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Controls on surface water chemistry in two lake-watersheds in the Adirondack region of New York: differences in nitrogen solute sources and sinks

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Abstract:

The southwestern Adirondack region of New York receives among the highest rates of atmospheric nitrogen (N) deposition in the USA. Atmospheric N deposition to sensitive ecosystems, like the Adirondacks, may increase the acidification of soils through losses of exchangeable nutrient cations, and the acidification of surface waters associated with enhanced mobility of nitrate (NO_3^-). However, watershed attributes, including surficial terrestrial characteristics, in-lake processing, and geological settings, have been found to complicate the relationships between atmospheric N deposition and N drainage losses. We studied two lake-watersheds in the southwestern Adirondacks, Grass Pond and Constable Pond, which are located in close proximity (~26 km) and receive similarly high N deposition, but have contrasting watershed attributes (e.g. wetland area, geological settings). Since the difference in the influence of N deposition was minimal, we were able to examine both within- and between-watershed influences of land cover, the contribution of glacial till groundwater inputs, and in-lake processes on surface water chemistry with particular emphasis on N solutes and dissolved organic carbon (DOC). Monthly samples at seven inlets and one outlet of each lake were collected from May to October in 1999 and 2000. The concentrations of NO_3^- were high at the Grass Pond inlets, especially at two inlets, and NO_3^- was the major N solute at the Grass Pond inlets. The concentrations of likely weathering products (i.e. dissolved Si, Ca^{2+}, Mg^{2+}, Na^+) as well as acid neutralizing capacity and pH values, were also particularly high at those two Grass Pond inlets, suggesting a large contribution of groundwater inputs. Dissolved organic N (DON) was the major N solute at the Constable Pond inlets. The higher concentrations of DON and DOC at the Constable Pond inlets were attributed to a large wetland area in the watershed. The DOC/DON ratios were also higher at the Constable Pond inlets, possibly due to a larger proportion of coniferous forest area. Although DON and DOC were strongly related, the stronger relationship of the proportion of wetland area with DOC suggests that additional factors regulate DON. The aggregated representation of watershed physical features (i.e. elevation, watershed area, mean topographic index, hypsometric-analysis index) was not clearly related to the lake N and DOC chemistry. Despite distinctive differences in inlet N chemistry, NO_3^- and DON concentrations at the outlets of the two lakes were similar. The lower DOC/DON ratios at the lake outlets and at the inlets having upstream ponds suggest the importance of N processing and organic N sources within the lakes. Although an inverse relationship between NO_3^- and DOC/DON has been suggested to be indicative of a N deposition gradient, the existence of this relationship for sites that receive similar atmospheric N deposition suggest that the relationship between NO_3^- and the DOC/DON ratio is derived from environmental and physical factors. Our results suggest that, despite similar wet N deposition at the two watershed sites, N solutes entering lakes were strongly affected by hydrology associated with groundwater contribution and the presence of wetlands, whereas N solutes leaving lakes were strongly influenced by in-lake processing. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS Adirondacks; atmospheric deposition; surface water; nitrate; DOC; DON; cations; anions; groundwater contribution; land cover

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INTRODUCTION

Atmospheric nitrogen (N) deposition has been chronically high in the northeastern USA since the early 1960s (Driscoll *et al.*, 2003a) and the Adirondack region of New York is among the areas receiving the highest rates of atmospheric N deposition in the USA. Atmospheric N deposition to ecosystems that are sensitive to inputs of strong acids, like the Adirondacks, can increase the acidification of soils through losses of exchangeable nutrient cations, and the acidification of surface waters associated with enhanced mobility of nitrate (NO_3^-) (Aber *et al.*, 1998; Fenn *et al.*, 1998; Driscoll *et al.*, 2001). Across the entire region of eastern New York State and New England, the spatial pattern of NO_3^- concentrations in surface waters coincides with the spatial pattern of N deposition, with values decreasing from the west to the east (Aber *et al.*, 2002). However, within subregions,

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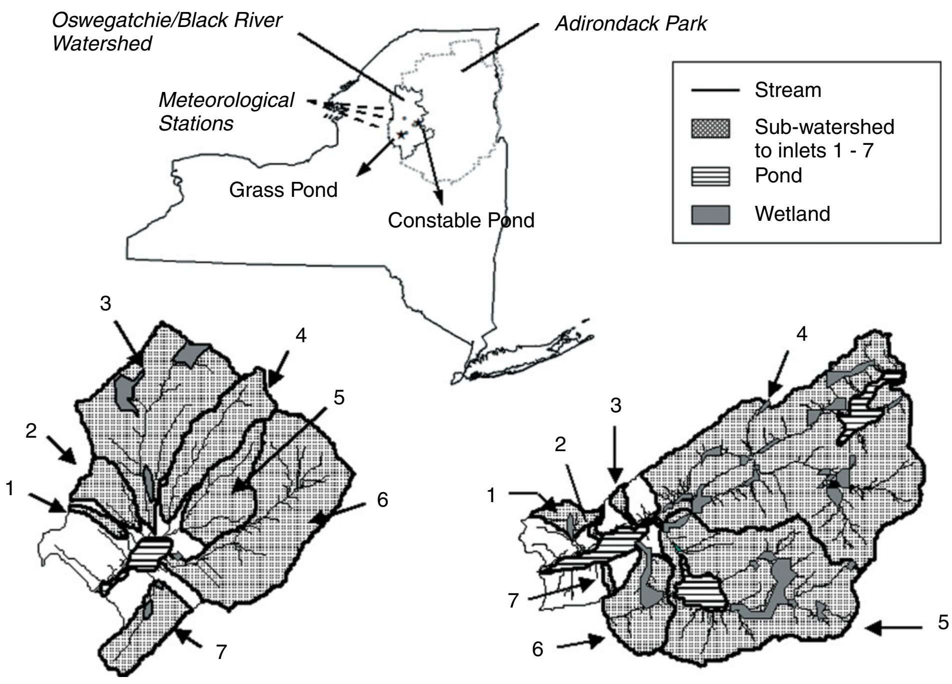
such as the Catskill Mountains of New York and the White Mountains of New Hampshire, NO_3^- drainage losses are highly varied and are not strongly related to N deposition (Aber *et al.*, 2002; Campbell *et al.*, 2004). Further, contrasting temporal trends have been observed in surface water NO_3^- concentrations across the region. For example, increases in stream water NO_3^- have been noted in West Virginia (Peterjohn *et al.*, 1996), whereas NO_3^- levels in stream water in New Hampshire (Likens *et al.*, 1996; Goodale *et al.*, 2003) and in several lakes in the Adirondacks (Driscoll *et al.*, 2003b) have declined. These spatial and temporal patterns indicate the high degree of complexity in the responses of forest ecosystems to N deposition.

