rates (in the denominator of Eq. 1). For example, years with high mid-summer DOC concentrations were associated with higher-than-normal runoff in spring and early summer (Canham et al. 2004), indicating that the net effect of higher runoff was to increase loading (outweighing an increase in the flushing of DOC out of the lake). On this basis, we incorporated a simple term in the analysis to allow for interannual variation in total loading from within the watershed. The year 2000 was set as a benchmark, and the analysis then estimated the variation in total within-watershed loading for the 2 other years (2006 and 2007) needed to account for the observed interannual variation in lake TN concentration (Canham et al. 2004).

Combining Eqs. 1–6, at steady state:

$$[\mathrm{TN}] = \frac{\begin{array}{c}\text{Lake surface inputs} + \text{Residential inputs}\\ + \sum_{j=1}^{M} \lambda \times \mathrm{ULE}_j + \sum_{i=1}^{N} \mathrm{Export}_c e^{-\alpha_c D_i^{\beta_c}}\end{array}}{\text{volume}(k + \text{flushing rate})}. \tag{6}$$

Watershed data sources

Methods of watershed delineation, identification of stream networks, and calculation of flow paths and flowpath distances from grid cells in each watershed followed the general methods used in our previous research (Canham et al. 2004, Canham and Pace 2009). We used two primary sources of data for watershed landcover classification. The 2001 national landcover data (NLCD) were used for uplands and developed areas (Homer et al. 2007), but the Adirondacks are unique in having very high resolution maps of wetland cover produced by the Adirondack Park Agency (APA), so those data were used for wetland delineation and classification (Roy et al. 1997, Primack et al. 2000). Areas of wetland in the NLCD landcover data that were mapped as herbaceous or forested wetlands, but not mapped by APA as wetland were reclassified to either herbaceous uplands or the upland forest type surrounding them.

Based on previous analyses, we initially distinguished between 5 upland vegetation cover types, 3 upland forest types (deciduous, mixed, and coniferous forests) and upland shrub and herbaceous vegetation. The NLCD classified developed land by intensity (low, medium and high), but there was very little medium and high density development within our watersheds, so those two classes were lumped. The APA classified wetlands based on National Wetlands Inventory (NWI) techniques (Cowardin and Golet 1995) and identified the dominant and subordinate strata in each wetland, along with modifiers for hydrology and disturbance (by beavers, etc.). We lumped the wetlands into 6 main structural types: emergent marshes (EM), typically dominated by cattails and sedges; deciduous shrub swamps (DSS), dominated by speckled alder (*Alnus rugosa*) and willows (*Salix* spp.); evergreen shrub swamps (ESS), primarily bogs dominated by a variety of ericaceous shrubs or by stunted black spruce (*Picea mariana*); deciduous forest swamps (DFS), typically dominated by red maple (*Acer rubrum* L.); conifer forest swamps (CFS), dominated by red spruce (*Picea rubens*), black spruce, or balsam fir (*Abies balsamea*); and "dead tree" swamps (DTS), in which most of the canopy trees were dead, usually as a result of beaver activity (Roy et al. 1997, Primack et al. 2000). Each of these 6 wetland types was further classified into "wet" and "dry" variants based on estimated frequency and duration of flooding (Primack et al. 2000).

These procedures produced a landcover classification with at most 19 distinct cover types. Our analysis allows us to estimate nutrient loading from the different cover types within the watershed, but with the limitation that the model requires estimation of 1–3 parameters (depending on model complexity) for each defined cover type (Eqs. 4 and 5). We thus used a series of successively simpler cover type classifications (using broader groups) and relied on the principle of parsimony (using model comparison methods) to find the simplest set of different cover type groupings that was supported by the data.

Compiled watershed datasets.—We classified each 10×10 m grid cell into either a non-source area (i.e., roads) or 1 of the different wetland or upland cover types for the 252 watersheds. For each cell, we used the 10 m resolution digital elevation model to calculate flowpath distance (as above) to the lakeshore. Data from ALSC provided the lake volume and lake flushing rate (based on watershed runoff calculations) (Kretser et al. 1989).

