Biogeochemistry (2005) 72: 283–314
DOI 10.1007/s10533-004-0361-1

Nitrogen input–output budgets for lake-containing watersheds in the Adirondack region of New York

MARI ITO[1,]*, MYRON. J. MITCHELL[1], CHARLES T. DRISCOLL[2] and KAREN M. ROY[3]
*[1]State University of New York, College of Environmental Science and Forestry, Syracuse, NY 13210-2877; [2]Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY 13244; [3]New York State Department of Environmental Conservation, Adirondack Lakes Survey Corporation, Ray Brook, NY 12977; *Address for correspondence (e-mail address: mito@mailbox.syr.edu; phone: +1-315-470-6916; fax: +1-315-470-6996)*

Received 23 December 2002; accepted in revised form 8 April 2004

Key words: Acid rain, Adirondack region, Atmospheric deposition, Budget analysis, Lakes, Nitrogen, Nitrogen retention, Watersheds

Abstract. The Adirondack region of New York is characterized by soils and surface waters that are sensitive to inputs of strong acids, receiving among the highest rates of atmospheric nitrogen (N) deposition in the United States. Atmospheric N deposition to Adirondack ecosystems may contribute to the acidification of soils through losses of exchangeable basic cations and the acidification of surface waters in part due to increased mobility of nitrate (NO_3^-). This response is particularly evident in watersheds that exhibit 'nitrogen saturation.' To evaluate the contribution of atmospheric N deposition to the N export and the capacity of lake-containing watersheds to remove, store, or release N, annual N input–output budgets were estimated for 52 lake-containing watersheds in the Adirondack region from 1998 to 2000. Wet N deposition was used as the N input and the lake N discharge loss was used as the N output based on modeled hydrology and measured monthly solute concentrations. Annual outputs were also estimated for dissolved organic carbon (DOC). Wet N deposition increased from the northeast to the southwest across the region. Lake N drainage losses, which exhibited a wider range of values than wet N deposition, did not show any distinctive spatial pattern, although there was some evidence of a relationship between wet N deposition and the lake N drainage loss. Wet N deposition was also related to the fraction of N removed or retained within the watersheds (i.e., the fraction of net N hydrologic flux relative to wet N deposition, calculated as [(wet N deposition minus lake N drainage loss)/wet N deposition]). In addition to wet N deposition, watershed attributes also had effects on the exports of NO_3^-, ammonium (NH_4^+), dissolved organic nitrogen (DON), and DOC, the DOC/DON export ratio, and the N flux removed or retained within the watersheds (i.e., net N hydrologic flux, calculated as [wet N deposition less lake N drainage loss]). Elevation was strongly related with the lake drainage losses of NO_3^-, NH_4^+, and DON, net NO_3^- hydrologic flux (i.e., NO_3^- deposition less NO_3^- drainage loss), and the fraction of net NO_3^- hydrologic flux, but not with the DOC drainage loss. Both DON and DOC drainage losses from the lakes increased with the proportion of watershed area occupied by wetlands, with a stronger relationship for DOC. The effects of wetlands and forest type on NO_3^- flux were evident for the estimated NO_3^- fluxes flowing from the watershed drainage area into the lakes, but were masked in the drainage losses flowing out of the lakes. The DOC/DON export ratios from the lake-containing watersheds were in general lower than those from forest floor leachates or streams in New England and were intermediate between the values of autochthonous and allochthonous dissolved organic matter (DOM) reported for various lakes. The DOC/DON ratios for seepage lakes were lower than those for drainage lakes. In-lake processes regulating N exports may include denitrification, planktonic depletion, degradation of DOM, and the contribution of autochthonous DOM and the influences of in-lake processes were also reflected in the relationships with hydraulic retention time. The N fluxes removed or stored within the lakes substantially varied among the lakes. Our analysis demonstrates that for these northern temperate lake-containing watershed ecosystems, many factors, including atmospheric N deposition, landscape features, hydrologic flowpaths, and retention in ponded waters, regulated the spatial patterns of net N hydrologic flux within the lake-containing watersheds and the loss of N solutes through drainage waters.

Introduction

There is considerable scientific, policy, and management interest in the transport and fate of nitrogen (N) in the environment due to high N deposition, elevated concentrations of N in surface waters, and undesirable effects on the environment. Lake-containing watersheds in the Adirondack region of New York are highly sensitive to acidic deposition with an acid neutralizing capacity (ANC) < 50 μeq l^{-1}, defined as being sensitive to inputs of strong acid (Driscoll et al. 2001). A synoptic survey conducted in the mid 1980s showed that 26% of the 1469 lakes surveyed with the surface area greater than 0.5 ha had negative ANC values (Kretser et al. 1989). The emissions of sulfur dioxide (SO_2) have decreased since 1973 after the 1970 Amendments to the Clean Air Act, while emissions of nitrogen oxides (NO_X) have remained essentially unchanged since 1980 (Driscoll et al. 2001). Atmospheric N deposition to sensitive ecosystems may contribute to the acidification of soils through losses of exchangeable nutrient cations, the acidification of surface waters associated with increases in nitrate (NO_3^-) (Aber et al. 1998; Fenn et al. 1998; Driscoll et al. 2001) and coastal eutrophication (Howarth et al. 1996). For forest ecosystems, these changes are presumably related to 'N saturation,' a hypothesized condition in which the availability of N exceeds the plant and microbial nutritional demand for N (Aber et al. 1989; Stoddard 1994). Thus, watershed N mass balances characterize N inputs and help assess the extent to which atmospheric N deposition is retained/lost from lake-containing watershed ecosystems.

The N exports from, and the N removal or retention within, the lake-containing watersheds may also be influenced by factors other than atmospheric N deposition. A review of N input–output budgets for 24 forested watersheds in the northeastern US found that characteristics such as hydrology, vegetation type, and landuse history affect the losses of dissolved inorganic nitrogen (DIN) and may markedly alter relationships between atmospheric N inputs and N outputs through drainage waters (Campbell et al. 2004). Land cover patterns (e.g., Prepas et al. 2001; Tufford et al. 1998) and watershed characteristics (e.g., D'Arcy and Carignan 1997; Gergel et al. 1999; Clow and Sueker 2000) have been used to predict concentrations or fluxes of N solutes or dissolved organic carbon (DOC) in surface waters. For example, wetland or peat cover reduces NO_3^- (McHale et al. 2000; Chapman et al. 2001) through denitrification and increases DOC drainage loss (Eckhardt and Moore 1990; Dillon and Molot 1997). Forest wetlands have elevated NH_4^+ in drainage waters in autumn (Johnson et al. 1997). The shrub wetland sites in the Adirondack region where nitrogen-fixing species speckled alder, *Alnus incana* ssp. *rugosa*, was present in high density showed the accumulation of NO_3^- in groundwater, suggesting the importance of this alder species in N cycles (Kiernan et al. 2003). Net N mineralization (Vitousek and Melillo 1979) and nitrification (Ohrui et al. 1999) were found to be higher in deciduous forests than coniferous forests, thus higher NO_3^- losses would be likely to be seen in deciduous forests. The increases in NO_3^- loss with increasing elevation could be expected due to steeper slope or shallower soils at higher elevations. The changes in-lake water chemistry with elevation corresponded with temperature, vegetation biomass, and soil depth and maturity in alpine, subalpine, and forested zones (Larson et al. 1999). For DOC, the fluxes have been shown to be higher in watersheds dominated by coniferous versus deciduous forests (Hope et al. 1994), and also related to watershed area (Wolock et al. 1997) and the drainage ratio (watershed area/lake area (WA/LA)) (Kortelainen 1993). The interrelationship found among slope, vegetation, and surficial geology and their relationships with surface water chemistry (Clow and Sueker 2000) suggest that a combination of multiple watershed attributes could influence surface water chemistry. Further, the concentrations or fluxes of N solutes and DOC can be altered within ponded waters. The N removal or retention increases with increasing hydraulic residence time in lakes or rivers (Kelly et al. 1987; Howarth et al. 1996; Nixon et al. 1996; Dettman 2001) and denitrification plays an important role in this N removal process (Kelly et al. 1987; Seitzinger 1987). In comparison with drainage lake-watersheds, the contributions of atmospheric N deposition or inflow from wetlands are expected to be more important in seepage lake-containing watersheds and the seepage lake-containing watersheds may respond to atmospheric N deposition differently in addition to the effect of differences in hydraulic residence time.

For dissolved organic matter (DOM), the C/N ratio may help characterize its sources (e.g., Wetzel 2001). The C/N ratios in stream water are generally lower (e.g., Qualls and Haines 1991; Goodale et al. 2000; Lovett et al. 2000) than the ratios in forest floor leachates (e.g., Qualls and Haines 1991; McDowell et al. 1998). Similarly, the autochthonous DOM was lower in C/N ratio than the allochthonous DOM reported for various lakes (Wetzel 2001). The C/N ratios could be also used as an indicator of N status associated with N saturation (Campbell et al. 2000) based on the observations in which the C/N ratio decreased with increasing N or NO_3^- output in streams (Campbell et al. 2000) and in soils and soil solutions (Gundersen et al. 1998).

The objectives of this study were to exhibit the spatial pattern of N drainage losses from 52 forested lake-containing watersheds in comparison with the pattern of wet N deposition and to evaluate the response of the lake-containing watersheds to atmospheric N deposition in the Adirondacks. In this study, the following hypotheses were evaluated: (a) atmospheric N deposition is an important regulator of surface water N chemistry, although it is not the sole determinant of N loss in the region, therefore, higher N drainage losses are found in the southwestern Adirondacks due to elevated wet N deposition; (b) the losses of N solutes and DOC are also influenced by watershed attributes: (b1) wetlands contribute to dissolved organic nitrogen (DON) and DOC, while they mitigate NO_3^- loss, (b2) NO_3^- loss increase with increasing elevation, which may reflect gradients of temperature, slope, vegetation, or soil and geological characteristics and depth, and (b3) NO_3^- loss is higher in watersheds covered with larger deciduous forest area, while DOC loss is greater in watersheds with larger coniferous forest area; and (c) the quality of DOM is altered and the DOC/DON ratio decreases with the influences of wetlands and in-lake processes. In the Adirondack region, deciduous forests include northern hardwoods, such as yellow birch (*Betula alleghaniensis*), American beech (*Fagus grandifolia*), and sugar maple (*Acer saccharum*) and coniferous forests typically include red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and paper birch (*Betula papyrifera*).

To evaluate those hypotheses, wet N deposition was estimated as the N input and the lake N drainage loss as the N output in the 52 lake-containing watersheds in the Adirondack region from 1998 to 2000. Net N flux removed or retained within the lake-containing watershed or 'net N hydrologic flux' was calculated as wet N deposition less than the lake N drainage loss. Net N hydrologic flux includes N fixation and biotic uptake of N, abiotic N retention, and gaseous losses via nitrification and denitrification. Nitrogen chemical species examined include NO_3^- and NH_4^+ in both wet deposition and discharges and DON in discharge. The drainage losses of DOC were also calculated to better understand the relationships between DOC and DON drainage losses. Further, the influence of in-lake processes was evaluated by estimating the NO_3^- fluxes draining into the lakes, excluding the influence of in-lake process, and the NO_3^- removed or retained within the lakes, using the model of Kelly et al. (1987). Relationships with land cover (wetland cover with vegetation-based classification and forest type), and simple watershed variables (elevation, WA), were examined as possible factors that could influence the NO_3^- fluxes draining into the lakes, excluding the influence of in-lake processes, as well as the lake N drainage losses of N solutes and DOC and the net N hydrologic fluxes. The definitions of the land cover and forest type classes are explained in the Methods section.