Concerns over the impacts of N deposition on acid-sensitive ecosystems have led to efforts to identify the factors that could regulate biogeochemical N cycling, including atmospheric N deposition (e.g. Miller *et al.*, 1993; Weathers *et al.*, 2000; Aber *et al.*, 2002), climate (e.g. Mitchell *et al.*, 1996; Murdoch *et al.*, 1998), aggregated land cover or physical features (e.g. Prepas *et al.*, 2001; Sueker *et al.*, 2001), surficial topography (Creed *et al.*, 1996; Creed and Band, 1998), the extent of catchments underlain by certain surficial materials, such as glacial till (e.g. Clow *et al.*, 1996) or geological N sources (Holloway and Dahlgren, 2001), tree species composition and related soils (e.g. Lovett and Rueth, 1999; Lovett *et al.*, 2004; Christopher *et al.*, 2006), land-use history (e.g. Compton and Boone, 2000; Goodale and Aber, 2001), and the status of 'N saturation' (e.g. Stoddard, 1994; Fenn *et al.*, 1998).

In the Adirondacks, wet N deposition exhibited significant, but limited, effects on N drainage losses and N retention for 52 Adirondack long-term monitoring (ALTM) lake-watersheds (Ito *et al.*, 2005). Factors other than atmospheric N deposition that were found to be important in regulating N drainage loss and retention included the presence of wetlands, vegetation composition, elevation, and the processing that occurred within ponded waters. Further, geological characteristics could be primary effects on surface water chemistry. For groundwater sources recharging to a lake in the southwestern Adirondacks, deep groundwater was highly enriched in NO_3^- and base cations with higher acid neutralizing capacity (ANC) and pH than shallow groundwater (Schafran and Driscoll, 1993). The enrichment in deep groundwater suggests the potential importance of geological and hydrological characteristics on surface water chemistry in the Adirondack region. Since wetlands constitute a large proportion ($\sim$14%) of the land surface in the Adirondacks (Roy *et al.*, 1996), surface water chemistry in this region is also expected to reflect the importance of NO_3^- reduction (McHale *et al.*, 2000, 2004; Chapman *et al.*, 2001) via denitrification and the increase in dissolved organic carbon (DOC) (Eckhardt and Moore, 1990; Dillon and Molot, 1997) that occur in wetlands. The relationships of wetlands to N solutes are complicated by the presence in some Adirondack shrub wetland sites of the nitrogen-fixing species speckled alder, *Alnus incana* ssp. *rugosa*. The presence of this alder in high density may contribute to the accumulation of NO_3^- in groundwater, suggesting that the N fixed can subsequently be nitrified (Kiernan *et al.*, 2003).

Grass Pond and Constable Pond are located in close proximity to each other ($\sim$26 km) and at similar elevations in the southwestern Adirondacks (Figure 1), where some of the highest rates of acidic deposition in the Adirondacks are found (Driscoll *et al.*, 1991; Ito *et al.*, 2002). In the present study, these two lake-watersheds were selected among the ALTM lakes to (a) minimize the difference in the influence of atmospheric N deposition and focus on other possible factors, such as wetlands, which could affect N solutes and (b) separate the terrestrial systems from the entire lake watershed systems by examining surface waters at both the lake inlets and outlets. Wet N deposition was predicted to be similar at these neighbouring sites (384 mol N ha^{-1} $year^{-1}$ and 366 mol N ha^{-1} $year^{-1}$ in Grass Pond and Constable Pond watersheds respectively for the period from 1998 to 2000; Ito *et al.*, 2002). Both sites are drainage lakes having distinct surface outlets and similar ratios of watershed area/lake surface area and hydraulic residence time (Table I). Previously, Grass Pond watershed was evaluated with respect to the role of atmospheric sulphur deposition and sediment accumulation by Holdren *et al.* (1984), and Constable Pond watershed was intensively examined as a part of a study of the North Branch of the Moose River (e.g. Goldstein *et al.*, 1987; Newton *et al.*, 1987).

Possible influencing factors that could be important in forested watersheds are illustrated in Figure 2, focusing on those found to be important in the region in the previous studies (e.g. Schafran and Driscoll, 1993; McHale *et al.*, 2000; Ito *et al.*, 2005). As illustrated, we examined watershed surficial characteristics (wetlands, land cover/forest type, soil characteristics, aggregated physical attributes of the watersheds, e.g. subwatershed area, elevation, mean topographic index (TI), and hypsometric-analysis index (HI) (Table II)), the contribution of groundwater inputs to the watersheds based on the thickness of glacial till underlying the watersheds, and climate effects. The TI expresses the likelihood of area of saturation based on topography (Beven *et al.*, 1995; Beven, 1997). The HI, which represents a geomorphologic feature, is the relative height at which a watershed is divided into two equal surface areas (Langbein, 1947; Strahler, 1952; Gatwood *et al.*, 2000). Changes in the concentrations of N solutes with water draining through the lakes were evaluated by comparing the lake inlet and outlet chemistry. In addition to N solutes, which include NO_3^-, ammonium (NH_4^+) and dissolved organic nitrogen (DON), DOC was examined to characterize its relationship to DON. Dissolved silica (dissolved Si), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), sulphate (SO_4^{2-}), chloride (Cl^-), pH, and ANC were also examined to help identify geologic sources and/or processes affecting surface water chemistry.



Grass Pond watershed
& 7 sub-watersheds

Constable Pond watershed
& 7 sub-watersheds

Figure 1. The locations of the Grass Pond and Constable Pond watersheds in the Adirondack Park, New York

Table I. Site characteristics of Grass Pond and Constable Pond watersheds

	Units	Watershed	
		Grass Pond	Constable Pond
Attribute			
Location		43°41′25″N 75°3′54″W	43°49′50″N 74°52′16″W
Area (WA)	ha	237	936
Elevation, lake	m	546	582
Lake surface area (LA)	ha	5·3	20·6
Drainage ratio (WA/LA)	ha ha^{-1}	44·7	45·4
Lake depth, max.	m	5·2	4·0
Hydraulic residence time	year	0·04	0·06
Deciduous forest[a]	% watershed	36	11
Mixed forest[a]	% watershed	53	38
Coniferous forest[a]	% watershed	1·8	31
Wetland area[a]	% watershed	5·3	9·6
Thick (>3 m) glacial till and stratified drift[a]	% watershed	23	0
Climate conditions and discharge			
Estimated precipitation (May to October)	cm		
1999		56·7	57·2
2000		62·0	62·4
Estimated mean temperature (May to October)	°C		
1999		14·9	14·8
2000		12·7	12·6
Estimated discharge (May to October)	cm		
1999		21·3	21·1
2000		30·0	30·2
Estimated wet N deposition	mol N ha^{-1} year^{-1}		
1999		312	297
2000		431	409

[a] Calculated from GIS data.