Statistical analyses

Our analysis is a form of inverse modeling using a spatial regression in which lake N concentration is the dependent variable, and the independent variables are (1) lake volume, (2) lake flushing rate, (3) N deposition to the surface of the lake, (4) the cover type and distance from the lake for each of the grid cells in the immediate watershed, (5) the annual N deposition to each of those grid cells, (6) the fraction of the flowpath distance from the cells to the lake that passes through either wetlands or saturated soils (i.e., TI > 12.5), (7) the number, type, and distance to lake of residential homes in the watershed, and (8) the year the lake was sampled (as a categorical variable). In order to increase the

Table 1. Watershed and lake basin properties for the 252 sampled lakes.

Property	Minimum	Median	Mean	Maximum
Lake TN (μg L^{-1})	21.2	229.0	255.4	710.2
Lake surface area (ha)	0.2	14.9	25.8	272.0
Lake volume ($m^3 \times 10^6$)	0.003	0.365	1.294	40.8
Lake mean depth (m)	0.4	2.6	3.2	15.4
Flushing rate (yr^{-1})	0.2	3.2	10.5	500.4
Watershed surface area (ha)†	0.9	141.2	277.9	6573.4
Percent of watershed in wetland (%)	0.4	12.7	13.9	57.9
Percent of watershed developed (%)	0.0	0.0	0.4	16.5
Weighted N deposition (kg ha^{-1})‡	4.6	7.1	7.0	9.3

† Exclusive of lake surface area.
‡ Over entire watershed (including lake).

speed of the iterative optimization process used to estimate model parameters (see below), we calculated for each cover type in each watershed the average flowpath distance to the lake for all cells of that cover type in each of 20 distance classes. The sizes of the distance classes were chosen to provide more precise discrimination of flowpath distances near the lake (starting at 10 m intervals), and increased in size with greater distance from the lake. Thus, rather than integrate across all grid cells in each watershed (the summation terms for watershed loading in Eq. 4), we summed across the 20 distance classes, using the mean flowpath distance for grid cells in that class. We solved for the parameter estimates that maximized the likelihood of the observed lake TN concentrations, using simulated annealing, an iterative, global optimization procedure. Residuals were normally distributed, so a normal distribution was used as the likelihood function. The analysis was done with software written by L. Murphy and C. D. Canham using Delphi (Borland International).

We compared alternative models using AIC corrected for small sample size (AIC_{corr}). We calculated asymptotic 2-unit support limits (analogous to traditional 95% confidence intervals) for each of the parameters by holding all other parameters at their maximum likelihood value, and then systematically increasing or decreasing the parameter of interest until the likelihood of the resulting model had dropped by 2 units. The fit of a model was evaluated using three metrics. Bias was evaluated by fitting a linear regression (without intercept) to the observed vs. predicted N concentrations: a slope of 1 indicates an unbiased model. Overall goodness of fit was evaluated using R^2, and the predictive power of the model was evaluated using root mean squared error (RMSE).

Results

We sampled a wide range of lakes in terms of size, depth, and flushing rate (Table 1). TN varied from 21 to 710 μg L^{-1} with median and mean values of 229 and 255 μg L^{-1}, respectively. The lakes were typically embedded in heavily forested watersheds, with highly variable amounts of wetland, but little developed area. Median watershed size was 141 ha with median percent wetland cover of 13% (Table 1). Median forest cover was 87%, reflecting the mixture of preserved areas and commercial forests that are the main land uses in the region. Less than half of the watersheds had any areas classified as developed, and only 50 of the lakes had any residential development somewhere in the watershed. N-deposition averaged approximately 7 kg ha^{-1} (area-weighted mean across the watershed), and varied two-fold among the sampled watersheds, although variation within the Park as a whole, due to deposition at the highest elevation, is much greater (Fig. 1).

Comparison of alternative models of N export and loading

We compared models that differed in the cover type classification, the presence or absence of distance decay (i.e., loss of N along flow paths), passage of flowpaths through wetlands, and inclusion of terms for inputs from residential development. These models varied substantially in complexity, with models including as many as 53 and as few as 12 parameters (Table 2). The best model based on AIC_c was also the simplest—a 12

Table 2. Comparison among alternate models. Models differed in (1) number of watershed cover types, (2) whether or not watershed loading varied with flowpath distance, (3) whether or not watershed loading varied as a function of the length of a flowpath that passed through a wetland, and (4) whether or not the model included separate estimates of loading from residential development within the watershed, and if so, the number of residential development categories used in the model. We report the number of parameters in the model (excluding the variance estimate for the normally-distributed likelihood function), the AIC for the model corrected for small sample size (AIC_{corr}), the R^2 of the model, and the difference in AIC between a given model and the best model (row 1) (ΔAIC). All of the models had unbiased fits, with slopes of the relationship between observed versus predicted lake TN ranging from 0.997 to 1.017.