Methods

Study sites

Nitrogen input–output budgets were developed for 52 lake-containing watersheds in the Adirondack region of New York, which is situated between 43°N and 45°N and between 73°W and 76°W over an elevation range from 380 to 880 m (Figure 1; Table 1). These lakes have been studied under the Adirondack long-term monitoring (ALTM) Program, which was started in 1982 with the sampling of 17 lakes (Driscoll et al. 1991) and increased to 52 lakes in 1992 (Driscoll et al. 2003). A variety of lakes are sampled in the ALTM program, including drainage and seepage, clearwater and colored, high ANC and acidic lakes. Four lake-containing watersheds that had previously been limed (i.e., $CaCO_3$ addition), Barns Lake, Little Clear Pond, Little Simon Pond, and Woods Lake, were included in our analysis because these sites did not show distinctive differences in N losses, compared with the remainder of the watersheds.

The humid continental climate in the Adirondacks is represented by precipitation that varies spatially with its increasing quantity from the northeast to the southwest. The bedrock geology in the Adirondacks is mainly gneisses and metasedimentary rocks with marble and other calcite bearing bedrock in a few scattered locations, mostly to the east (Driscoll et al. 1991). Mantled glacial till forms the geology of the mountains and uplands, thinner in the upslope and gradually thicker toward the valleys. The surficial geology at lower elevations often includes glacial meltwater deposits of stratified sand and gravel. The soils in the Adirondacks are primarily Spodosols and are generally shallow and acidic, especially in the organic-rich upper horizons (Driscoll et al. 1991). The lake-containing watersheds are predominantly forested. Northern hardwoods

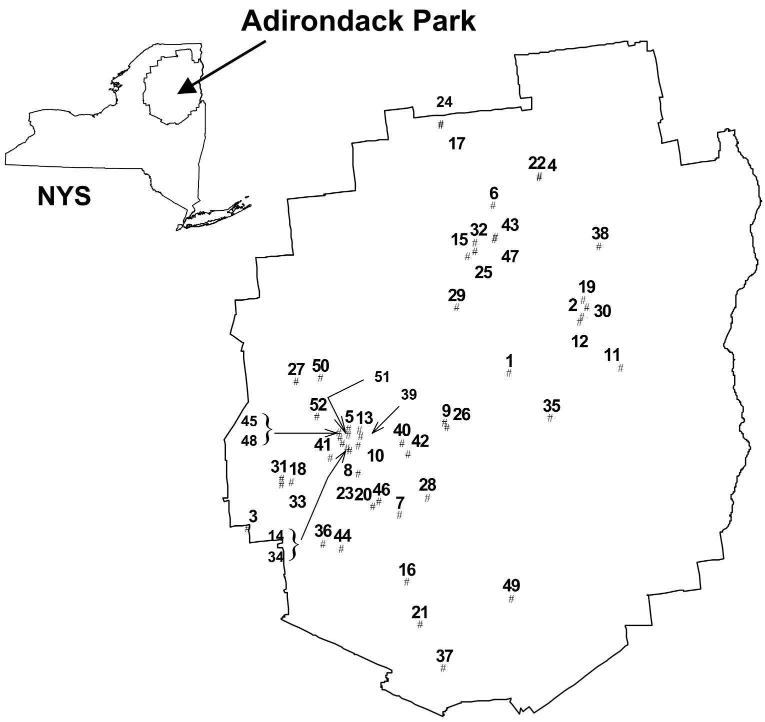

Figure 1. The locations of 52 lake-containing watersheds in the Adirondack Park, New York. The numbers correspond to the site numbers in Table 1.

Table 1. The locations and elevations of the Adirondack lake-containing watersheds examined in this study. The site numbers correspond to the locations shown in Figure 2

		Latitude (N)			Longitude (W)			Elevation
Site No.	Pond Name	Degree	Minute	Second	Degree	Minute	Second	Meter
1	Arbutus Lake	43	59	00	74	15	0	530
2	Avalanche Lake	44	7	51	73	58	13	873
3	Barnes Lake[a]	43	33	52	75	13	36	396
4	Big Hope Pond	44	30	43	74	7	30	522
5	Big Moose Lake	43	50	0	74	50	60	635
6	Black Pond	44	26	12	74	18	5	498
7	Brook Trout Lake[b]	43	36	0	74	39	45	722
8	Bubb Lake[b]	43	46	29	74	50	49	553
9	Carry Pond [a]	43	50	54	74	29	21	649
10	Cascade Lake[b]	43	47	21	74	48	46	553
11	Clear Pond	43	59	38	73	49	40	583
12	Lake Colden	44	7	9	73	58	59	842
13	Constable Pond[b]	43	49	50	74	48	27	582
14	Dart Lake	43	47	36	74	52	16	536
15	East Copperas Pond	44	18	43	74	22	20	479
16	G Lake	43	25	5	74	38	10	619
17	Grass Pond (a)[a]	44	39	26	74	29	54	384
18	Grass Pond (b)[b]	43	41	25	75	3	54	546
19	Heart Lake	44	10	47	73	58	3	661
20	Indian Lake[b]	43	37	24	74	45	44	654
21	Jockeybush Lake	43	18	8	74	35	9	599
22	Little Hope Pond	44	30	57	74	7	31	521
23	Limekiln Lake[b]	43	42	48	74	48	47	576
24	Little Clear Pond[a]	44	39	38	74	29	53	408
25	Little Echo Pond[a]	44	17	60	74	24	0	481
26	Long Pond	43	50	15	74	28	50	570
27	Loon Hollow Pond[b]	43	57	41	75	2	43	607
28	Lost Pond[b]	43	38	48	74	33	30	584
29	Little Simon Pond	44	9	42	74	26	36	545
30	Marcy Dam Pond	44	9	32	73	57	11	715
31	Middle Branch Lake[b]	43	41	52	75	6	8	494
32	Middle Pond	44	20	13	74	22	19	484
33	Middle Settlement Pond[b]	43	41	2	75	5	60	526
34	Moss Lake[b]	43	46	52	74	51	11	536
35	Nate Pond	43	51	33	74	5	36	614
36	North Lake[b]	43	31	22	74	56	53	555
37	Otter Lake	43	10	60	74	30	0	535
38	Owen Pond	44	19	23	73	54	12	515
39	Queer Lake	43	48	49	74	48	25	597
40	Raquette Lake Reservoir	43	47	42	74	39	5	570
41	Lake Rondaxe	43	45	23	74	54	59	524
42	Sagamore Lake	43	45	57	74	37	43	580
43	Sochia Pond[a]	44	21	8	74	17	41	500
44	South Lake[b]	43	30	35	74	52	37	615
45	Squash Pond[b]	43	49	32	74	53	11	648
46	Squaw Lake[b]	43	38	10	74	44	20	645
47	Sunday Pond[a]	44	20	41	74	18	2	485

Table 1. Continued.

		Latitude (N)			Longitude (W)			Elevation
Site No.	Pond Name	Degree	Minute	Second	Degree	Minute	Second	Meter
48	West Pond[b]	43	48	41	74	53	0	585
49	Willis Lake	43	22	17	74	14	47	397
50	Willys Lake[b]	43	58	20	74	57	20	630
51	Windfall Pond[b]	43	49	00	74	50	60	601
52	Woods Lake[b]	43	52	00	74	58	0	678

([a]indicates a seepage lake; the lake without a is a drainage lake; [b]indicates a lake-containing watershed for which the analysis was performed using special data, including the data of vegetation-based classification available on a finer scale.)

compose approximately one half of the forest vegetation, including yellow birch (*B. alleghaniensis)*, American beech (*F. grandifolia*), and sugar maple (*A. saccharum*). At higher elevations above 650–800 m, red spruce (*P. rubens*) and balsam fir (*Abies balsamea*) with paper birch (*Betula papyrifera*) are common (Adirondack Ecological Center 1997). The trees in many stands were 50–70 years old with old-growth forests containing trees of 200–400 years old (Driscoll et al. 1991). Wetlands constitute about 14% of the land surface of the Adirondacks (Roy et al. 1996). Most wetlands are forested, while non-forested wetlands include bogs, fens, and open marshes.

Sampling and chemical analyses

Lake surface water samples were collected monthly at or near the outlets of the 52 ALTM lakes from 1998 to 2000 and maintained at 1 °C until analyzed for nitrate (NO_3^-) by ion chromatography, ammonium (NH_4^+) by a Wescan ammonium analyzer or colorimetric automated phenate, total N by persulfate digestion, and DOC by ultraviolet promoted persulfate oxidation. The concentration of DON was calculated as the difference between the concentrations of total N and DIN (NO_3^- plus NH_4^+).

Mass balance and other calculations

Annual input–output budgets were calculated for total N, NO_3^-, and NH_4^+ from 1998 to 2000. Annual outputs were also calculated for DON and DOC. Here, we consider only wet deposition of NO_3^-–N and NH_4^+–N as the input in our input–output analyses. The input was calculated by multiplying the precipitation amount by ion concentration in precipitation. Other forms of atmospheric N deposition, including gas or vapor, aerosol, and cloud droplet, and the deposition of organic compounds could be also important contributors to total atmospheric deposition. At one of the Adirondack lake-containing watersheds (Arbutus lake-containing watershed) in the Huntington Wildlife Forest (HWF) in the central Adirondacks, estimated dry and organic N deposition accounted for approximately 28 and 24% of total N deposition, respectively (calculated from Park et al. 2003). The spatial pattern of dry deposition is generally complex and difficult to characterize (Clarke et al. 1997). Although high-elevation forests may receive elevated atmospheric deposition as precipitation, cloud droplets, and aerosols due to orographic effects and the forest canopy (Miller and Friedland 1999), few studies have reported cloud and fog deposition (Weathers et al. 1988; Anderson et al. 1999). Organic N deposition, including both DON and particulate organic N (PON), could constitute 7–80% of the total N deposition in terrestrial and coastal ecosystems (Neff et al. 2002) likely with a reduced contribution of the dissolved organic fraction if PON was excluded. However, there have been few studies on atmospheric deposition of organic N, and differences in analytical approaches, sampling protocols, and sample treatment after collection (Cornell et al. 2003) make evaluation of this input difficult. The focus of our study on atmospheric N deposition was thus set as above, considering the presently available information and the uncertainty associated with possible contributions of other N components to atmospheric deposition in the region. Therefore, our estimates of atmospheric N deposition should be regarded as the lower limits. Accordingly, those of N fluxes removed or stored in the watersheds as proportions of N inputs could be viewed as the upper limits of those proportions.

Precipitation amounts and the NO_3^- concentrations in precipitation were estimated by adjusting the data from the HWF, a National Atmospheric Deposition Program/National Trends Network (NADP/NTN) site, located in the central Adirondacks, using the empirical models of Ito et al. (2002). These models were specifically developed for the Adirondack region, based on the geographic location and elevation as independent variables. Compared with the measured values, the empirical models had adjusted R^2 ranging from 0.14 (August) to 0.73 (January) for precipitation and in the range between 0.76 (January–March) and 0.995 (April–June) for the NO_3^- concentrations. The NH_4^+ concentrations were estimated using the measured data from the HWF since there was no specific spatial pattern for NH_4^+ over the Adirondacks (Ito et al. 2002). The drainage loss was calculated by multiplying the discharge by solute concentration in-lake water. Discharge rates were estimated using a hydrologic simulation model, BROOK90 (Federer 2001), which was developed for small, forested watersheds. This model was previously used to estimate the water flux in the gauged Arbutus lake-containing watershed in the central Adirondacks, for which standard deviations on a daily basis, daily relative root mean squared error, and overall mean bias error were 2.47, 2.88 and −0.073, respectively (Mitchell et al. 2001a). These values were comparable with the results from the Hubbard Brook Experimental Forest (White Mountains, New Hampshire) for which the model was originally developed (Mitchell et al. 2001a). For the analyses in our study, separate simulations were made for individual watersheds using the inputs of daily precipitation and minimum and maximum temperatures estimated from the measured daily weather data at the HWF adjusted by the empirical models of Ito et al. (2002). Such estimates are most appropriate for the drainage lakes in our study. This approach was also used to estimate hydrologic solute losses for seepage lakes although we recognized that these systems would be highly influenced by groundwater solute fluxes. The monthly fluxes of NO_3^-, DON and DOC, which were a product of calculated monthly discharge values (the sum of daily simulated values) and measured monthly concentrations, were summed to obtain annual values. These annual values were used to show broad spatial patterns of N budgets across the Adirondacks and also to examine the role of specific watershed attributes in affecting N drainage losses, N removal or storage in the watersheds, and NO_3^- draining into the lakes. As summarized by Campbell et al. (2004), while gaseous N flux on the small watershed scale is difficult to measure due to a large spatial variability within watersheds and problem associated with measurement methodology, N fixation and denitrification were thought to be negligible relative to drainage losses in small basins. Therefore, for the N budgets, the input was wet deposition of NO_3^- and NH_4^+ and the output was the sum of the drainage losses of NO_3^-, NH_4^+, and DON from the lake. Net N flux removed or retained in the lake-containing watershed or 'net N hydrologic flux' was calculated by subtracting the lake N drainage loss from wet N deposition. The fraction of net N hydrologic flux was the fraction of wet N deposition removed or retained within the lake-containing watershed relative to wet N deposition and calculated as (net N hydrologic flux/wet N deposition). Water flux is reported in cm yr^{-1} and chemical fluxes including wet deposition, drainage loss, net hydrologic flux, and flux draining into the lake are in mol ha^{-1} yr^{-1} .