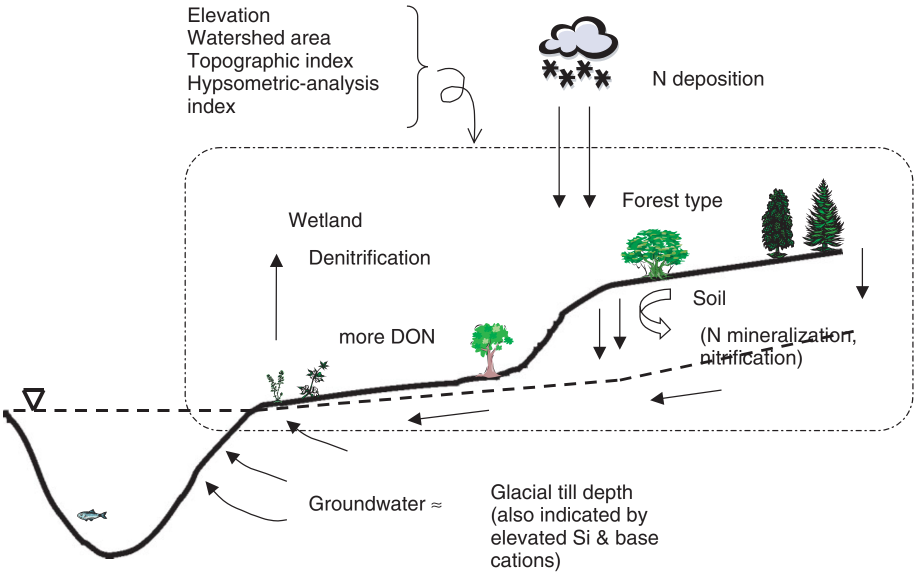


Figure 2. A conceptual model for biogeochemical processes influencing surface water N and DOC chemistry at the study sites

Table II. Characteristics for seven subwatersheds of Constable Pond and Grass Pond

Subwatershed	Area (ha)	Elevation[a] (m)	Mean TI[b]	HI[c]	Average stream gradient (m km^{-1})	Forest[d] (%)			Wetland[d] (%)		
						Deciduous	Mixed	Coniferous	Total	Shrub	Forested
Constable Pond											
1	16	608	6·33	0·19	74	0	9	69	23	19	4
2	2	594	6·60	0·26	50	0	11	86	0	0	0
3	4	614	5·78	0·34	117	0	76	21	2	0	2
4	453	673	5·93	0·36	53	8	43	30	9	2	6
5	276	658	6·19	0·36	50	20	38	22	9	2	7
6	62	658	6·01	0·23	111	14	42	22	17	9	8
7	3	615	5·84	0·35	150	0	26	74	0·01	0·01	0
Grass Pond											
1	2	591	5·58	0·41	174	77	23	0	0	0	0
2	10	587	5·77	0·65	124	73	27	0	0	0	0
3	60	597	5·97	0·67	66	47	42	0	11	0·2	11
4	25	618	5·49	0·53	111	35	65	0	0	0	0
5	21	612	5·60	0·42	143	31	69	0	0	0	0
6	64	616	5·77	0·56	84	35	64	0·3	0	0	0
7	15	601	5·32	0·19	73	0	71	22	6	1	6

[a] Elevation is the mean value of the maximum and minimum elevations of the subwatershed.
[b] TI: topographic index.
[c] HI: hypsometric-analysis index.
[d] The percentage of subwatershed area occurring as the respective land cover type.

This study thus focused on the following questions: (a) Are the influences of the contribution of groundwater inputs to NO_3^- concentrations comparable to the influences of watershed surficial characteristics and processes? (b) Among surficial characteristics and processes, is the extent of wetland area a major regulator of NO_3^-, DON, and DOC concentrations at lake inlets? (c) Are within-lake sources and processes important regulators of lake outlet N chemistry?

METHODS

Study sites

The Grass Pond and Constable Pond watersheds are located within the Oswegatchie/Black River drainage in the southwestern Adirondack region of New York (Figure 1; Table I). The climate is classified as humid-continental; at the three nearby meteorological stations of National Climate Data Center (Big Moose, Old Forge, and Stillwater Reservoir), mean annual precipitation was 115 cm and 141 cm and mean annual temperature was 5·6 °C and 4·2 °C in 1999 and 2000 respectively. The bedrock geology in the Adirondacks is mainly gneisses and metasedimentary rocks with marble and other calcite-bearing bedrock in a few scattered locations. The soils are generally shallow and acidic, especially in the organic-rich upper horizons, and the soils are primarily Spodosols (Driscoll *et al.*, 1991).

Northern hardwoods are predominant in the mostly forested vegetation, including yellow birch (*Betula* *alleghaniensis*), American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*) and paper birch (*Betula papyrifera*). Coniferous vegetation in the watersheds includes red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*). The site characteristics of Grass Pond and Constable Pond watersheds are summarized in Table I and are described in more detail elsewhere (e.g. Holdren *et al.*, 1984; McMartin, 1985; Cronan *et al.*, 1987; Newton *et al.*, 1987). The seven inlets of Grass Pond and Constable Pond were numbered clockwise from 1 to 7 around each lake (hereinafter, Grass 1 to 7 and Constable 1 to 7; Figure 1). There are upstream ponds flowing into Constable Pond in Constable 4 and 5 (Figure 1).

Chemical analysis of surface waters

Surface water samples were collected monthly at or near the surface of the seven inlets and one outlet of each pond by the Adirondack Lakes Survey Corporation (ALSC) from May to October in 1999 and 2000. The samples were maintained at 1 °C and filtered with pre-combusted glass-fibre (Whatman GF/F) filter prior to analysis. The samples were analysed at SUNY-ESF or Syracuse University for NO_3^- by suppressed ion chromatography, NH_4^+ by colorimetric automated phenate, total N by persulphate digestion, and DOC by ultraviolet-promoted persulphate oxidation. The DON concentration was calculated as the difference between the concentrations of total N and dissolved inorganic nitrogen (NO_3^- plus NH_4^+). The lake water samples were also analysed for SO_4^{2-}, Cl^- (by ion chromatography), pH (potentiometrically with glass electrode), SiO_2 (by colorimetric molybdate), Ca^{2+}, Mg^{2+}, Na^+ (by atomic absorption spectrophotometry), and ANC (by strong acid titration with Gran plot analysis).

Analysis of surficial geology and soils

The Grass Pond and Constable Pond watersheds are underlain by similar bedrock and glacial till of similar mineralogy. Chemistry of this surficial glacial materials included SiO_2 (70·9 wt%), CaO (2·6 wt%), K_2O (3·8 wt%), MgO (1·4 wt%), Na_2O (2·6 wt%), Al_2O_3 (11·8 wt%), among others. More details on chemistry of the glacial till of this area were presented by Gherini *et al.* (1989). Surficial geology (glacial drift and depth to bedrock) in the Grass Pond watershed was mapped in the summer of 1989, based on samples from pits and field observation as well as aerial photographs. Measured depths in the thick till area ranged from 4 to 24 m. As part of this mapping effort, five seismic lines were run in the area mapped as thick till. Four soil pits were excavated to a depth of approximately 1 m. Samples were collected by horizon and analysed for grain-size distribution, exchangeable bases, exchangeable acidity, and percentage heavy minerals (specific gravity >2·95). The Constable Pond watershed was mapped in the summer of 1983 in the same manner as the Grass Pond watershed. There were five soil pits sampled in the Constable Pond watershed for analysis (Newton *et al.*, 1987; unpublished data).