Model Features							
No. cover types†	Flowpath distance	Loss due to wetlands along flowpath?	Residential development types	No. parameters	AIC_{corr}	R^2	ΔAIC
3	None	No	0	12	4124.0	0.250	0.0
3	Exponential	No	0	15	4131.6	0.247	7.6
13	None	No	0	32	4158.4	0.274	34.4
13	None	No	3	38	4172.4	0.276	48.4
13	None	No	1	34	4162.2	0.276	38.2
13	None	No	5	44	4186.5	0.278	62.5
13	None	Yes	3	40	4177.0	0.277	53.0
13	None	Yes¶	3	40	4176.9	0.277	52.9
13	Exponential‡	Yes	5	53	4218.2	0.264	94.2
13	Exponential§	Yes	5	53	4203.6	0.294	79.6

† The 3 cover type models grouped the watershed into upland, wetland, and developed cover types. The 13 cover type models consisted of 5 upland types, (deciduous forest, mixed forest, conifer forest, shurbland, and herbaceous communities), 1 "developed" land cover type, an "open water" cover type, and 6 wetland cover types (emergent marshes, deciduous forest swamps, conifer forest swamps, dead tree swamps, deciduous shrub swamps, and evergreen shrub swamps).

‡ Used total flowpath distance to the nearest lakeshore.

§ Excluded length of flowpath along streams, if flowpath included a stream.

¶ Used grid cells with topographic index (TI) values $>$ 12.5, rather than cover type maps, to delimit wetlands.

parameter model consisting of three cover types (upland vegetation, wetlands, and developed areas) with no distance decay along flowpaths, no loss dependent on presence of wetlands along flowpaths, and no additional inputs specifically attributable to residential development. This model explained 25% of the variance among lake nitrogen concentrations (Table 2). The model fit was unbiased (i.e., the slope of predicted versus observed was 1). While some of the alternative models had higher R^2, the simplest model was by far the most parsimonious based on ΔAIC (Table 2). All the models had limited ability to resolve the variability in the data as evidenced by the low overall R^2 values. Despite the large unexplained variation in lake TN, the parameter estimates from the models were typically well constrained (Table 3) and provide quantitative estimates of loading that would be difficult to determine by other approaches. Note that lakes were sampled in multiple years and the terms introduced to account for interannual variation were significant, with effective loading lowest in 2000 and highest 2007.

The main utility of the analysis is in comparing models to evaluate specific alternative hypotheses about watershed control of lake nutrient concentrations. In addition, the individual parameter estimates provide a quantitative assessment of the relative importance of different processes in controlling lake TN concentration, and in assessing patterns of N transport and processing within the watershed and the lake. Estimates of export per unit area were highest for developed areas and wetlands, while upland vegetation (primarily forest) had the lowest areal export. Export increased as a function of N-deposition for uplands and developed areas but not wetlands (Fig. 2). Export at zero N-deposition was 7.1, 3.2, and 0.5 kg ha^{-1} for developed, wetland, and upland areas, respectively (Table 3). Despite their low areal export, uplands dominate the overall export of N, and therefore, the loading of N to lakes. This is simply because upland forests are by far the dominant land cover.

Subdividing land cover types for wetlands and uplands provided cover-specific loading esti-

Table 3. Maximum likelihood estimates (MLE) and 2-unit support intervals (SI) for parameters of the most parsimonious model for lake N concentration (first model in Table 2).