Hydraulic residence time was calculated by dividing the total lake volume by mean annual runoff. In-lake processes may be important in those lakes with extended hydrologic residence time. The evaluation of in-lake processes requires intensive work, making difficult the comparison of multiple sites across a wide region. Since N fixation is light-dependent and N fixers migrate vertically during a day and are subject to wind rafting (Levine and Lewis 1984; 1985; Lewis and Levine 1984), N fixation varies in a day, over time, and spatially in a single lakes as well as on a larger scale. While we do not have detailed data explaining N fixation within each of these lakes, planktonic N-fixation in lakes is generally low in lakes with low or moderate productivity (Wetzel 2001). N loss by denitrification was found to exceed the input of N by fixation, when both processes were measured (Seitzinger 1988), although few lakes were assessed for denitrification. Considering these issues, the importance of in-lake processes for NO_3^- was evaluated using the model of Kelly et al. (1987), which was originally developed in part for the Adirondack lake-containing watersheds. Based on this approach, we estimated the NO_3^- removed within the lakes and the NO_3^- fluxes flowing from the watershed drainage area into the lakes, calculated as the sum of the NO_3^- fluxes draining out of the lakes and the NO_3^- removed within the lakes.

The spatial maps of wetlands (with vegetation-based classifications, as explained below), land cover (deciduous, mixed, coniferous forests, deciduous forest with open canopy, open with vegetation, open), and the boundary of the Adirondack Park were obtained from the Adirondack Park Agency (Roy et al. 1997). The land cover data were based on Landsat thematic mapper (TM) data. Deciduous forest was defined as the area dominated by trees where 75% or more of the tree species shed foliage simultaneously in response to seasonal change. Coniferous forest was defined as the area dominated by trees where 75% or more of the tree species maintain their leaves all year and canopy is never without green foliage. Mixed forest was defined as the area dominated by trees where neither deciduous nor coniferous species represent more than 75% of the cover present. Wetlands were defined as the areas where the soil or substrate is periodically saturated with or covered with water. Shrubland was defined as the area characterized by natural or semi-natural woody vegetation with aerial stems, generally less than 6-m tall, with individuals or clumps not touching to interlocking, which include coniferous and deciduous species of true shrubs, young trees, and trees or shrubs that are small or stunted. The classification of wetlands was made according to the National Wetlands Inventory techniques (Cowardin et al. 1979) on aerial photography overlay (Roy et al. 1996). Most commonly identified wetland cover types (with representative plant species in parentheses) were emergent marsh (cattail, grasses, sedges), alder/willow (speckled alder, willow), broad-leaved and needle-leaved deciduous scrub/shrub (speckled alder, willow, eastern larch), broad-leaved and needle-leaved coniferous scrub/shrub (leatherleaf, black spruce), broad-leaved and needle-leaved deciduous forested (red maple, eastern larch), and needle-leaved coniferous forested (balsam fir, red or black spruce) wetlands (Roy et al. 1996). For 20 lake-containing watersheds for which spatial data of wetland types with detailed vegetation-based classification on a finer scale (1:24,000) were available (marked in Table 1), watershed boundaries were delineated using the US Geological Survey digital elevation models with a pixel width of 10 m by external computation based on the flow accumulation values calculated by TARDEM (Tarboton 2000) and were used for the examination of possible relationships of the export and removal/retention of N and DOC with land cover and wetlands. The proportion of watershed area occurring as the respective land cover or wetland type was expressed by percentage. The spatial data were processed in Arc/Info version 8.0.2 and ArcView version 3.2 (Environmental Systems Research Institute, Inc.).

Univariate linear regression and correlation analyses were applied to examine possible influences on the drainage losses of N and DOC and NO_3^- draining into the lakes of wet N deposition as well as landscape (elevation, watershed area) and land cover (e.g., deciduous, mixed, coniferous forest, wetland area) factors and correlations between the factors. Stepwise linear regression analyses were also employed to test any combined effects of factors. For wetland area, stepwise regression analyses were applied separately with different levels of classification: (a) total wetland area or the area of different wetland types based on ‘ classification (i.e., (b) forested and scrub/shrub wetland area; (c) deciduous scrub/shrub, coniferous scrub/shrub, deciduous forested wetland, and coniferous forested wetland area, and (d) emergent marsh, wetland with N-fixing species, other deciduous scrub/shrub wetland, needle-leaved coniferous scrub/shrub wetland, deciduous and coniferous forested wetland area). However, the stepwise regression analyses showed either similar regression relationships as univariate linear regression analyses or exhibited no significant relationships. Thus, the results of univariate regression analyses are emphasized as they provided useful information on the major influencing factors. Statistical analyses were conducted using SAS (SAS 1994).

Results and Discussion

Nitrogen budgets and atmospheric N deposition

The mean annual precipitation to the 52 Adirondack lake-containing watersheds, estimated based upon the models of Ito et al. (2002), ranged between 103 and 125 cm yr^{-1}, with values increasing from the northeast to the southwest and with elevation (Figure 2a). Estimated discharge ranged from 63 to 87 cm yr^{-1} and reflected the spatial pattern of precipitation (Figure 2b). The modeled water yield did not vary markedly among the lake-containing watersheds, ranging between 61 and 69% of the precipitation input. Thus, the variability in water fluxes did not account for any major differences in N export and retention in these Adirondack lake-containing watersheds.

The estimated wet N deposition varied from 288 to 396 mol N ha^{-1} yr^{-1} (mean: 349 mol N ha^{-1} yr^{-1}) in the 52 lake-containing watersheds, with values increasing from the northeast to the southwest and with elevation (Figure 2c; Table 2). The wet NO_3^- deposition was between 191 and 284 mol N ha^{-1} yr^{-1} (mean: 244 mol N ha^{-1} yr^{-1}), representing 67–73% of the wet N deposition (mean: 70%). The wet N deposition was near or above the threshold value of wet N (NO_3^- + NH_4^+) deposition of 300 mol N ha^{-1} yr^{-1} (or eq ha^{-1} yr^{-1} as reported) which Stoddard (1994) suggested may initiate substantial watershed losses of N. Since the wet N deposition values below this threshold (288–297 mol N ha^{-1} yr^{-1}) at six sites were close to the threshold value, it would not be possible to determine whether there is a distinct level of wet deposition below which N saturation will not occur in the Adirondack watersheds. These six low deposition sites had the mean lake N drainage loss of 255 mol N ha^{-1} yr^{-1} (ranging from 206 to 323 mol N ha^{-1} yr^{-1}), which was only slightly lower than the mean value (270 mol N ha^{-1} yr^{-1}, seen as below) for all lake-containing watersheds.

The lake N drainage losses had a much wider range (between 120 and 478 mol N ha^{-1} yr^{-1}, mean: 270 mol N ha^{-1} yr^{-1}) than the wet N deposition, and did not exhibit a distinct spatial pattern Figure 2d; Table 2). The N solute losses from the seven seepage lakes (marked in Tables 1, 2, and 5) ranged from

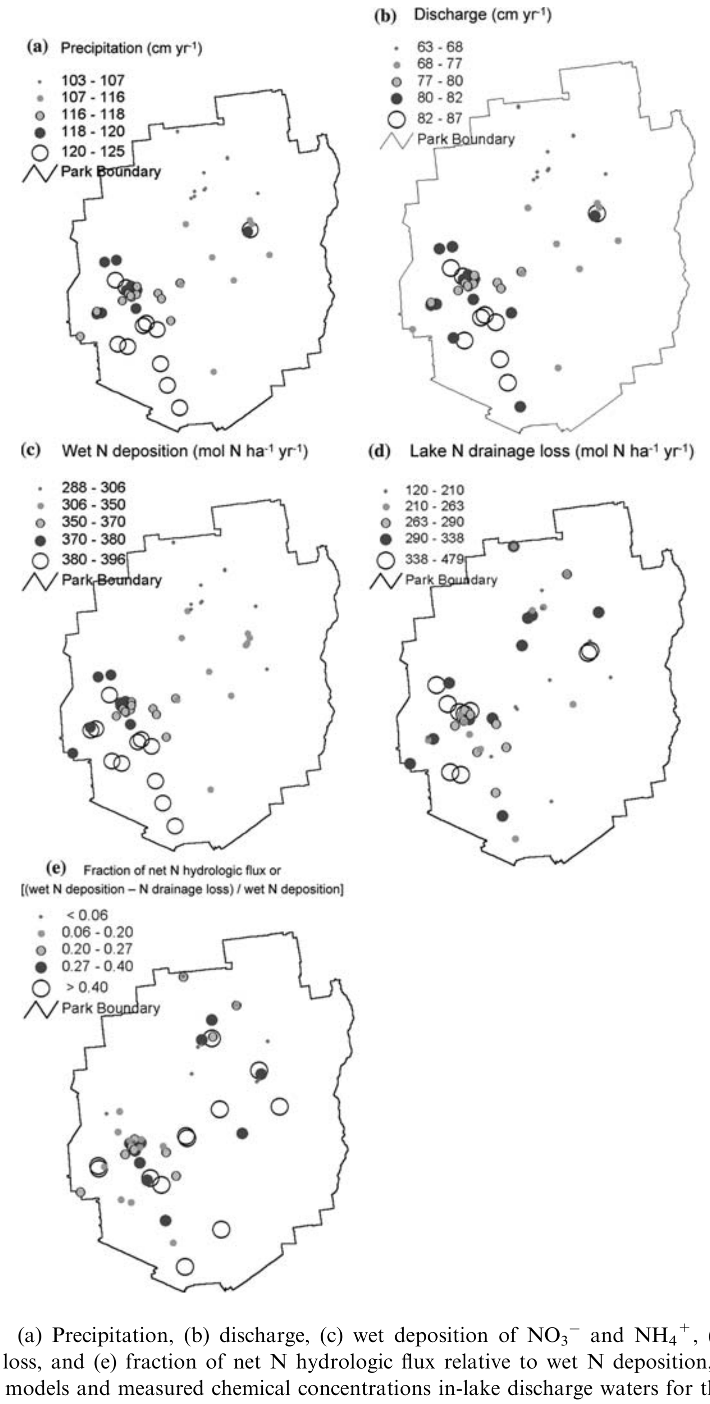

Figure 2. (a) Precipitation, (b) discharge, (c) wet deposition of NO_3^- and NH_4^+, (d) lake N drainage loss, and (e) fraction of net N hydrologic flux relative to wet N deposition, estimated based on models and measured chemical concentrations in-lake discharge waters for the Adirondack lake-containing watersheds.