Data analysis

Precipitation quantities and minimum and maximum air temperatures were estimated using the empirical models of Ito *et al.* (2002) and daily weather data from the Huntington Wildlife Forest (HWF), a National Atmospheric Deposition Program/National Trends Network site, located in the central Adirondacks. Discharge rates for the entire Grass Pond and Constable Pond watersheds were estimated using the BROOK90 hydrological model (Federer, 2001), which was developed for small, forested watersheds. This model was previously used to estimate the water flux in a gauged watershed in the central Adirondacks and the model fit was comparable to the results from the Hubbard Brook Experimental Forest (White Mountains, New Hampshire) for which the model was originally developed (Mitchell *et al.*, 2001). For the analyses in our study, simulations were made using the inputs of daily precipitation and minimum and maximum temperatures as estimated above.

The boundaries of the lake watersheds and the subwatersheds to the lake inlets (defined from the lake inlet sampling locations) were delineated using the US Geological Survey digital elevation models (DEMs) with a pixel width of 10 m by external computation based on the flow accumulation values calculated by TARDEM (Tarboton, 2000). Mean TI, HI, and stream gradient were calculated using DEMs for each subwatershed. The spatial maps of wetlands (with vegetation-based classifications), land cover, land history, 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 data. The definitions of deciduous, coniferous, and mixed forests, and wetlands and the classification of wetlands are provided in Ito *et al.* (2005). The locations of wetlands in the seven subwatersheds of both the Grass Pond and Constable Pond watersheds are shown in Figure 1.

After the boundaries of watersheds and subwatersheds were delineated, the spatial data were processed using ArcInfo Workstation Arc versions 8·0·2 and 8·3, ArcView versions 3·2 and 3·3, and ArcMap 8·3 (Environmental Systems Research Institute, Inc.). The proportion of watershed area occurring as the respective land cover or wetland type, or underlain by thick glacial till, was expressed as a percentage.

Univariate linear regression analyses were applied to examine possible influences on the lake water chemistry of watershed characteristics (e.g. deciduous, mixed, coniferous forest, wetland area), after correlation analyses between the factors were conducted as tests for multicollinearity. There were some significant correlations between total wetland area and a subcategory of wetlands (e.g. total wetland versus scrub/shrub wetland areas for the Constable Pond subwatersheds) or between forested wetland and deciduous forest areas in the Constable Pond subwatersheds ($r = 0{\cdot}85$, $p = 0{\cdot}015$). But these pairs of variables were not simultaneously used as independent variables because they were at a different level of classification, e.g. (i) total forest area and

(ii) deciduous versus coniferous forest areas. For the Grass Pond subwatersheds, the correlation between shrub wetland and coniferous areas was significant ($r = 0{\cdot}96$, $p = 0{\cdot}0008$), which may be due to Grass Pond subwatershed 7 containing relatively large areas of both conifers and shrub wetlands among Grass Pond subwatersheds. There were no significant correlations between other variables. Regression analyses also included testing for normality (Shapiro and Wilk W statistics), constant variance (residual plots and the test of first- and second-moment specification), and outliers (residual plots and externally Studentized residuals). Stepwise linear regression analyses were also employed to examine any combined effects of factors. However, stepwise regression analyses either showed similar regression relationships as univariate linear regression analyses or exhibited no significant relationships, except when the DOC/DON ratio was used as a dependent variable. Therefore, the results of univariate regression analyses were emphasized as they provided useful information on the major influencing factors. Statistical analyses were performed using SAS version 8·01 (SAS, 2002).

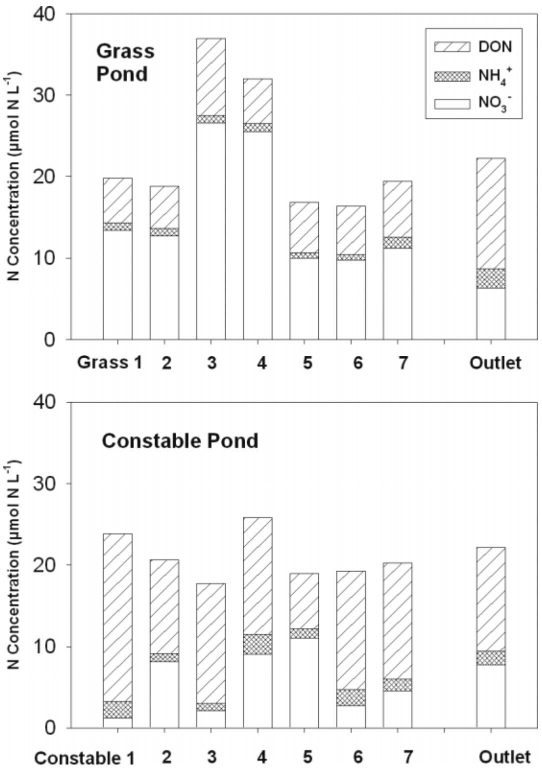


Figure 3. Mean monthly concentrations of NO_3^-, NH_4^+, and DON at seven lake inlets and one outlet of each of Grass Pond and Constable Pond

RESULTS AND DISCUSSION

Nitrogen solutes and dissolved organic carbon at lake inlets

NO_3^- was the major N solute at all seven Grass Pond inlets (59–80% of total N; mean: 66%). The mean monthly concentrations of NO_3^- were higher at the Grass Pond inlets (mean: 16 µmol N l^{-1}) than the Constable Pond inlets (mean: 6 µmol N l^{-1}) (Figure 3; Table III). Grass 3 and 4 exhibited particularly high NO_3^- concentrations, compared with the other Grass Pond inlets. At the Constable Pond inlets, the concentrations of DON were much higher (mean: 14 µmol N l^{-1}) than at the Grass Pond inlets (mean: 6 µmol N l^{-1}) (Figure 3; Table III). The predominance of DON in dissolved nitrogen (36–86% of total N; mean: 66%) at the Constable Pond inlets was consistent with other studies

Table III. Mean concentrations (with standard errors are in parentheses) calculated from monthly values of NO_3^-, NH_4^+, DON, and DOC and DOC/DON ratio at seven inlets and at the outlet of Constable Pond and Grass Pond from May to October