Parameter	MLE	Two-unit SI Lower	Upper
Upland export − intercept (a_c) (Eq. 5)	0.493	0.366	0.607
Upland export − slope (b_c) (Eq. 5)	0.132	0.116	0.146
Wetland export − intercept (a_c) (Eq. 5)	3.226	2.591	3.773
Wetland export − slope (b_c) (Eq. 5)	0.000	0.000	0.065
Developed export − intercept (a_c) (Eq. 5)	7.088	2.501	12.100
Developed export − slope (b_c) (Eq. 5)	0.055	0.000	0.705
Interannual variation − 2000†	1.000	...	...
Interannual variation − 2006	1.201	1.123	1.286
Interannual variation − 2007	1.542	1.456	1.620
Downstream loss‡	0.601	0.469	0.734
In-lake decay − k' (Eq. 2b)	2.654	2.404	2.956
In-lake decay − γ (Eq. 2b)	0.175	0.152	0.195

† Parameter estimate for year 2000 fixed at a value of 1.
‡ Fraction of upstream lake discharge.

mates. However, models that subdivided wetlands based on structural vegetation types had very wide support intervals and hence did not provide better predictions of loading. This is likely due to the small area of any given wetland type over the region, but may also reflect the possibility that vegetation structure used to classify wetlands is not a good predictor of N export. In one model analysis we categorized wetlands as intermittently wet versus permanently wet using the topographic index (TI > 12.5). This analysis was not an improvement over other approaches. Contrary to the results for different wetland types, models that subdivided uplands into 3 different forest types plus two open vegetation types (see Methods) had narrow support intervals. However, the loading from the 5 upland cover types was similar so that aggregating uplands as one cover type in the simplest model (i.e., 12 parameter model Table 2) does not result in a significant loss of information or predictive ability.

The most parsimonious models were those with no distance decay of loading from watershed source areas (Table 2). As a result, areas of the same cover type high in the watershed contribute the same amount to loading as areas low in the watershed. This result is consistent with our previous studies of DOC and iron (Canham et al. 2004, Maranger et al. 2006) where the entire watershed, not just areas nearest lakes,

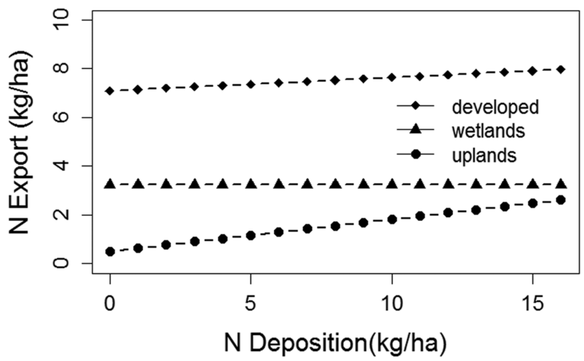

Fig. 2. Predicted nitrogen export as a function of N deposition for developed areas, wetlands, and upland source areas within the watershed.

provided source areas for export to lakes. To explore this point further, we considered if flowpaths from upland areas that passed through wetlands would show evidence of removal (or possibly enhancement) of N loading. We found no evidence for this hypothesis. We considered four different models that included this effect, and none of these proved more parsimonious than simpler models (Table 2).

We accounted for residential development in several of the models, but there was no evidence that the type, number, or distance from the lakeshore of residential development had a measurable impact on lake-N concentration (Table 2). We originally hypothesized that the density of residential development would be an indicator of the potential number of failing septic systems that might be point sources of significant loading of nitrogen. While the vast majority of the lakes have no residential development within the immediate watershed, models that included parameters for inputs specifically from residential development were not supported by the data.

Watershed retention of atmospheric N deposition

Atmospheric nitrogen that is deposited to uplands and wetlands may accumulate (e.g., in plants, soils), be lost to the atmosphere, or be lost to aquatic systems. The first two processes (accumulation or loss to the atmosphere) represent watershed retention of N. The watershed balance approach used in our analysis allowed us to estimate retention for different cover types. Retention was different between wetlands and