154 to 313 mol N ha^{-1} yr^{-1}, with a mean value of 242 mol N ha^{-1} yr^{-1} (Table 2), which was slightly lower than the average for all the 52 lake-containing watersheds. As summarized in Table 3, the mean drainage losses of NO_3^-, NH_4^+, and DON were 136, 33, and 101 mol N ha^{-1} yr^{-1}, respectively. The drainage losses of NO_3^-, NH_4^+, and DON thus accounted for 47, 13, and 40% of the total N solute losses by drainage water on average, respectively, (Table 3). For the seepage lakes, the NO_3^- losses were in general lower than the NO_3^- outputs for the drainage lakes, while the solute losses of NH_4^+ and DON were higher than for the drainage lakes (Table 3). Accordingly, the mean losses of NO_3^-, NH_4^+, and DON from the seepage lakes comprised 15, 48, and 58% of total N solute loss, respectively, while the mean loss of NO_3^-, NH_4^+, and DON from drainage lakes were 52, 11, and 37% of the total N solute loss, respectively.

The fraction of the net N hydrologic flux relative to wet N deposition (i.e., the fraction of wet N deposition removed or retained in the lake-containing watersheds) ranged from −0.41 to 0.61 (mean: 0.22) Figure 2e; Table 2) with negative values indicating additional sources of N within the watersheds or underestimates of atmospheric N deposition. While there was no clear spatial pattern, the lake-containing watersheds in the western region generally had low, but positive values. The fraction of net N hydrologic flux relative to wet N deposition was negative in seven sites, including two lake-containing watersheds at high elevations. The fractions of net N hydrologic flux in seepage lakes ranged from −0.06 to 0.52 (mean: 0.23) (Table 2). While our estimates used only wet N deposition, other forms of atmospheric deposition, including gas or vapor, aerosol, and cloud droplet, may be important sources of N, especially at high elevations (Miller and Friedland 1999). Since the spatial pattern of net N hydrologic flux was different from that of wet N deposition, landscape attributes affect net N hydrologic flux in the Adirondack lake-containing watersheds.

There was some evidence that wet N deposition influenced lake N drainage loss and net N hydrologic flux in the lake-containing watersheds. The lake NO_3^- drainage loss increased and the fraction of the net NO_3^- hydrologic flux (i.e., the fraction of wet NO_3^- deposition removed or retained within the lake-containing watersheds) decreased with wet N deposition (R^2 = 0.21, p = 0.0006 and R^2 = 0.09, p = 0.029, respectively; Table 4, Figure 3). For the 45 drainage lake-containing watersheds, the relationship between wet N deposition and NO_3^- drainage loss was also significant, but weaker (R^2 = 0.14, p = 0.011) than the relationship for all the 52 lake-containing watersheds. The wet N deposition was also related with the total N drainage loss (R^2 = 0.10, p = 0.024; Table 4), but not with the fraction of the net N hydrologic flux. The positive relationship between wet N deposition and the NO_3^- or total N drainage loss in the Adirondack lake-containing watersheds was consistent with the pattern found across eastern New York and New England where stream and lake NO_3^- followed N deposition (Aber et al. 2003). The sites above 800 m had higher lake NO_3^- drainage loss and negative

Table 2. Annual nitrogen budgets and DON and DOC drainage losses for the lake-containing watersheds, estimated based on models and measured chemical concentrations in lake drainage waters, in the Adirondack region of New York

Site No.	Pond Name	Wet N deposition (Note 1)	N drainage loss (Note 2)	Fraction of net N hydrologic flux (Note 3)	NO_3^- deposition	NO_3^- drainage loss	Fraction of net NO_3^- hydrologic flux	NH_4^+ deposition	NH_4^+ drainage loss	Fraction of net NH_4^+ hydrologic flux	DON drainage loss	DOC drainage loss
		(mol N ha^{-1} yr^{-1})										(mol C ha^{-1} yr^{-1})
1	Arbutus Lake	318	175	0.45	219	72	0.67	100	19	0.81	85	2672
2	Avalanche Lake	340	478	−0.41	229	327	−0.43	111	34	0.69	117	3731
3	Barnes Lake[a]	382	291	0.24	277	32	0.88	105	81	0.23	178	2720
4	Big Hope Pond	289	212	0.27	192	49	0.75	96	35	0.63	128	4392
5	Big Moose Lake	374	289	0.23	265	181	0.32	109	24	0.78	85	3071
6	Black Pond	297	206	0.31	200	74	0.63	97	24	0.75	108	2074
7	Brook Trout Lake	392	199	0.49	278	71	0.74	114	28	0.75	100	2021
8	Bubb Lake	367	240	0.34	260	111	0.57	106	27	0.74	102	2265
9	Carry Pond[a]	356	171	0.52	248	50	0.80	108	42	0.61	79	1547
10	Cascade Lake	364	292	0.20	258	197	0.24	106	16	0.85	79	2193
11	Clear Pond	305	120	0.61	206	42	0.80	100	16	0.84	62	2066
12	Lake Colden	337	360	−0.07	228	280	−0.23	110	15	0.86	65	2733
13	Constable Pond	366	343	0.06	259	234	0.10	107	22	0.79	87	3404
14	Dart Lake	365	289	0.21	259	172	0.34	106	22	0.79	94	2866
15	East Copperas Pond	304	293	0.04	207	32	0.84	97	94	0.03	167	6209
16	G Lake	388	276	0.29	277	171	0.38	111	20	0.81	85	2198
17	Grass Pond (a)[a]	288	217	0.25	194	29	0.85	94	60	0.36	127	4165
18	Grass Pond (b)	384	328	0.15	276	210	0.24	108	21	0.80	97	2503
19	Heart Lake	310	162	0.48	208	76	0.63	102	20	0.80	66	1689
20	Indian Lake	386	277	0.28	275	165	0.40	111	21	0.81	90	3531
21	Jockeybush Lake	390	317	0.19	279	199	0.29	111	28	0.74	90	1636
22	Little Hope Pond	288	265	0.08	192	79	0.59	96	40	0.59	146	6596
23	Limekiln Lake	372	238	0.36	265	144	0.46	108	18	0.83	76	1979
24	Little Clear Pond[a]	289	307	−0.06	195	34	0.83	95	98	−0.04	175	3652

25	Little Echo Pond[a]	306	313	−0.02	208	25	0.88	98	78	0.20	210	8331
26	Long Pond	344	185	0.46	240	22	0.91	104	27	0.74	137	7928
27	Loon Hollow Pond	374	370	0.01	265	179	0.32	108	82	0.24	109	3001
28	Lost Pond	364	289	0.21	257	150	0.42	107	35	0.67	105	3490
29	Little Simon Pond	320	324	−0.01	220	225	−0.02	100	15	0.85	84	2079
30	Marcy Dam Pond	316	199	0.37	213	155	0.27	104	7	0.93	37	1840
31	Middle Branch Lake	379	197	0.48	272	71	0.74	107	32	0.70	93	2805
32	Middle Pond	303	219	0.28	206	52	0.75	97	62	0.36	105	2807
33	Middle Settlement Pond	384	218	0.43	276	78	0.72	108	56	0.48	84	2013
34	Moss Lake	365	285	0.22	259	190	0.27	106	19	0.82	76	2654
35	Nate Pond	328	211	0.36	225	86	0.62	103	23	0.77	102	3205
36	North Lake	390	362	0.07	281	247	0.12	109	18	0.84	97	3335
37	Otter Lake	384	214	0.44	275	142	0.48	109	16	0.85	56	1747
38	Owen Pond	288	323	−0.12	191	236	−0.23	96	19	0.80	68	2756
39	Queer Lake	369	266	0.28	261	160	0.39	108	28	0.74	78	1979
40	Raquette Lake Reservoir	357	303	0.15	252	178	0.29	106	13	0.87	111	4454
41	Lake Rondaxe	368	272	0.26	262	167	0.36	106	22	0.79	83	2552
42	Sagamore Lake	360	284	0.21	253	179	0.29	107	16	0.85	90	4804
43	Sochia Pond[a]	301	240	0.20	203	37	0.82	97	83	0.15	119	1983
44	South Lake	396	362	0.09	284	256	0.10	112	23	0.79	83	2098
45	Squash Pond	379	352	0.07	269	183	0.32	110	33	0.70	136	5545
46	Squaw Lake	383	217	0.43	272	91	0.66	111	20	0.82	106	2307
47	Sunday Pond[a]	300	154	0.49	203	20	0.90	97	28	0.71	106	1333
48	West Pond	372	253	0.32	264	103	0.61	108	33	0.69	118	4178
49	Willis Lake	342	183	0.47	241	23	0.91	101	27	0.73	133	3395
50	Willys Lake	371	314	0.15	263	219	0.17	109	21	0.81	74	1710
51	Windfall Pond	372	453	−0.22	263	337	−0.28	108	43	0.60	73	2336
52	Woods Lake	387	345	0.11	275	237	0.14	112	25	0.78	83	2596

([a]indicates a seepage lake; no mark for a drainage lake).

(Note 1) Wet N deposition indicates the wet deposition of NO_3^- and NH_4^+ for the entire watershed.

(Note 2) N drainage loss indicates the N flux flowing out of the lake through drainage waters.

(Note 3) Fraction of net N hydrologic flux indicates the fraction of net N hydrologic flux relative to wet N drainage loss, calculated as [(wet N deposition – lake N drainage loss)/(wet N deposition)].

Table 3. Lake drainage losses of NO_3^-, NH_4^+, and DON in all 52 lakes, 45 drainage lakes, and 7 seepage lakes. (The fraction of total N indicates the fraction of respective N chemical species in total N drainage loss)

	All lakes				Drainage lakes				Seepage lakes			
	Flux (mol N ha^{-1} yr^{-1})		Fraction of total N (%)		Flux (mol N ha^{-1} yr^{-1})		Fraction of total N (%)		Flux (mol N ha^{-1} yr^{-1})		Fraction of total N (%)	
N Chemical species	Mean	(Range)	Mean	(Range)	Mean	(Range)	Mean	(Range)	Mean	(Range)	Mean	(Range)
NO_3^-	136	(19–337)	47	(8–78)	152	(19–337)	52	(11–78)	32	(20–50)	15	(8–29)
NH_4^+	33	(7–98)	13	(4–35)	28	(7–94)	11	(4–32)	67	(28–98)	48	(26–70)
DON	101	(37–210)	40	(16–74)	94	(37–167)	37	(16–74)	142	(79–210)	58	(46–69)

Table 4. Significant relationships for the drainage losses of NO_3^-, NH_4^+, DON, total N, and DOC, the C/N export ratio, net NO_3^- hydrologic flux the fraction of net NO_3^- hydrologic flux, and NO_3^- draining into the lake as dependent variable based on univariate regression analyses

Influencing factor or independent variable	Unit	Coefficient		R^2	n
		Constant	Slope		
For NO_3^- drainage loss (mol N ha^{-1} yr^{-1})					
Wet N deposition	mol N ha^{-1} yr^{-1}	−250.8	1.108	0.21**	52
wet NO_3^- deposition	mol N ha^{-1} yr^{-1}	−157.7	1.203	0.19**	52
Elevation	m	−158.4	0.515	0.33**	52
Mixed forest area [a] (Note 1)	%	341.8	−3.969	0.38*	20
Coniferous forest area [a] (Note 1)	%	134.8	3.175	0.23	20
For NH_4^+ drainage loss (mol N ha^{-1} yr^{-1})					
Wet N deposition	mol N ha^{-1} yr^{-1}	99.2	−0.189	0.09	52
Wet NO_3^- deposition	mol N ha^{-1} yr^{-1}	82.7	−0.202	0.08	52
Elevation	m	93.2	−0.105	0.20**	52
Wetland with N-fixing species [a]	%	22.9	2.289	0.23	20
Deciduous shrub wetland [a]	%	22.7	2.234	0.22	20
For DON drainage loss (mol N ha^{-1} yr^{-1})					
Wet N deposition	mol N ha^{-1} yr^{-1}	195.2	−0.270	0.09	52
Elevation	m	194.0	−0.163	0.22**	52
Total wetland area [a]	%	81.0	1.203	0.28*	20
For DOC drainage loss (mol C ha^{-1} yr^{-1})					
Total wetland area [a]	%	1922	85.22	0.44**	20
Emergent marsh [a]	%	2512	493.2	0.22	20
Coniferous forest wetland [a]	%	2197	168.0	0.25	20
Shrub wetland [a]	%	2157	155.6	0.29*	20
For total N drainage loss (mol N ha^{-1} yr^{-1})					
Wet N deposition	mol N ha^{-1} yr^{-1}	43.6	0.649	0.10	52
Wet NO_3^- deposition	mol N ha^{-1} yr^{-1}	96.0	0.714	0.09	52
Elevation	m	128.9	0.247	0.10	52
Deciduous forest area [a] (Note 1)	%	241.4	2.646	0.22	20
Mixed forest area [a] (Note 1)	%	456.3	−3.765	0.38*	20
For drainage export ratio of C/N					
Water residence time	yr	33.2	−4.219	0.13*	52
log(water residence time)	yr	26.2	−8.862	0.20**	47
Total wetland area [a]	%	24.8	0.479	0.30*	20
Coniferous shrub wetland [a]	%	26.7	7.625	0.30*	20
Shrub wetland [a]	%	25.2	1.091	0.31*	20
For net NO_3^- hydrologic flux (mol N ha^{-1} yr^{-1})					
Elevation	m	353.4	−0.429	0.28**	52
log(depth/residence time)	m yr^{-1}	219.4	−106.8	0.22**	47
For the fraction of net NO_3^- hydrologic flux (mol N ha^{-1} yr^{-1})					
Elevation	m	1.63	−0.0021	0.34**	52
Wet N deposition	mol N ha^{-1} yr^{-1}	1.46	−0.003	0.09	52
log(depth/residence time)	m yr^{-1}	0.928	−0.453	0.21*	47

Table 4. Continued.