		NO_3^- (µmol l^{-1})		NH_4^+ (µmol l^{-1})		DON (µmol N l^{-1})		DOC (µmol C l^{-1})		DOC/DON	
		1999	2000	1999	2000	1999	2000	1999	2000	1999	2000
Constable Pond											
Inlet	1	2 (1)	0.4 (0)	3 (2)	1 (1)	22 (3)	19 (3)	1657 (203)	1311 (209)	75	69
	2	10 (5)	7 (2)	1 (0)	1 (1)	12 (6)	11 (2)	780 (95)	758 (84)	65	69
	3	3 (2)	2 (0)	1 (0)	1 (0)	15 (4)	15 (1)	1051 (134)	944 (55)	70	63
	4	11 (3)	8 (2)	2 (1)	3 (2)	16 (3)	13 (2)	689 (78)	565 (42)	43	43
	5	13 (4)	10 (3)	1 (0)	1 (0)	7 (2)	7 (2)	289 (22)	294 (10)	41	42
	6	3 (1)	3 (2)	3 (1)	1 (0)	17 (3)	12 (1)	1150 (143)	1028 (50)	68	86
	7	5 (4)	4 (2)	2 (1)	1 (0)	22 (13)	8 (2)	659 (125)	582 (43)	30	73
Outlet		9 (4)	7 (3)	1 (0)	2 (1)	14 (3)	11 (2)	475 (50)	478 (39)	34	43
Grass Pond											
Inlet	1	17 (3)	10 (2)	1 (0)	1 (0)	5 (2)	6 (2)	280 (29)	277 (27)	56	46
	2	14 (2)	11 (2)	1 (1)	1 (0)	6 (3)	4 (1)	189 (22)	170 (17)	32	42
	3	32 (4)	22 (4)	1 (0)	1 (0)	8 (3)	11 (3)	274 (44)	407 (117)	34	37
	4	28 (3)	24 (3)	1 (1)	1 (0)	7 (2)	4 (2)	231 (40)	222 (20)	33	55
	5	12 (2)	8 (2)	1 (0)	1 (0)	5 (1)	8 (3)	253 (13)	257 (17)	50	32
	6	11 (4)	8 (2)	1 (0)	1 (0)	6 (1)	6 (2)	320 (19)	340 (27)	53	56
	7	20 (12)	4 (2)	1 (1)	1 (1)	7 (1)	7 (2)	337 (12)	393 (38)	48	56
Outlet		5 (3)	7 (3)	2 (1)	3 (1)	14 (1)	13 (2)	380 (34)	347 (35)	27	27

reporting that DON can constitute an important fraction in dissolved N in stream and soil waters in forested ecosystems (e.g. Sollins *et al.*, 1980; Qualls *et al.*, 1991; Hedin *et al.*, 1995; Arheimer *et al.*, 1996; Currie *et al.*, 1996; Hagedorn *et al.*, 2000; McHale *et al.*, 2000). In contrast, much higher concentrations of NO_3^- than DON were found at Grass 3 and 4. The mean monthly concentration of DOC was also higher at the Constable Pond inlets (837 μmol C l^{-1}) than the Grass Pond inlets (283 μmol C l^{-1}) (Table III). Among the Constable Pond inlets, the NO_3^- concentrations were higher at Constable 4 and 5, which have relatively large subwatershed areas with upstream ponds in their subwatersheds (Table III). The concentrations of DON and DOC were markedly lower at Constable 5 than at the other inlets. The NH_4^+ concentrations were low (<3 μmol N l^{-1}) at the inlets of both lakes, with concentrations being slightly higher at the Constable Pond inlets.

Nitrogen solutes and dissolved organic carbon at the lake inlets versus outlets: in-lake processing?

A comparison of solute concentrations between the lake inlets and outlets suggests that NO_3^- was retained, DON increased, and the DOC/DON molar ratio decreased as water was transported through Grass Pond (Table III). Monthly concentrations of NO_3^- and the DOC/DON ratio at the Grass Pond outlet exhibited much less temporal variation than at the Grass Pond inlets, consistent with a study that compared lake and stream sites in southern Norway (Kaste *et al.*, 2003). At the Constable Pond outlet, mean NO_3^- concentrations calculated from monthly values were lower than at Constable 2, 4 and 5, but were higher than at the other inlets. The concentrations of NO_3^- and DON at the Constable Pond outlet were similar to those at the Grass Pond outlet, whereas DOC concentrations and DOC/DON ratios were higher at the Constable Pond outlet than at the Grass Pond outlet. The similarity of NO_3^- and DON between the outlets of the two lakes, despite substantial differences in NO_3^- and DON between the inlets of the two lakes, suggest that: (i) there are differences in the relative importance of other water sources to the lakes, including ephemeral inflows, which were not examined, and groundwater contributions (Staubitz and Zarriello, 1989); and/or (ii) in-lake N processes play an important role as the water drains from the lake inlets through the outlets.

The DOC/DON ratios were higher at the Constable Pond inlets than the Grass Pond inlets primarily due to the higher DOC concentrations at the Constable Pond inlets (Table III). Among the Constable Pond inlets, the DOC/DON ratios were lower at Constable 4 and 5, which contain upstream ponds, and the ratios at these two inlets were comparable to those of the Constable Pond outlet. The mean DOC/DON ratio at Constable 7 was also low in 1999. Since DON at Constable 7 in 1999 had a much larger standard error than at other inlets and in 2000, the DOC/DON at Constable 7 in 1999 is not discussed further in comparison with those at Constable 4 and 5. The C/N ratios tend to be higher for dissolved organic matter (DOM) derived from terrestrial sources than autochthonous DOM from phytoplankton and aquatic plants (Clair *et al.*, 1994; Chapman *et al.*, 2001). Further, in a forest–grassland catchment of Switzerland, the DOC/DON ratios were found to decrease due to decreasing DOC export with increasing watershed scale from the subcatchments to the headwater catchment, despite relatively constant DON export (Hagedorn *et al.*, 2000). The decreases in DOC, lowering the DOC/DON ratios in lake waters, could be due to the removal of allochthonous DOC by metal-mediated coagulation (Schnitzer and Khan, 1972; Effler *et al.*, 1985; Schindler *et al.*, 1992), photo-oxidation of allochthonous DOC, or microbial degradation of photochemically transformed DOC (Kopáček *et al.*, 2003). The DOC/DON ratios at Constable 4 and 5 were mostly between the C/N ratios of autochthonous and allochthonous organic matter in lakes (approximately 12 and 45 to 50, respectively; Wetzel, 2001), suggesting that in-lake processes in upstream ponds may have been responsible for the lower DOC/DON ratios in Constable 4 and 5. The DOC/DON ratios at other Constable Pond inlets mostly exceeded 60 (Table III), which were higher than those reported for other streams in the eastern USA (Qualls and Haines, 1991; Goodale *et al.*, 2000; Lovett *et al.*, 2000), but comparable to the ratios in streams from remote sites in Chile (Hedin *et al.*, 1995) and in forest floor leachates (Qualls and Haines, 1991; Hedin *et al.*, 1995; McDowell *et al.*, 1998).

The higher DOC concentrations at the Constable Pond outlet than at the Grass Pond outlet might have resulted from much higher DOC concentrations at the Constable Pond inlets than at the Grass Pond inlets, thus reflecting terrestrial processes, such as those associated with wetlands and/or forest type (e.g. conifer). Yet, in-lake processes appeared to have some effects on DON and DOC at the outlets as well, because the DON and DOC concentrations also changed following transport through the lakes.

Year-to-year variations of chemistry

In both lake watersheds, the concentrations of NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, and Cl^-, as well as pH and ANC, were higher in 1999 than in 2000 at most lake inlets and outlets (Tables III–V). For example, the NO_3^- concentrations were higher in 1999 than 2000 by 17 to 75% at Grass Pond inlets (except at Grass 7: 351%), although the concentrations at the outlet were lower (−27%). At Constable Pond, the NO_3^- concentrations were higher in 1999 than 2000 by 18 to 54%, except at Constable 1 (432%). The concentrations of SO_4^{2-} and dissolved Si in the Grass Pond watershed and DON and DOC in the Constable Pond watershed were also higher in 1999 than in 2000 (Tables III–V).