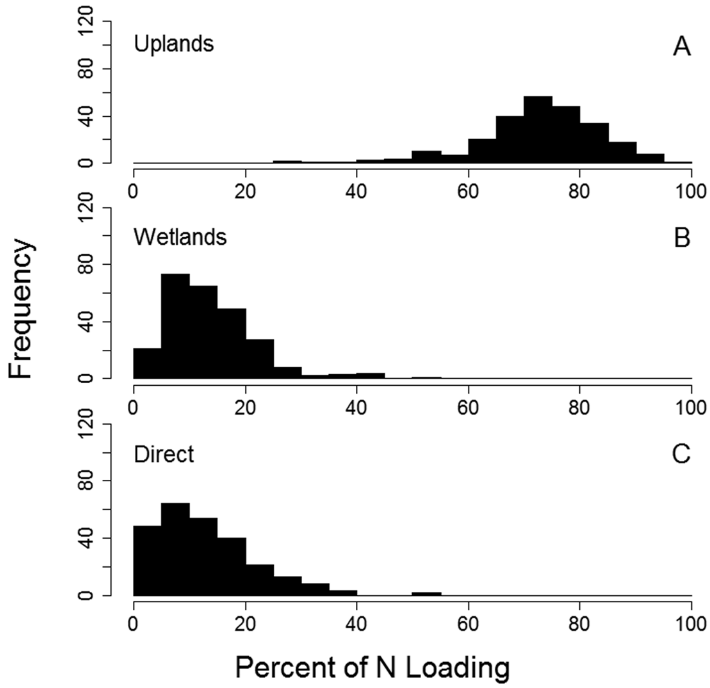

Fig. 3. Histograms of percent of N-loading to lakes from uplands, wetlands, and direct atmospheric inputs.

uplands as indicated by the slopes of the export parameters (Table 3), which are equal to one minus retention. Wetlands on average retained all deposited N (note export slope = 0) while uplands on average retained 87% of the deposited N with tight lower and upper support intervals for this estimate (Table 3). For developed areas, support intervals were very wide and so there is little precision in the estimate of 96% retention.

Aggregate sources of watershed N loading

Forest loading was the dominant source of nitrogen for nearly all lakes (Fig. 3) accounting on average for 73% of the total input. Wetlands (average 13% of total input) and direct deposition (also averaging 13% of total input) accounted for most of the balance of the inputs (Fig. 3). Direct deposition of atmospheric N was a significant source of N loading particularly for 34 lakes where direct N deposition to the lake surface accounted for 25 to 53% of total inputs (Fig. 3).

Some lakes lie downstream of other lakes, and in the analysis we accounted for N exported from upstream lakes. On average 40% of the N exported from an upstream lake was loaded to the downstream lake, with the balance lost or retained along the flow path (Table 3). We did not account for stream distance between lakes and so this estimate is averaged across the whole dataset.

In-lake processing

Nitrogen losses within lakes varied as a function of mean depth (Fig. 4). This loss represents a combination of sedimentation, ac-

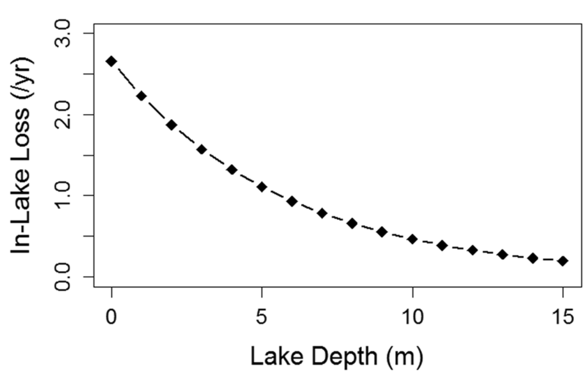

Fig. 4. Predicted in-lake losses (yr^{-1}) as a function of lake depth (m).

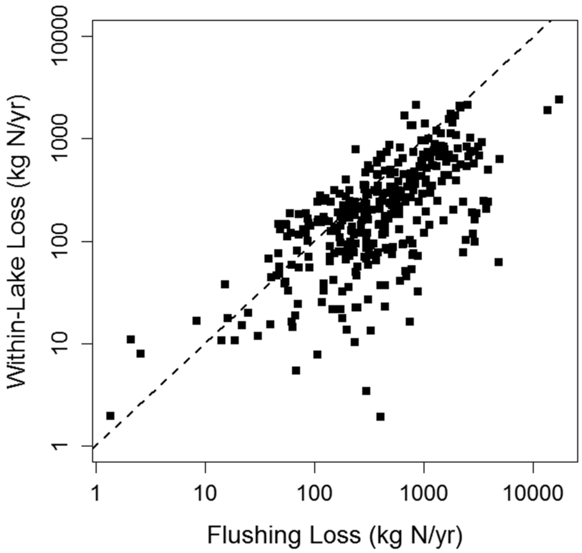

Fig. 5. Predicted N-losses from lakes due to discharge (flushing) and within lake processes (sedimentation, denitrification). Dashed line represents equal flushing and within-lake losses.

cumulation in biomass, and denitrification. Assuming that biomass accumulation for lakes near steady state is negligible, the main losses were likely sedimentation, as denitrification rates are typically low in oligotrophic lakes except under the highest levels of N-deposition (McCrackin and Elser 2010).