Influencing factor or independent variable	Unit	Coefficient: Constant	Coefficient: Slope	R^2	n
NO_3^- draining into the lake (mol N ha^{-1} yr^{-1})					
Wet N deposition	mol N ha^{-1} yr^{-1}	−533.7	2.232	0.25**	52
Wet NO_3^- deposition	mol N ha^{-1} yr^{-1}	−359.2	2.476	0.23**	52
Elevation	m	−214.9	0.805	0.24**	52
Deciduous forest area [a]	%	183.2	6.502	0.31*	20
Mixed forest area [a]	%	663.1	−8.119	0.42*	20
Coniferous forest wetland [a]	%	410.0	−25.388	0.25	20
Forested wetland [a]	%	408.0	−19.225	0.25	20

For R^2,* indicates significance $p < 0.01$ and $**p < 0.001$. No mark for $p < 0.05$. n is the number of lake-containing watersheds used for the analysis; [a] indicates the proportion of watershed area occurring as the respective land cover type expressed by percentage.
(Note 1) The apparent relationships between total N and NO_3^- lake drainage loss versus land cover type might have also include the effect of in-lake processes, compared with the relationships of NO_3^- draining into the lake (which excluded the influence of in-lake processes) versus forest type, as discussed in the text.

fraction of net NO_3^- hydrologic flux, possibly due to elevational effects (e.g., steeper slopes and shallower soils) and the underestimation of atmospheric input (e.g., cloud water), while seepage lake sites had lower NO_3^- loss and higher net NO_3^- hydrologic flux (Figures 4a, b), reflecting longer hydraulic residence time and hence high capacity for net N hydrologic flux. The lake NO_3^- drainage losses were expected to be low at the sites having large wetland area due to denitrification loss, but the lake-containing watersheds with wetland area > 14% (the proportion of the land surface occupied by wetlands for the entire region is 14%; Roy et al. (1996)) did not exhibit clear patterns. The absence of a relationship is discussed further below. These results are consistent with our hypothesis that atmospheric N deposition is an important regulator of N solutes in surface waters, although it is not the sole determinant of N loss in the Adirondack region.

The lake DOC drainage losses ranged from 1333 to 8331 mol C ha^{-1} yr^{-1} (mean: 3100 mol C ha^{-1} yr^{-1}). These maximum and minimum DOC output values were from seepage lake-containing watersheds. The DOC losses from the seepage lakes had a mean value of 3390 mol C ha^{-1} yr^{-1}, which was comparable to the mean value for all the lake-containing watersheds but was in contrast with higher DON outflux in seepage lake-containing watersheds than in drainage lake-containing watersheds. The DOC concentrations were strongly related with the DON concentrations ($R^2 = 0.57$, $p < 0.0001$; Figure 4). Note that seepage lakes were enriched in DON for a given level of DOC compared to drainage lakes. This pattern is likely a function of hydraulic residence time and associated contributions of in-lake processes in seepage lakes, as discussed below.

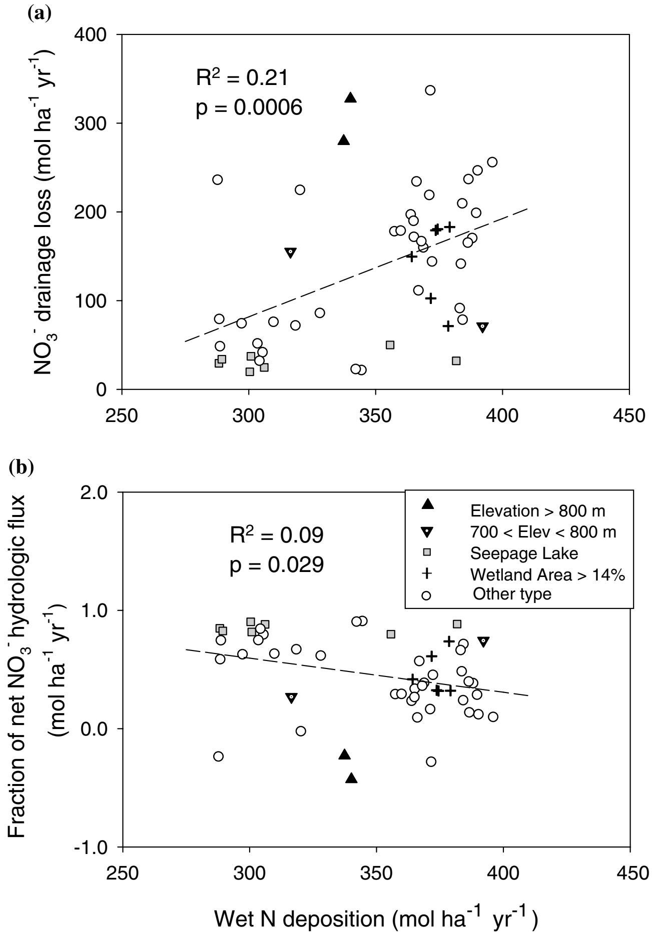

Figure 3. The relationships between (a) NO_3^- drainage loss versus wet N deposition and (b) the fraction of net NO_3^- hydrologic flux relative to wet N deposition versus wet N deposition in the Adirondack lake-containing watersheds.

Both the DON and DOC lake drainage losses decreased with increasing wet N deposition ($R^2 = 0.09$, $p = 0.035$; $R^2 = 0.07$, $p = 0.060$), although the relationship between the DOC drainage loss and the wet N deposition was not statistically significant ($p > 0.05$). The volume-weighted concentrations of DON or DOC were also inversely related with volume-weighted N concentrations in precipitation ($R^2 = 0.12, p = 0.011$; $R^2 = 0.12, p = 0.013$), which were stronger than the flux relationships of the DON or DOC with wet N deposition, respectively. Previous studies of N treatment effects on the concentrations or fluxes of DON and DOC in soil leachates have been inconclusive. Based on 1 year of observations following N additions to the Harvard Forest, Massachusetts, Currie et al. (1996) did not find significant changes in DON and

DOC concentrations, despite a significant change in the DOC/DON ratio in soil solutions. However with 4 years of observations, McDowell et al. (1998) found that DON concentrations significantly increased with little change in DOC concentrations. On the other hand, N addition did not consistently influence the leaching of DON and DOC at five sites across Europe (NITREX project) (Gundersen et al. 1998). These findings differed from our results. The decrease in DON or DOC loss with increasing wet N deposition in the Adirondacks was not attributable to elevated DON or DOC associated with wetlands. While wet N deposition increased with increasing elevation (R^2 = 0.11, p = 0.016), the proportion of the watershed area occurring as wetlands was not a function of elevation. The inverse relationship might be explained by acid-induced changes in DOC quantity and quality (i.e., decreases in allochthonous DOC with acidification) (Donahue et al. 1998). Alternatively, the decrease in DOC may be due to retarded decomposition of stable nitrogenous compounds formed from lignin by-product under higher N deposition (Berg et al. 1995; Fenn et al. 1998). For the seepage lake-containing watersheds, the DON losses were high (>100 mol N ha^{-1} yr^{-1}) relative to wet N deposition, except for one site (Carry Pond), which had a relatively low DON loss. In contrast, the DOC losses were relatively low (≤ 4000 mol C ha^{-1} yr^{-1}) regardless of wet N deposition, except for one site (Little Echo Pond) with a markedly high DOC loss (Table 2).

Land cover and terrestrial factors

We were able to evaluate how various watershed attributes that we hypothesized to be important have affected drainage losses of N and DOC in the Adirondack region. Wetlands are abundant in the Adirondacks and we expected them to influence N and C drainage losses. Both DON and DOC drainage losses increased with increasing proportion of total wetland area in the lake-containing watersheds (R^2 = 0.28, p = 0.0176 and R^2 = 0.44, p = 0.0014, respectively; Table 4). The volume-weighted concentrations of DON and DOC also increased with the proportion of total wetland (R^2 = 0.34, p = 0.0070 and R^2 = 0.48, p = 0.0008, respectively). Note that the relationship of DOC with wetland area was stronger than the relationship with DON. This difference between DON and DOC was consistent with a study in upland catchments in Scotland where stream DOC was significantly correlated with the percentage of peat cover, while the correlation between DON and the percentage of peat cover was not significant (Chapman et al. 2001). Chapman et al. (2001) suggested that difference in the relationships of peat cover with DON versus DOC was due to the factors other than wetlands in controlling DON, such as transformation or production within the stream channel.

The vegetation-based classification of wetlands improved the relationships with N solutes or DOC to a limited extent. The proportion of shrub wetland

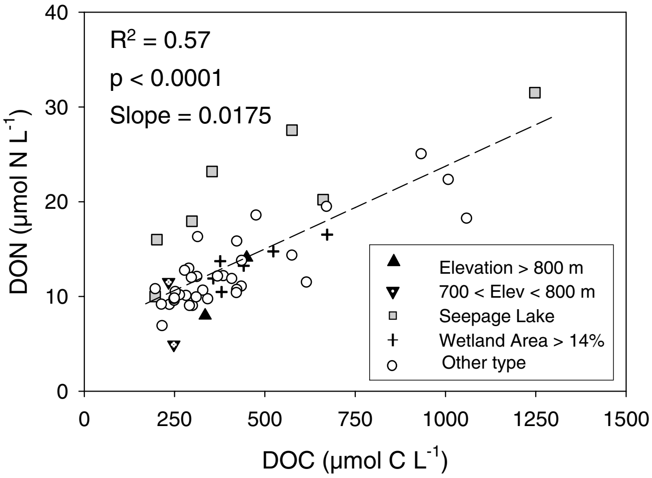

Figure 4. The relationship between the DON and DOC concentrations for the Adirondack lake-containing watersheds.

area and coniferous forest wetland area in the lake-containing watersheds were significantly and positively related to the DOC fluxes ($R^2 = 0.29$, $p = 0.014$ and $R^2 = 0.26$, $p = 0.023$, respectively; Table 4) and concentrations ($R^2 = 0.30$, $p = 0.011$ and $R^2 = 0.27$, $p = 0.018$, respectively), but not the DON fluxes or concentrations ($p > 0.05$). While the presence of alders in shrub wetlands that fix atmospheric N could be expected to affect the concentrations of NO_3^- (Ohrui et al. 1999; Hurd and Raynal 2004) and NH_4^+, the proportion of shrub wetland area with N-fixing species and the proportion of deciduous shrub wetland area were only related to the NH_4^+ fluxes ($R^2 = 0.23$, $p = 0.031$ and $R^2 = 0.22$, $p = 0.039$, respectively; Table 4) and concentrations ($R^2 = 0.24$, $p = 0.028$ and $R^2 = 0.22$, $p = 0.035$, respectively) and did not show significant relationships with other N chemical species.