The period from May to October in 2000 was wetter and colder than in the same months in 1999 (Table I). The combination of greater precipitation and lower temperature in 2000 resulted in substantially higher estimated discharges in 2000 than in 1999 from May to

Table IV. Mean concentrations (with standard errors are in parentheses) calculated from monthly values of dissolved Si, Ca^{2+}, Mg^{2+}, and Na^{+} ions at seven inlets and at the outlet of Constable Pond and Grass Pond from May to October

		Dissolved Si (μmol l^{-1})		Ca^{2+} (μmol l^{-1})		Mg^{2+} (μmol l^{-1})		Na^{+} (μmol l^{-1})	
		1999	2000	1999	2000	1999	2000	1999	2000
Constable Pond									
Inlet	1	118 (18)	104 (16)	25 (2)	26 (1)	10 (1)	8 (0)	28 (3)	22 (3)
	2	143 (19)	153 (11)	31 (4)	28 (1)	10 (1)	8 (0)	25 (1)	22 (2)
	3	112 (19)	133 (13)	31 (4)	27 (1)	9 (1)	8 (0)	26 (2)	23 (2)
	4	77 (9)	69 (4)	30 (2)	28 (1)	9 (1)	9 (0)	24 (2)	19 (2)
	5	58 (7)	57 (3)	36 (1)	35 (1)	11 (1)	11 (0)	23 (1)	20 (1)
	6	91 (14)	71 (12)	26 (2)	24 (1)	9 (1)	8 (1)	26 (3)	19 (3)
	7	118 (8)	123 (15)	25 (4)	24 (2)	7 (0)	8 (1)	25 (2)	21 (3)
Outlet		56 (6)	57 (5)	49 (7)	35 (2)	12 (1)	11 (1)	32 (6)	21 (2)
Grass Pond									
Inlet	1	192 (17)	161 (14)	39 (2)	35 (1)	11 (1)	10 (0)	48 (3)	41 (4)
	2	201 (14)	186 (20)	37 (0)	33 (1)	12 (1)	11 (1)	55 (3)	48 (6)
	3	291 (20)	253 (33)	78 (5)	66 (4)	31 (3)	27 (3)	84 (6)	72 (12)
	4	252 (22)	226 (31)	70 (4)	56 (4)	30 (3)	24 (4)	70 (8)	56 (10)
	5	125 (11)	103 (6)	26 (1)	22 (1)	8 (1)	7 (0)	33 (3)	27 (3)
	6	103 (9)	106 (14)	23 (1)	20 (0)	7 (1)	6 (0)	28 (3)	23 (3)
	7	125 (14)	120 (12)	18 (1)	16 (1)	5 (1)	5 (0)	28 (2)	26 (2)
Outlet		84 (9)	103 (7)	39 (1)	36 (1)	16 (1)	13 (1)	44 (4)	38 (4)

Table V. Mean concentrations (with standard errors are in parentheses) calculated from monthly values of SO_4^{2-}, Cl^{-}, ANC, H^{+}, and pH at seven inlets and at the outlet of Constable Pond and Grass Pond from May to October

		SO_4^{2-} (μmol l^{-1})		Cl^{-} (μmol l^{-1})		ANC (μeq l^{-1})		H^{+} (μmol l^{-1})		pH	
		1999	2000	1999	2000	1999	2000	1999	2000	1999	2000
Constable Pond											
Inlet	1	32 (10)	38 (6)	14 (2)	11 (2)	−25 (10)	−33 (7)	34 (7)	42 (4)	4·5	4·4
	2	80 (7)	69 (4)	13 (3)	11 (0)	−42 (4)	−43 (3)	48 (2)	46 (3)	4·3	4·4
	3	59 (6)	51 (2)	12 (3)	12 (3)	−38 (3)	−36 (3)	43 (3)	43 (2)	4·4	4·4
	4	48 (5)	50 (2)	10 (1)	8 (0)	−1 (6)	−11 (4)	16 (3)	20 (4)	4·8	4·7
	5	53 (2)	54 (1)	8 (1)	8 (0)	4 (2)	2 (4)	6 (1)	8 (1)	5·2	5·1
	6	37 (5)	33 (3)	11 (2)	10 (2)	−12 (9)	−26 (7)	26 (6)	34 (5)	4·6	4·5
	7	53 (9)	55 (4)	10 (2)	9 (1)	−13 (9)	−24 (3)	26 (4)	31 (2)	4·6	4·5
Outlet		48 (3)	48 (1)	9 (1)	8 (0)	46 (28)	5 (6)	3 (1)	8 (3)	5·5	5·1
Grass Pond											
Inlet	1	57 (4·2)	51 (1)	9 (1)	9 (0)	20 (2)	18 (2)	2 (0)	3 (1)	5·7	5·5
	2	58 (0·5)	57 (1)	9 (1)	8 (0)	26 (3)	23 (6)	1 (0)	2 (1)	6·0	5·7
	3	57 (0·9)	53 (2)	9 (1)	9 (1)	164 (18)	127 (28)	0.1 (0)	0 (0)	7·0	6·7
	4	62 (0·4)	60 (2)	10 (1)	9 (0)	115 (15)	80 (22)	0.2 (0)	0 (0)	6·7	6·4
	5	61 (1·1)	55 (2)	10 (1)	9 (0)	−6 (3)	−6 (2)	15 (2)	14 (1)	4·8	4·9
	6	59 (1·1)	54 (2)	9 (1)	8 (0)	−17 (14)	−18 (2)	24 (3)	25 (2)	4·6	4·6
	7	49 (3·0)	43 (4)	10 (2)	9 (2)	−24 (2)	−22 (2)	31 (2)	28 (2)	4·5	4·6
Outlet		48 (0·7)	46 (2)	8 (1)	6 (1)	46 (7)	34 (7)	1 (0)	1 (1)	6·2	5·9

October (Table I). Accordingly, the higher solute concentrations observed in 1999, especially NO_3^{-}, Ca^{2+}, and Mg^{2+}, may be due to: (a) greater relative contribution of groundwater inputs with high solute concentrations due to the lower precipitation and discharge rates in 1999; (b) higher N mineralization and nitrification rates due to warmer temperature in 1999; (c) changes in hydrologic flowpaths due to differences in precipitation; (d) a lower water table in wetland areas in the drier summer of 1999, resulting in lower rates of denitrification (e.g. Hefting *et al.*, 2004, for water table control of N cycling); and/or (e) higher evapotranspiration rates due to higher temperature in 1999, resulting in increased solute concentrations. Although the contribution of dry deposition was not determined, wet chemical deposition did not explain the higher solute concentrations in 1999, because wet deposition was estimated to be lower in 1999 than in 2000 (Table I). These results suggest the importance of climate influences on solute chemistry.

Contribution of groundwater inputs: a major influencing factor at Grass Pond inlets?