Hydrologic flushing losses of N were typically greater than within lake loss as indicated by the 1:1 line in Fig. 5. Most Adirondack lakes have high rates of flushing because the lakes tend to be small, shallow, stream-fed systems. Large lakes and seepage lakes have longer residence times and in these systems within-lake losses were more important.

Discussion

The spatially explicit mass-balance approach used in our study has a number of strengths and some limitations. For our approach most of the parameters are directly related to processes of interest, including watershed export from different cover types, and the nature of losses from lakes (e.g., flushing, sedimentation, denitrification). Most importantly, the analysis provides estimates of retention and export of nitrogen from cover types based on hundreds of watersheds. Hence, the parameters are robust regional estimators of wide applicability in forested landscapes with minimal development. Further, the mass balance constraints allow assessment of the most important source areas and the possible consequences of changing sources (e.g., loss of wetlands or disturbance of forests). The principal weakness of our study is that the analysis explains only a modest portion of the variance in mid-summer total nitrogen concentrations among lakes. One likely reason is that the estimates of TN for lakes are based on a single mid-summer sample so that the observations have relatively high uncertainty and may not account for important but unknown seasonal variability in TN. Multiple samples over time from within a given lake would provide an estimate of TN better suited to an analysis targeted at an annual mean. Such an analysis would be possible if variables like TN or other lake chemistry properties could be measured frequently by remote sensing or in situ devices. The potential for more frequent measures of water chemistry variables is emerging using sensors and remote sensing (e.g., Hanson 2007, Pan et al. 2011) and as spatial data become more readily available, the approach presented in our study should be widely applicable.

The modest portion of variance explained for TN also contrasts with better fits previously obtained for dissolved organic carbon (DOC) and iron using a similar approach (Canham and Pace 2009). The differences may be related to the dominance of hydrological fluxes interacting with soils in controlling organic carbon and iron loading to lakes relative to more complex uptake, transformation, and loss processes associated with nitrogen. We did not explicitly consider inputs to watersheds via nitrogen fixation or losses from watersheds via denitrification. Nitrogen fixation rates are roughly similar to N-deposition (Cleveland et al. 1999, Hurd et al. 2005). Denitrification losses are also about equal to N-fixation based on studies of forests in the region (e.g., Groffman et al. 2001). Interactions of deposition with N-fixation and denitrification are a possible source of variation among watersheds and may also be related to the low predictability of lake TN.

Among year variability was accounted for in our analysis with parameters that quantified effective interannual differences in total watershed loading (Table 2). Hydrological variability is the likely cause of these interannual differences, and we observed similar variability for DOC (Canham et al. 2004). In dry years nitrogen concentrations tend to be lower while in wet years there is greater deposition and greater flushing of the watershed that presumably leads to greater export and higher TN in lakes. We do not know the precise time scale over which variability in precipitation influences TN. For example, based on precipitation data from Lake Placid, New York, 2007 was the wettest year, but the wettest spring (season prior to sampling) was in 2000. Conducting all lake sampling in a single year would minimize this extrinsic source of variation but would fail to reveal the potential magnitude and causes of interannual variability.

A principal finding of our study, and contrary to expectation, is that the nearshore environment is neither a principal source nor sink of nitrogen to these remote lakes. Models that allowed loss of N along flow paths were never superior to simpler models that apportioned export simply as a function of cover type within the entire watershed. Further, the inclusion of parameters to describe the relative saturation of soils (i.e., the topographic index) did not improve model fits. In theory nitrate moving into saturated soils should be lost to processes like denitrification as demonstrated by numerous studies (Hill 1996, Mayer et al. 2007, Ranalli and Macalady 2010). However, this biogeochemical processing will have much less impact on total nitrogen if dissolved organic nitrogen is the principal agent of transport and downstream loading, particularly in these remote, largely undeveloped watersheds (Perakis and Hedin 2002).