Since the rates of both net N mineralization (Vitousek and Melillo 1979; Nadelhoffer et al. 1985) and nitrification (Ohrui et al. 1999) are found to be higher in deciduous forests than coniferous forests, the NO_3^- drainage loss was expected to be higher in deciduous forests. In the Adirondack lake-containing watersheds, total N drainage loss increased with increasing proportion of deciduous forest area ($R^2 = 0.22$, $p = 0.038$) (Table 4), while the NO_3^- drainage loss had no relationship with deciduous forest area ($p > 0.05$) (Table 4). As discussed below, the influence of in-lake processes might have obscured possible effects of forest types on N solute losses. Further, because the GIS data of landcover type (e.g., coniferous, mixed, and deciduous forests) used for this analysis, except for the GIS data of wetlands with vegetation-based classification, were only available on a coarse scale (about 32 m per pixel width) and did not include the information on actual species composition, no definitive conclusion can be drawn from these relationships. The influences of wetlands and forest types were further examined for the estimated NO_3^- fluxes draining into the lakes, excluding the in-lake effects, as below.

Although the information on tree species was not available for our study sites, other than for wetland areas, tree species have been shown to affect nutrient cycling due to differences in the quality of litter inputs and decomposition rates. The litter inputs from sugar maple have lower lignin:N ratios (6.5–14) than other tree species, including American beech, Red oak (Lovett and Rueth 1999), and red spruce with lignin:N ratios between 15 and 31 (Aber et al. 2003). Sugar maple stands have higher rates of net nitrification than American beech (Lovett and Rueth 1999; Lovett and Mitchell 2004) or red oak (Finzi et al. 1998), which appear to be related to the lignin:N ratios. Since decomposition rates over the long-term are reduced with N-rich litter (Fenn et al. 1998), vegetation type may also influence the production of DOM with different litter quality. In the Adirondack lake-containing watersheds, the DOC drainage losses increased with increasing proportion of coniferous forest wetland area ($R^2 = 0.25$, $p = 0.023$; Table 3). The DOC concentrations also increased with increasing proportion of coniferous forest wetland area ($R^2 = 0.27$, $p = 0.018$). Hope et al. (1994) reported that the DOC fluxes were higher in coniferous forests than deciduous forests, which may be associated with the litter types and decomposition rates. The absence of the relationship between DOC and coniferous forest area (other than wetland area with conifers) might be due to a coarse resolution of the forest type map, compared with the wetland maps.

The NO_3^- drainage loss, net NO_3^- hydrologic flux, the fraction of net NO_3^- hydrologic flux relative to wet NO_3^- deposition, and DON drainage loss were all strongly related with elevation ($R^2 = 0.33$, 0.28, 0.34, and 0.22, respectively; $p < 0.0001$ for the first three correlations and $p = 0.0004$ for the DON output relationship). Aber et al. (2003) found that the relationships of NO_3^- in surface waters with elevation were free from covariation between N deposition and elevation across northeastern US. The relationships of N losses with elevation could also be derived from factors other than N deposition, including watershed landscape characteristics. Relationships of lake chemistry with watershed characteristics, such as watershed area (WA), have been previously reported (e.g., Houle et al. 1995; Wolock et al. 1997; Gergel et al. 1999; Larson et al. 1999; Prepas et al. 2001). In the Adirondack lake-containing watersheds, since watershed area or elevation range did not explain the spatial patterns of NO_3^-, DON, or DOC drainage losses and DOC/DON ratio, other factors that were not examined in our study, such as temperature, soil and geological characteristics, and their related hydrological and biogeochemical processes, might have been responsible. For example, the positive relationship between the NO_3^- drainage loss and elevation or the inverse relationship between the net NO_3^- hydrologic flux and elevation may be explained by steeper slopes (e.g., Clow and Sueker 2000) and shallower soils at higher elevations where NO_3^- may be readily leached to surface waters. There results support our hypotheses on the importance of watershed attributes especially elevation and the presence of wetlands in affecting N and C solute losses in the drainage waters of the Adirondacks.

In-lake processes

Hydraulic retention time is an important factor that regulates the amount of planktonic NO_3^- depletion (Owen et al. 1999) and denitrification (e.g., Kelly et al. 1987). In lakes and rivers (Howarth et al. 1996) and estuaries (Nixon et al. 1996), the percentage of N retention (or N exported) is a function of the ratio of mean depth to water residence time, based on a model of Kelly et al. (1987) for NO_3^-. In the Adirondack lakes, the ratio of mean depth to water residence time (z/t) on the log-arithmetic scale was positively related with the NO_3^- drainage loss ($R^2 = 0.20$, $p = 0.001$) and inversely related with the net NO_3^- hydrologic flux and the fraction of net NO_3^- hydrologic flux ($R^2 = 0.22$, $p = 0.0009$ (Figure 5) and $R^2 = 0.21$, $p = 0.001$, respectively, excl. $z/t > 90$; Table 3). These results suggest that in-lake processes were important in controlling the removal or retention and drainage loss of NO_3^- in the Adirondack lake-containing watersheds. Previously for the Arbutus lake-containing watersheds, direct mass balance measurements that compared the N fluxes draining into the major inlet versus at the lake outlet showed a 48% reduction of NO_3^- and a 30% reduction in total N (Mitchell et al. 2001b). For analyzing all of the Adirondack lake-containing watersheds in the present study, the NO_3^- fluxes removed within the lakes estimated based on the model of Kelly et al. (1987) ranged from 2 to 352 mol N ha^{-1} yr^{-1} (mean:

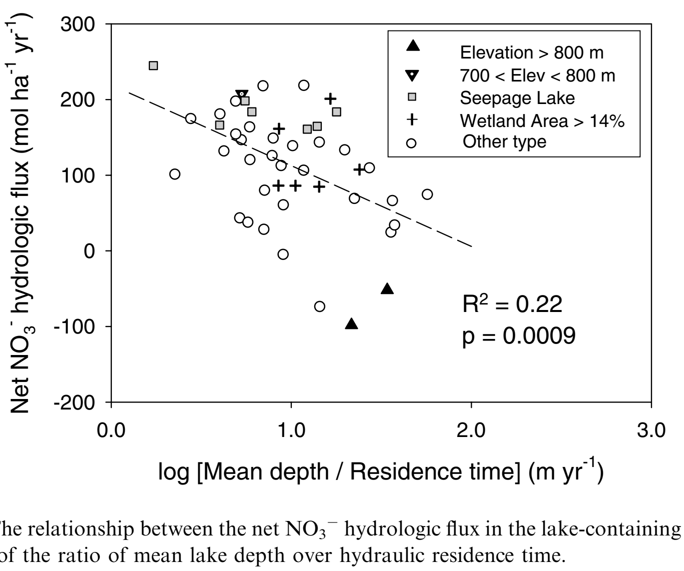

Figure 5. The relationship between the net NO_3^- hydrologic flux in the lake-containing watershed and the log of the ratio of mean lake depth over hydraulic residence time.

100 mol N ha^{-1} yr^{-1}), excluding Queer Lake, which had markedly high value (Table 5). The mean removal of NO_3^- within the lakes accounted for 28% (ranging from 1 to 95%, excluding Queer Lake) of wet N deposition to the

Table 5. Annual nitrate fluxes removed in and draining into the lake. The site numbers correspond to the locations shown in Figure 2

Site No.	Pond Name	NO_3^- removed within the lake (Note 1)	NO_3^- draining into the lake (Note 2)
			mol N ha^{-1} yr^{-1}
1	Arbutus Lake	113	185
2	Avalanche Lake	126	453
3	Barnes Lake[a]	155	187
4	Big Hope Pond	28	77
5	Big Moose Lake	105	285
6	Black Pond	79	153
7	Brook Trout Lake	111	182
8	Bubb Lake	117	228
9	Carry Pond[a]	75	125
10	Cascade Lake	181	378
11	Clear Pond	59	101
12	Lake Colden	68	348
13	Constable Pond	54	289
14	Dart Lake	9	181
15	East Copperas Pond	97	129
16	G Lake	121	291
17	Grass Pond (a)[a]	17	47
18	Grass Pond (b)	48	257
19	Heart Lake	149	225
20	Indian Lake	51	216
21	Jockeybush Lake	232	431
22	Little Hope Pond	75	154
23	Limekiln Lake	203	347
24	Little Clear Pond[a]	23	57
25	Little Echo Pond[a]	34	59
26	Long Pond	15	37
27	Loon Hollow Pond	175	355
28	Lost Pond	52	202
29	Little Simon Pond	207	432
30	Marcy Dam Pond	2	157
31	Middle Branch Lake	36	107
32	Middle Pond	87	139
33	Middle Settlement Pond	133	211
34	Moss Lake	70	260
35	Nate Pond	70	156
36	North Lake	55	301
37	Otter Lake	59	201
38	Owen Pond	20	256
39	Queer Lake	588	748

Table 5. Continued.

Site No.	Pond Name	NO_3^- removed within the lake (Note 1)	NO_3^- draining into the lake (Note 2)
			mol N ha^{-1} yr^{-1}
40	Raquette Lake Reservoir	15	193
41	Lake Rondaxe	11	178
42	Sagamore Lake	26	205
43	Sochia Pond[a]	77	114
44	South Lake	302	558
45	Squash Pond	144	327
46	Squaw Lake	189	281
47	Sunday Pond[a]	9	29
48	West Pond	100	202
49	Willis Lake	27	50
50	Willys Lake	352	571
51	Windfall Pond	194	531
52	Woods Lake	343	580

[a]indicates a seepage lake; no mark for a drainage lake.
(Note 1) NO_3^- removed within the lake indicates the NO_3^- flux removed by in-lake processes, calculated using the model of Kelly et al. (1987).
(Note 2) NO_3^- draining into the lake was calculated as [NO_3^- lake drainage loss plus NO_3^- removed by in-lake processes].

lake-containing watershed and 43% (ranging from 1 to 83%) of NO_3^- draining into the lake estimated using the model of Kelly et al. (1987).

Based on this calculation, NO_3^- draining into the lakes ranged from 29 to 580 mol N ha^{-1} yr^{-1} (mean: 236 mol N ha^{-1} yr^{-1}), excluding Queer Lake (Table 5). The estimated NO_3^- flux draining into the lakes increased with increasing wet N deposition, wet NO_3^- deposition, and elevation, as found for the lake NO_3^- drainage loss (Table 4). The estimated NO_3^- draining into the lakes also increased with increasing deciduous forest area, which could be due to higher net N mineralization (Vitousek and Melillo 1979; Nadelhoffer et al. 1985) and nitrification (Ohrui et al. 1999) under deciduous overstory than in coniferous forests. The estimated NO_3^- draining into the lakes decreased with increasing proportion of the watershed occurring as wetlands (Table 4), presumably due to denitrification. The absence of the relationships between NO_3^- drainage loss from the lake versus deciduous forest or wetland area could have been due to the overriding effect of in-lake processes on NO_3^-.