The major source of dissolved Si is the weathering of silicate minerals (Johnson, 1984). Dissolved Si concentrations at the lake outlets and at Constable 4 and 5, which have upstream ponds in their subwatersheds, were lower than those at other inlets, suggesting the influences of the processing within the lake, such as coagulation or the assimilation by diatoms (Wetzel, 2001). However, in the terrestrial environment, dissolved Si is relatively conservative, other than changes through such processes as the cementation forming secondary minerals, and is not highly subject to ion exchange (Drever and Clow, 1995; Kelly *et al.*, 1998). Silicate mineral weathering may regulate surface water concentrations of base cations and ANC as well (Clow *et al.*, 1996). Dissolved Si has been used to examine chemical weathering rates (Drever and Zobrist, 1992; Stonestrom *et al.*, 1998; White *et al.*, 1999), and could thus be used as an indicator of the contribution of groundwater inputs, together with other likely weathering products, such as base cations, ANC, and specific conductance (Hendershot *et al.*, 1992; Hinton *et al.*, 1994). At Grass 3 and 4, whereas vegetation uptake could decrease N concentrations during the growing season, high NO_3^- concentrations were observed from May to October, along with dissolved Si concentrations that were also much higher than other inlets of Grass Pond and the Constable Pond inlets (Tables III and IV). The mean NO_3^- concentrations increased with increasing dissolved Si concentrations at the Grass Pond inlets (Table VI; Figure 4). The Si/NO_3^- molar ratios at the Grass Pond inlets were within relatively small ranges, i.e. 6–14 (mean: 10) and 10–27 (mean: 15) in 1999 and 2000 respectively. The concentrations of other likely weathering products (Ca^{2+}, Mg^{2+}, and Na^+), as well as ANC and pH, were also higher at Grass 3 and 4 than at the other inlets of Grass Pond and the Constable Pond inlets (Tables IV and V). At the Grass Pond inlets, NO_3^- concentrations also increased with increasing concentrations of other mineral weathering products, including Ca^{2+} (Table VI). The strong correlations between dissolved Si and Ca^{2+} (Table VI) suggest a source of Ca^{2+} influenced by extensive mineral weathering at the Grass Pond inlets. Observations of groundwater seepage in Grass 3 and 4 at the end of the dry summer in 2002 suggested the importance of the influence of groundwater inputs in these two subwatersheds.

At the Constable Pond inlets, the dissolved Si concentrations were lower (Table IV) and no relationship existed between NO_3^- and dissolved Si (Figure 4). The Si/NO_3^- ratio varied greatly among the inlets, ranging from 5 to 60 (mean: 26) and from 6 to 281 (mean: 65) in 1999 and 2000 respectively. There was no significant relationship between dissolved Si and Ca^{2+}, and positive correlations between NO_3^- and Ca^{2+} at the Constable Pond inlets were not as strong as for the Grass Pond inlets (Table VI).

The Integrated Lake Watershed Acidification Study, conducted in this same region of the Adirondacks, showed that the thickness of unconsolidated surficial sediments influenced water flowpaths and that thick glacial till cover can support a large groundwater reservoir (April and Newton, 1984). In an Adirondack lake-watershed with thick glacial till (Panther Lake), precipitation infiltrated glacial till during most hydrologic events. As a result of the long hydraulic residence time within till deposits, the water reacted with the till minerals, and eventually drained into the lake via groundwater seepage.

Table VI. Selected results of regression analyses

Variables		Year	Grass Pond inlets			Constable Pond inlets		
			Relationship[a]	r^2	p	Relationship[a]	r^2	p
NO_3^-	Dissolved Si	1999	(+)	0·74	0·01	—	—	—
		2000	(+)	0·81	0·006	—	—	—
NO_3^-	Ca^{2+}	1999	(+)	0·76	0·01	(+)	0·58	0·046
		2000	(+)	0·92	0·0006	(+)	0·56	0·05
Ca^{2+}	Dissolved Si	1999	(+)	0·92	0·0007	—	—	—
		2000	(+)	0·92	0·0006	—	—	—
NO_3^-	pH	1999	(+)	0·64	0·032	(+)	0·42	0·1
		2000	(+)	0·84	0·003	(+)	0·53	0·060
NO_3^-	DON	1999	(−)	0·54	0·061	(−)	0·53	0·063
		2000	—	—	—	(−)	0·56	0·050
NO_3^-	DOC	1999	—	—	—	(−)	0·69	0·021
		2000	—	—	—	(−)	0·81	0·0006
DON	DOC	1999	—	—	—	(+)	0·45	0·10
		2000	(+)	0·54	0·06	(+)	0·79	0·007
SO_4^{2-}	% Total wetland area	1999	—	—	—	(−)	0·74	0·013
		2000	—	—	—	(−)	0·72	0·016
DON/DOC	NO_3^-	1999	(−)	0·53	0·06	—	—	—
		2000	—	—	—	—	—	—
DON/DOC	pH	1999	(−)	0·86	0·002	(−)	0·56	0·05
		2000	—	—	—	(−)	0·52	0·06
DON/DOC	Ca^{2+}	1999	(−)	0·77	0·008	—	—	—
		2000	—	—	—	(−)	0·42	0·1

[a] Relationship: positive (+), negative (−), or no '—' relationship ($p > 0.10$).

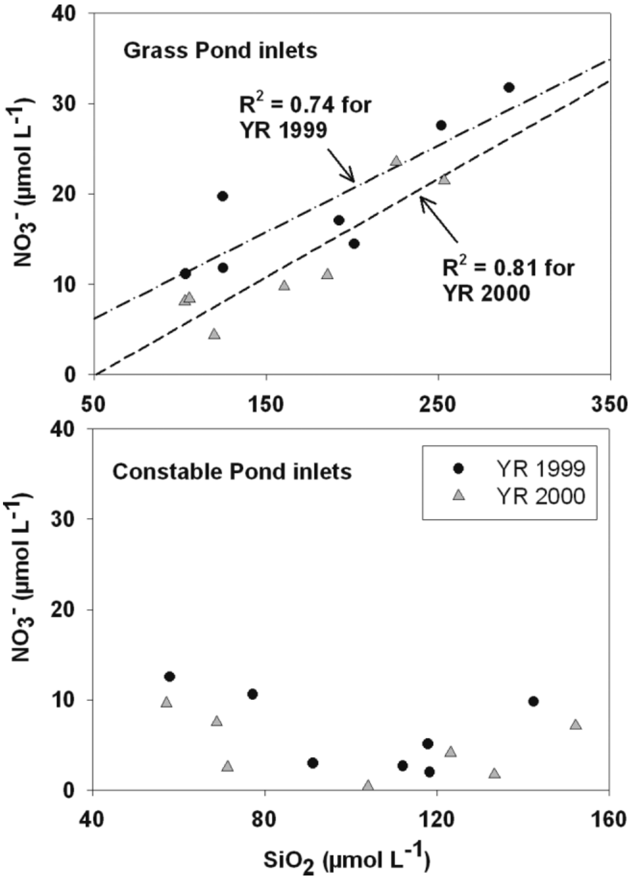


Figure 4. The relationships between the concentrations of NO_3^- and dissolved Si at the inlets of Grass Pond and Constable Pond

High pH (7·9) and ANC (1740 μeq l^{-1}) in deep groundwater within the glacial till at Panther Lake watershed suggested a high rate of supply of base cations and ANC from minerals in glacial till (feldspar and hornblende) (Newton *et al*., 1987). In Yosemite National Park, California, the concentrations of the weathering products in surface water were related with the extent of catchments underlain by surficial material, mostly glacial till (Clow *et al*., 1996).