Wetlands and developed areas generated the greatest export of nitrogen per unit area. These rates are approximately 7-fold (wetlands) and 14-fold (developed areas) higher than the export estimated for upland vegetation at low nitrogen deposition, with lower differences in export at higher deposition (Fig. 2). Despite lower export per unit area, forests are still the major source of nitrogen for most of the lakes, accounting for an average of 73% of total loading to the sample of lakes. And the ultimate source of nitrogen export from these forests is clearly atmospheric deposition. Consequently, there is a direct link between atmospheric deposition, the biogeochemistry of nitrogen in forests, and nitrogen concentration of lakes. This link results from the generation of dissolved organic nitrogen in forest litter and soils and the export of this material to aquatic systems. While wetlands and developed areas have high N export per unit area, for the watershed as a whole, forest processing, retention, and export are critical for controlling total N transfer to these lakes.

Most of the N deposited on the landscape is retained, based on our analysis using watershed mass balances. This result is consistent with other studies that measure N deposition to watersheds and output in streams (Weathers et al. 2000). Unfortunately, our analysis does not address whether Adirondack watersheds are becoming N saturated (Aber et al. 2003) because we do not have sufficient temporal data to document change over time. Trends for monthly samples taken by the Adirondack Lake Survey Corporation indicate that nitrate is not increasing in Adirondack lakes (Driscoll et al. 2003), providing evidence that the leakage of inorganic N from Adirondack watersheds is generally low at present. Our analysis does suggest that lakes with high watershed to lake area ratios would be most susceptible to the effects of N saturation because of the importance of N export from forests. Watershed to lake area ratios (WA:LA) ranged from 1.3 to 323, with a median of 8.6. Our analyses confirm that every area of the watershed contributes to loading, hence the range in WA:LA provides a large scope for variation in loading, with a range near 10^4 among all watersheds (Fig. 6). The spatial configuration of watersheds, for example the presence of extensive riparian wetlands, should not strongly influence total N loading to lakes unless shifts in the form of N (organic vs. inorganic) exported cause changes in biogeochemical processing along flow paths. This could happen if the export of nitrate increased.

Conceptually, in our analysis lake retention of nitrogen is equal to within-lake losses. This flux was lower than flushing in most lakes (Fig. 5). The fraction of N retained equals within-lake losses over the sum of these losses plus flushing. This fraction averaged ($\pm$1 SD) 0.35 $\pm$ 0.19. The mean and variability of these estimates are

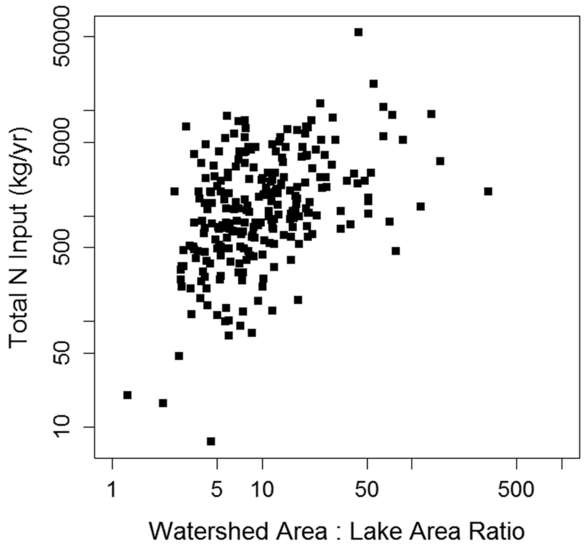

Fig. 6. Predicted total nitrogen input to the lakes versus the watershed area to lake area ratio.

similar to data summarized by Harrison et al. (2009) for temperate lakes. The pattern of within-lake loss rates among lakes (Fig. 3) was related to mean depth and is likely the result of processes that regulate similar seasonal patterns of nitrate loss in European lakes (Weyhenmeyer et al. 2007).

In summary, while there is significant variation in N deposition across the region, there is only an indirect relationship between N deposition and lake nitrogen concentrations because of differences in watershed configuration that control both inputs and losses to individual lakes. The processing and export of nitrogen from forests, rather than regional variation in total deposition, drives most of the loading of N to lakes. These inputs are balanced primarily by hydrological losses. Wetlands, developed areas, and details of flowpaths were less important than we originally expected. Although there was considerable unexplained variation, lake TN varies because of watershed size relative to lake size that affects both loading and hydrological losses. Our results are based on a spatially explicit, statistical analysis, and the modeled fluxes we estimate are those most consistent with hundreds of measured lake nitrogen concentrations. Such fluxes are difficult to quantify even for a limited number of watersheds, and provide a basis for future measurement and analysis of the relationships of terrestrial and aquatic ecosystems under elevated nitrogen deposition.

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