The lake drainage export ratio of DOC to DON in the ALTM lake-containing watersheds ranged from 12.6 to 58.0 on a molar basis (mean: 30.8), with 60% of the lake-containing watershed having the ratios between 25 and 40. The DOC/DON ratios were slightly higher in streams at the Coweeta Hydrologic Laboratory, North Carolina (simple mean calculated: 36 on a molar basis; 31 on a mass basis) (Qualls and Haines 1991), in the White Mountain National Forest, New Hampshire (20–62 (simple mean calculated:

37) on a molar basis; 17–53 (simple mean calculated: 32) on a mass basis) (Goodale et al. 2000), but lower in Catskills Mountains (mean DOC/TON ratio: 21 on a molar basis; 18 on a mass basis) (Lovett et al. 2000), and much higher in remote sites in Chile (45–57 (simple mean calculated: 53); 39–49 (simple mean calculated: 45) on a mass basis) (Hedin et al. 1995). Compared with the ratios in stream water, the ratios in forest floor leachates were found to be higher at Harvard Forest, Massachusetts (47–51 on a molar basis; 40–44 on a mass basis) (McDowell et al. 1998), at the Coweeta (45–63 (simple mean calculated: 56); 39–54 (simple mean calculated: 48) on a mass basis) (Qualls and Haines 1991), and lower at 3 NITREX sites across Europe (22–37 (simple mean: 28); 19–32 (simple mean: 24) on a mass basis) (calculated from Gundersen et al. 1998) and in northeast Bavaria, Germany (simple mean calculated: 29 on a molar basis; 25 on a mass basis) (Michalzik and Matzner 1999). The C/N ratios were found to be higher for DOM derived from terrestrial origins, in comparison with values contributed by phytoplankton and aquatic plants (Clair et al. 1994; Chapman et al. 2001). The drainage export ratios of DOC/DON were mostly between the values for autochthonous (approximately 12) and allochthonous DOM (approximately 45–50) reported for various lakes (Wetzel 2001), which suggests that in-lake processes affected the composition of organic matter in the Adirondack lakes. For seepage lake-containing watersheds, the DOC/DON ratio was generally lower, ranging from 12.6 to 39.6 (mean: 22.5) due to higher DON concentrations than those for drainage lake-containing watersheds.

The C/N ratio as an indicator of N status associated with N saturation has been suggested (Campbell et al. 2000) based on the inverse relationships between the N or NO_3^- loss and the C/N ratio observed in streams (Campbell et al. 2000) and in soils and soil solutions (Gundersen et al. 1998). However, we observed no relationship between the N or NO_3^- drainage loss and DOC/DON. The net NO_3^- hydrologic flux increased with decreasing DOC/DON ratio ($R^2 = 0.07$, $p = 0.05$) and with increasing DON drainage loss ($R^2 = 0.20$, $p = 0.001$). No relationship existed between the net NO_3^- hydrologic flux and DOC. Harriman et al. (1998) suggested that the inverse relationship between net NO_3^- hydrologic flux (or NO_3^- retention in watershed, as reported) and DOC/DON ratio might be indicative of N immobilization into the soil N pool. However, the NO_3^- removed within the lakes also increased with decreasing DOC/DON ($R^2 = 0.11$, $p = 0.015$) in the Adirondacks, suggesting the importance of in-lake processes by which NO_3^- is removed or retained and more N-rich, autochthonous DOM is released (DOM produced in lakes tends to have lower C/N ratios), in addition to the processes occurring in wetlands that are abundant in the region. In contrast, there was no relationship between in-lake NO_3^- removal and the lake DON drainage loss, suggesting that the relationship between net NO_3^- hydrologic flux and the lake DON drainage loss was not solely attributable to in-lake processes. Vitousek et al. (1998) hypothesized that DON loss could be a mechanism to delay N saturation, but the relationship between within-watershed retention or removal of NO_3^- in lake-containing watersheds and DON drainage loss could not alone support this hypothesis without further direct evidence.

As shown above, the lake outfluxes or concentrations of both DON and DOC decreased with increasing wet N deposition or N concentrations in precipitation. The decrease in proportion of allochthonous DOC could be attributed to a removal of allochthonous DOC by metal-mediated coagulation enhanced with acidification (Effler and Schafran 1985; Schindler et al. 1992; Schnitzer and Khan 1994/1972), photooxidation of allochthonous DOC, for which the efficiency increases with decreasing pH, and microbial degradation of photochemically transformed DOC(Kopáček et al. 2002).

Total N exported or N denitrified is a function of hydraulic residence time (Nixon et al. 1996; Dettmann 2001). In the Adirondack lakes, total N, NO_3^- or DON drainage loss, total N or NO_3^- net hydrologic flux, or the fraction of total N or NO_3^- net hydrologic flux was not significantly related to the log mean hydraulic residence time alone ($p > 0.05$). However, the DOC drainage loss was inversely related with the log hydraulic residence time ($R^2 = 0.10$, $p = 0.04$; excl. the residence time < 0.05 yr). Allochthonous DOM, which has higher C/N ratios, is generally more dominant than autochthonous DOM in lakes and the utilization of allochthonous DOC increases with longer retention time by 0.5–2% per day (Wetzel 2001). Thus, the inverse relationship between DOC and hydraulic residence time may reflect the degradation of allochthonous DOC with increasing hydraulic residence time. The absence of the relationship with DON, compared with DOC, suggests the importance of the influences of other factors on DON export. Alternatively, since DON from wetlands and groundwater is mostly associated with humic compounds (Wetzel 2001), DON may be more resistant to abiotic processes and microbial degradation than DOC in the lakes, thereby affecting the relationship of DON with residence time.

Conclusions

Nitrogen input–output budgets allowed us to assess the contribution of atmospheric wet N deposition to N drainage loss and N retention within the Adirondack lake-containing watersheds. Spatial patterns found for wet N deposition over the Adirondacks were less evident for N drainage loss and net hydrologic flux. The significant relationships between wet N deposition and N drainage loss or the fraction of net N hydrologic flux relative to wet N deposition (i.e., the fraction of wet N deposition removed or stored in the watersheds) suggest that wet N deposition influenced N drainage loss and net N hydrologic flux to a limited extent. As hypothesized, in addition to wet N deposition, other factors also influenced the drainage losses of NO_3^-, NH_4^+, DON, and DOC, the DOC/DON export ratio, and net N hydrologic flux. The drainage losses of NO_3^-, NH_4^+, and DON, net NO_3^- hydrologic flux, and the fraction of net NO_3^- hydrologic flux were strongly related to elevation, but the DOC drainage loss was not related. Both the DON and DOC drainage losses from the lakes increased with the proportion of watershed area occurring as wetlands, but the relationship with DOC was stronger. The effects of wetlands and forest type on NO_3^- loss became more apparent when the NO_3^- flux draining into the lakes was calculated by excluding the influence of in-lake NO_3^- processing. The DOC/DON export ratios from the lake-containing watersheds were in general lower than those from forest floor leachates or streams in New England and were intermediate between those of autochthonous and allochthonous organic matter reported for various lakes. The DOC/DON ratios for seepage lakes were lower than those for drainage lakes. The influences of in-lake processes regulating N exports, which may include denitrification, degradation of DOM, and contribution of autochthonous DOM in the lakes, were also reflected in the relationships with hydraulic retention time. The N removed by in-lake processes varied substantially among the lakes. Further evaluations of those processes that influence N solute generation and losses within the terrestrial and aquatic components of watersheds will be required for fully understanding spatial patterns of N biogeochemistry both within and among regions.

Acknowledgments

This research was supported by the New York State Energy Research Development Authority and the National Science Foundation. The boundary map of the Adirondack Park was obtained from the Adirondack Park Agency and BROOK90 was from Compass Brook of C.A. Federer. We thank R. Costanza, S. Capone, T. Dudones, and other ALSC staff for sample collection and additional data, P. McHale, D. Lyons, C. Martinez, and other people for their assistance in chemical analyses, and C. Demers with the climate data at HWF. We also thank E. Dettmann for his comment on hydraulic residence time. We appreciate the comments of anonymous reviewers which improved the manuscript.

References

Aber J.D., Goodale C.L., Ollinger S.V., Smith M.-L., Magill A.H., Martin M.E., Hallett R.A., Stoddard J.L. and NERC Participants. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? BioScience 53: 375–390.

Aber J.D., McDowell W., Nadelhoffer K., Magill A., Berntson G., Kmakea M., McNulty S., Currie W., Rustad L. and Fernandez I. 1998. Nitrogen saturation in temperate forest ecosystems – hypothesis revisited. BioScience 48: 921–934.

Aber J.D., Nadelhoffer K.J., Steudler P. and Melillo J.M. 1989. Nitrogen saturation in northern forest ecosystems. BioScience 39: 378–386.

Adirondack Ecological Center 1997. Overview of the Adirondack Ecosystem.

Anderson J.B., Baumgardner R.E., Mohnen V.A. and Bowser J.J. 1999. Cloud chemistry in the eastern United States, as sampled from three high-elevation sites along the Appalachian Mountains. Atmos. Environ. 33: 5105–5114.

Berg B., McClaugherty C., VirzoDeSanto A., Johansson M.-B. and Ekbohm G. 1995. Decomposition of forest litter and soil organic matter – a mechanism for soil organic matter buildup? Scand. J. Forest Res. 10: 108–119.

Campbell J.L., Hornbeck J.W., McDowell W.H., Buso D.C., Shanley J.B. and Likens G.E. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry 49: 123–142.

Campbell J.L., Hornbeck J.W., Mitchell M.J., Adams M.B., Castro M.S., Driscoll C.T., Kahl J.S., Kochenderfer J.N., Likens G.E., Lynch J.A., Murdoch P.S., Nelson S.J. and Shanley J.B. 2004. Input–output budgets of inorganic nitrogen for 24 forest watersheds in the northeastern United States: a review. Water Air Soil Poll. 151: 373–396.

Chapman P.J., Edwards A.C. and Cresser M.S. 2001. The nitrogen composition of streams in upland Scotland: some regional and seasonal differences. Sci. Total Environ. 265: 65–83.

Clair T.A., Pollock T.L. and Ehrman J.M. 1994. Exports of carbon and nitrogen from river basins in Canada's atlantic provinces. Global Biogeochem. Cycles 8: 441–450.

Clarke J.F., Edgerton E.S. and Martin B.E. 1997. Dry deposition calculations for the clean air status and trends network. Atmos. Environ. 31: 3667–3678.

Clow D.W. and Sueker J.K. 2000. Relations between basin characteristics and stream water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado. Water Resour. Res. 36: 49–61.

Cornell S.E., Jickells T.D., Cape J.N., Rowland A.P. and Duce R.A. 2003. Organic nitrogen deposition on land and coastal environments: a review of methods and data. Atmos. Environ. 37: 2173–2191.

Cowardin L.M., Carter V., Golet F.C. and LaRoe E.T. 1979. Classification of Wetlands and Deepwater Habitats of the United States. FWS/OBS-79. Office of Biological Services, US Fish and Wildlife Service, US. Department of the Interior, Washington, DC, pp. 103.

Currie W.S., Aber J.D., McDowell W.H., Boone R.D. and Magill A.H. 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry 35: 471–505.

D'Arcy P. and Carignan R. 1997. Influence of catchment topography on water chemistry in southeastern Québec Shield lakes. Can. J. Fish. Aquat. Sci. 54: 2215–2227.

Dettmann E.H. 2001. Effect of water residence time on annual export and denitrification of nitrogen in estuaries: a model analysis. Estuaries 24: 481–490.

Dillon P.J. and Molot L.A. 1997. Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. Water Resour. Res. 33: 2591–2600.

Donahue W.F., Schindler D.W., Page S.J. and Stainton M.P. 1998. Acid-induced changes in DOC quality in an experimental whole-lake manipulation. Environ. Sci. Technol. 32: 2954–2960.

Driscoll C.T., Driscoll K.M., Roy K.M. and Mitchell M.J. 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. Environ. Sci. Technol. 37: 2036–2042.

Driscoll C.T., Lawrence G.B., Bulger A.J., Butler T.J., Cronan C.S., Eagar C., Lambert K.F., Likens G.E., Stoddard J.L. and Weathers K.C. 2001. Acidic deposition in the northeastern US: sources and inputs, ecosystem effects, and management strategies. BioScience 51: 180–198.

Driscoll C.T., Newton R.M., Gubala C.P., Baker J.P. and Christensen S. 1991. Adirondack mountains. In: Charles D.F. (ed.), Acidic Deposition and Aquatic Ecosystems: Regional Case Studies. Springer-Verlag, New York, pp. 133–202.

Eckhardt B.W. and Moore T.R. 1990. Controls on dissolved organic carbon concentrations in streams, southern Québec. Can. J. Fish. Aquat. Sci. 47: 1537–1544.

Effler S.W., Schafran G.C. and Driscoll C.T. 1985. Partitioning light attenuation in an acidic lake. Can. J. Fish. Aquat. Sci. 42: 1707–1711.

Federer C.A. 2001. BROOK90: A Simulation Model for Evaporation, Soil Water, and Streamflow. Versions 4, 3.3, and 3.2. Compass BrookVersions 4, Durham NH.

Fenn M.E., Poth M.A., Aber J.D., Baron J.S., Bormann B.T., Johnson D.W., Lemly A.D., McNulty S.G., Ryan D.F. and Stottlemyer R. 1998. Nitrogen excess in North American

ecosystems: predisposing factors, ecosystem responses, and management strategies. Ecol. Appl. 8: 706–733.
Finzi A.C., Canham C.D. and van Breemen N. 1998. Canopy tree - soil interactions within temperate forests: species effects on soil carbon and nitrogen. Ecol. Appl. 8: 440–446.
Gergel S.E., Turner M.G. and Kratz T.K. 1999. Dissolved organic carbon as an indicator of the scale of watershed influence on lakes and rivers. Ecol. Appl. 9: 1377–1390.
Goodale C.L., Aber J.D. and McDowell W.H. 2000. The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. Ecosystems 3: 433–450.
Gundersen P., Emmett B.A., Kjønaas O.J., Koopmans C.J. and Tietema A. 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. Forest Ecol. Manage. 101: 37–55.
Harriman R., Curtis C. and Edwards A.C. 1998. An empirical approach for assessing the relationship between nitrogen deposition and nitrate leaching from upland catchments in the United Kingdom. Water Air Soil Poll. 105: 193–203.
Hedin L.O., Armesto J.J. and Johnson A.H. 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory. Ecology 76: 493–506.
Hope D., Billett M.F. and Cresser M.S. 1994. A review of the export of carbon in river water: fluxes and processes. Environ. Poll. 84: 301–324.
Houle D., Carignan R. and Lachance M. 1995. Dissolved organic carbon and sulfur in southwestern Quebec lakes: relationships with catchment and lake properties. Limnol. Oceanogr. 40: 710–717.
Howarth R.W., Billen G., Swaney D., Townsend A., Jaworski N., Lajtha K., Downing J.A., Elmgren R., Caraco N., Jordan T., Brendse F., Freney J., Kudeyarov V., Murdoch P. and 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.
Hurd T.M. and Raynal D.J. 2004. Nitrogen solutes and surface-groundwater interactions in riparian wetlands dominated by alder shrubs or coniferous trees. Hydrol. Process. (In press).
Ito M., Mitchell M.J. and Driscoll C.T. 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. Atmos. Environ. 36: 1051–1062.
Johnson L.B., Richards C., Host G.E. and Arthur J.W. 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. Freshwater Biol. 37: 193–208.
Kelly C.A., Rudd J.W.M, Hesslein R.H., Schindler D.W., Dillon P.J., Driscoll C.T., Gherini S.A. and Hecky R.E. 1987. Prediction of biological acid neutralization in acid-sensitive lakes. Biogeochemistry 3: 129–140.
Kiernan B.D., Hurd T.M. and Raynal D.J. 2003. Abundance of *Alnus incana ssp. rugosa* in Adirondack Mountain shrub wetlands and its influence on inorganic nitrogen. Environ. Poll. 123: 347–354.
Kopáček J., Hejzlar J., Kana J., Porcal P. and Klementová Š 2003. Photochemical and biological degradation of dissolved organic carbon and its impact on alkalinity production in acidified lakes. Limnol. Oceanogr. 43: 106–117.
Kortelainen P. 1993. Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. Can. J. Fish. Aquat. Sci. 50: 1477–1483.
Kretser W., Gallagher J. and Nicolette J. 1989. Adirondack Lakes Survey, 1984–1987: An Evaluation of Fish Communities and Water Chemistry. Adirondack Lakes Survey Corp., Ray Brook, NY.
Larson G.L., Lomnicky G., Hoffman R., Liss W.J. and Deimling E. 1999. Integrating physical and chemical characteristics of lakes into the glacially influenced landscape of the northern Cascade Mountains, Washington State, USA. Environ. Manage. 24: 219–228.
Levine S.H. and Lewis W.M. 1984. Diel variation of nitrogen fixation in Lake Valencia, Venezuela. Limnol. Oceanogr. 29: 887–893.

Levine S.N. and Lewis W.M. 1985. The horizontal heterogeneity of nitrogen fixation in Lake Valencia, Venezuela. Limnol. Oceanogr. 30: 1240–1245.

Lewis W.M. and Levine S.N. 1984. The light response of nitrogen fixation in Lake Valencia, Venezuela. Limnol. Oceanogr. 29: 894–900.

Lovett G.M. and Mitchell M.J. 2004. Sugar maple and nitrogen cycling in the forests of eastern North America. Frontiers Ecol. Environ. 2: 81–88.

Lovett G.M. and Rueth H. 1999. Soil nitrogen transformations in beech and maple stands along a nitrogen deposition gradient. Ecol. Appl. 9: 1330–1344.

Lovett G.M., Weathers K.C. and Sobczak W.V. 2000. Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. Ecol. Appl. 10: 73–84.

McDowell W.H., Currie W.S., Aber J.D. and Yano Y. 1998. Effects of chronic nitrogen amendments on production of dissolved organic carbon and nitrogen in forest soils. Water Air Soil Poll. 105: 1998.

McHale M.R., Mitchell M.J., McDonnell J.J. and Cirmo C.P. 2000. Nitrogen solutes in an Adirondack Forest Watershed: importance of dissolved organic nitrogen. Biogeochemistry 48: 165–184.

Michalzik B. and Matzner E. 1999. Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem. Eur. J. Soil Sci. 50: 579–590.

Miller E.K. and Friedland A.J. 1999. Local climate influences on precipitation, cloud water, and dry deposition to an Adirondack subalpine forest: insights from observations 1986–1996. J. Environ. Qual. 28: 270–277.

Mitchell M.J., Driscoll C.T., Owen J.S., Schaefer D., Michener R. and Raynal D.J. 2001a. Nitrogen biogeochemistry of three hardwood ecosystems in the Adirondack Mountains of New York. Biogeochemistry 56: 93–133.

Mitchell M.J., McHale P.J., Inamdar S. and Raynal D.R. 2001b. Role of within lake processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack Mountains of New York State, USA. Hydrol. Process. 15: 1951–1965.

Nadelhoffer K.J., Aber J.D. and Melillo J.M. 1985. Fine roots, net primary production, and soil nitrogen availability: a new hypothesis. Ecology 66: 1377–1390.

Neff J.C., Holland E.A., Dentener F.J., McDowell W.H. and Russell K.M. 2002. The origin, composition and rates of organic nitrogen deposition: a missing piece of the nitrogen cycle? Biogeochemistry 57/58: 99–132.

Nixon S.W., Ammerman J.W., Atkinson L.P., Berounsky V.M., Billen G., Boicourt W.C., Boynton W.R., Church T.M., Ditoro D.M., Elmgren R., Garber J.H., Giblin A.E., Jahnke R.A., Owens N.J.P., Pilson M.E.Q. and Seitzinger S.P. 1996. The fate of nitrogen and phosphorus at the land–sea margin of the North Atlantic Ocean. Biogeochemistry 35: 141–180.

Ohrui K., Mitchell M.J. and Bischoff J.M. 1999. Effect of landscape position on N mineralization and nitrification in a forested watershed in the Adirondack Mountains of New York. Can. J. Forest Resour. 29: 497–508.

Owen J.S., Mitchell M.J. and Michener R.H. 1999. Stable nitrogen and carbon isotopic composition of seston and sediment in two Adirondack lakes. Can. J. Fisheries Aquat. Sci. 56: 2186–2192.

Park J.-H., Mitchell M.J., McHale P.J., Christopher S.F. and Myers T.P. 2003. Impacts of changing climate and atmospheric deposition on N and S losses from a forested watershed of the Adirondack Mountains, New York State. Glob. Change Biol. 9: 1602–1619.

Prepas E.E., Planas D., Gibson J.J., Vitt D.H., Prowse T.D., Dinsmore W.P., Halsey L.A., McEachern P.M., Paquet S., Scrimgeour G.J., Tonn W.M., Paszkowski C.A. and Wolfstein K. 2001. Landscape variables influencing nutrients and phytoplankton communities in Boreal Plain lakes of northern Alberta: a comparison of wetland- and upland-dominated catchments. Can. J. Fish. Aquat. Sci. 58: 1286–1299.

Qualls R.G. and Haines B.L. 1991. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. Soil Sci. Soc. Am. J. 55: 1112–1123.

Roy K.M., Allen E.B., Barge J.W., Ross J.A., Curran R.P., Boguchi D.J., Franzi D.A., Kretser W.A., Frank M.M., Spada D.M. and Banta J.B. 1997. Influences of wetlands and lakes in the Adirondack Park of New York State: a catalog of existing and new GIS data layers for the 400,000-hectare Oswegatchie/Black River Watershed. Final report prepared for the State Wetlands Protection Program, US Protection Agency, Grant No. CD992087-01. 71.

Roy K.M., Curran R.P., Barge J.W., Spada D.M., Boguchi D.J., Allen E.B. and Kretser W.A. 1996. Watershed protection for Adirondack wetlands: a demonstration-level GIS characterization of subcatchments of the Oswegatchie/Black River watershed. Final report (February 1996) prepared for the State Wetlands Protection Program, US Environmental Protection Agency, Contract No. W-002777-01-0. 49.

SAS Institute 1994. Statistical Analysis Software For Microcomputers. SAS Institute Inc., Cary, NC.

Schindler D.W., Stainton M.P., Kelly C.A., Bayley S.E., Curtis P.J. and Parker B.R. 1992. Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in Precambrian Shield lakes. Hydrobiologia 229: 1–21.

Schnitzer M. and Khan S.U. (1994/1972). Humic Substances in the Environment. Marcel Dekker, New York, NY pp. 327.

Seitzinger S.P. 1987. Nitrogen biogeochemistry in an unpolluted estuary: the importance of benthic denitrification. Marine Ecology – Progress Series 41: 177–186.

Seitzinger S.P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnol. Oceanogr. 33: 702–724.

Stoddard J.L. 1994. Long-term changes in watershed retention of nitrogen: its causes and consequences. In: Baker L.A. (ed.), Environmental Chemistry of Lakes and Reservoirs. American Chemical Society, Washington, DC, pp. 223–284.

Tarboton D.G. 2000. TARDEM: a suite of programs for the analysis of digital elevation data. Utah State University, Logan, Utah.

Tufford D.L., KcKellar H.N. Jr. and Hussey J.R. 1998. In-stream nonpoint source nutrient prediction with land-use proximity and seasonality. J. Environ. Qual. 27: 100–111.

Vitousek P.M., Hedin L.O., Matson P.A., Fownes J.H. and Neff J. 1998. Within-system element cycles, input–output budgets, and nutrient limitation. In: Pace M.L. and Groffman P.M. (eds), Successes, Limitations and Frontiers in Ecosystem Science. Springer-Verlag, New York.

Vitousek P.M. and Melillo J.M. 1979. Nitrate losses from disturbed forests: patterns and mechanisms. Forest Sci. 25: 605–619.

Weathers K.C., Likens G.E., Bormann F.H., Bicknell S.H., Bormann B.T., Daube B.C. Jr. Eaton J.S., Galloway J.N., Keene W.C., Kimball K.D., McDowell W.H., Siccama T.G., Smiley D. and Tarrant R. 1988. Cloud water chemistry from ten sites in North America. Environ. Sci. Technol. 22: 1018–1026.

Wetzel R.G. 2001. Limnology: Lake and River Ecosystems. 3rd ed. Academic Press, San Diego, pp. 1006.

Wolock D.M., Fan J. and Lawrence G.B. 1997. Effects of basin size on low-flow stream chemistry and subsurface contact time in the Neversink River Watershed, New York. Hydrol. Process. 11: 1273–1286.