Portions of Grass Pond subwatersheds 3, 4, and 7 have thick (>3 m) deposits of glacial till (Figure 5), whereas the other parts of these three subwatersheds, as well as Grass 1, 2, 5, and 6 and all seven Constable Pond subwatersheds, are underlain by thin glacial till. In Grass 3 and 4 in particular, 43% and 46% of the respective subwatershed areas are covered by thick glacial till, some of which lies under the stream channel in the lower part of the subwatersheds. In Grass 7, only 24% of the subwatershed is covered with thick glacial till and much of the area underlain by thick till in Grass 7 is in the upstream reach (Figure 5), which would limit the influence of groundwater inputs from thick glacial till. Groundwater seepage was not evident at the end of dry summer season in Grass 7.

High NO_3^- concentrations in the stream water in the summer or autumn, or during the baseflow period, have been also observed in other northern temperate forest catchments (Burns *et al*., 1998; McHale *et al*., 2002; Schiff *et al*., 2002). The contribution of groundwater inputs can elevate NO_3^- concentrations in surface waters by some combination of two mechanisms.

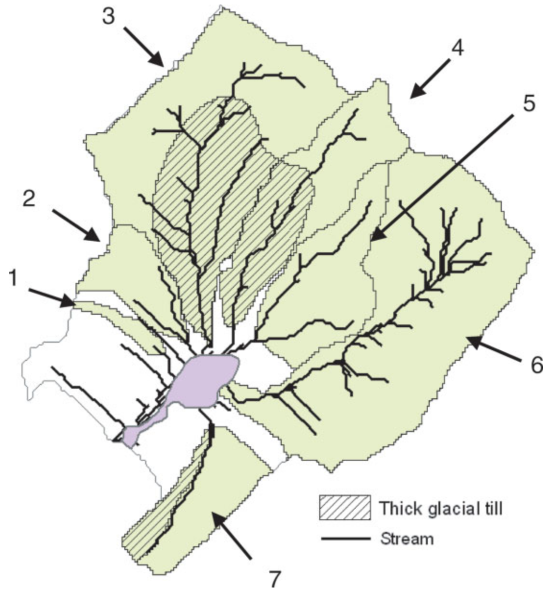


Figure 5. The coverage of thick glacial till in seven Grass Pond subwatersheds

First, the groundwater itself contains high NO_3^- concentrations and the large contribution of groundwater inputs from thick glacial till could further increase surface water NO_3^-. Examples of such relationships have been reported in southeastern Canada, where a catchment exporting high NO_3^- had much higher groundwater NO_3^- concentrations than a catchment with the lower stream water NO_3^- (Schiff *et al*., 2002). In Dart Lake, located in the same region of the Adirondacks as the watersheds in the present study, groundwater transported within the deep surficial deposits was characterized by higher concentrations of NO_3^-, together with high base cation concentrations, ANC, and pH, as well as lower concentrations of organic anions and SO_4^{2-} (Schafran and Driscoll, 1993). In an alpine catchment in Colorado, positive correlations between NO_3^- concentrations and the chemical species indicating weathering contributions (including dissolved Si, Ca^{2+}, and ANC) were used to show that the NO_3^- was derived from basin sources, not from snowpack or atmospheric deposition (Williams *et al*., 1997). Possibilities for N sources also include geologic origins, as were found in certain areas in California (Holloway and Dahlgren, 2001), but similar geological sources are not likely in the Adirondack region. It is not likely that N sources are associated with direct human impacts, because these watersheds are located in relatively pristine locations with no housing. In nearby Dart Lake, high NO_3^- observed in deep groundwater did not suggest possible NO_3^- sources deep in the geological structure, but was attributed to the lack of removal by vegetative and/or microbial activity (Schafran and Driscoll, 1993).

Second, elevated pH and base cation levels due to substantial inputs of groundwater with high pH and base cation concentrations could promote NO_3^- production. Nitrogen mineralization and net nitrification rates have been found to be higher at higher soil pH (Ste-Marie and Paré, 1999) and base cation levels (Ohrui *et al.*, 1999).

Influences of watershed physical features and land cover on nitrogen solutes and dissolved organic carbon

The concentrations of N solutes, DOC, and other chemical species in soils and drainage waters have been shown to be influenced by watershed physical characteristics, such as watershed area and elevation (e.g. Houle *et al.*, 1995; Wolock *et al.*, 1997; Gergel *et al.*, 1999; Johnson *et al.*, 2000; Prepas *et al.*, 2001). Unlike these studies, for the Grass Pond and Constable Pond subwatersheds, the concentrations of N solutes or DOC were not related to watershed area, elevation, mean TI, HI, or average stream gradient (Table II), although HI was lower for the subwatersheds having larger area proportions as shrub wetlands. The probability distributions of TI and hypsometric (area–altitude) curves were not related to the concentrations of N solutes and DOC. These results suggest that the aggregated representation of physical features could not account for lake N and C chemistry in these two lake watersheds. In addition, using the 1916 fire protection map that recorded recent major fire disturbances between 1890 and 1910, and the maps of the wind storms of 1950 and 1995, there was no indication that these factors had differential influences on surface water chemistry at any of the inlets for either lake.

Soils. Comparisons of soil characteristics between Grass 3 and 6 showed that exchangeable aluminium (Al) and hydrogen ion (H^+) concentrations in deeper mineral horizons were lower at Grass 3 than Grass 6 (Table VII), which would be consistent with the greater contribution of groundwater inputs with high pH and concentrations of weathering by-products at Grass 3 and 4 than at the other inlets. The average grain size in Grass 3 was high in sand, whereas Grass 6 had a high silt fraction. The much more coarse-textured soils in Grass 3 may have facilitated the percolation of water through the soils and into the glacial till. The higher silt fraction in Grass 6 was attributed to a well-developed aeolian mantle found in a soil pit in Grass 6 (site 102). The aeolian mantle occurs throughout the region as a discontinuous mantle of wind-blown silt (loess) covering areas of both till and stratified drift (Newton, unpublished data).

The concentrations of exchangeable Ca and Mg and the cation exchange capacity (CEC) in the A1 horizon were much higher at Grass 6 than at Grass 3, which was probably due to a higher percentage of organic material in the Grass 6 soil profile. Since organic horizons, which have the highest base saturation, are also the most acidic, pore water pH was not as high as expected for soils with high CEC and base saturation that result from high mineral matter content. The higher organic material in Grass 6 could be due to microclimate factors.

Wetlands. Anoxic conditions in wetlands facilitate losses of NO_3^- through gaseous losses via denitrification, while increasing the production of DOM (Jugsujinda *et al.*, 1998; Yu and Patrick, 2003). The influences of wetlands on N solutes and DOC were examined based on the proportion of total wetland area in subwatersheds as well as by separating wetlands into two types, shrub and forested wetlands, which often differ in location and function. Since the wetland proportions in the subwatersheds of Constable Pond were larger, the effect of wetlands was expected to be more evident in the Constable Pond watershed. However, the concentrations of NO_3^-, DON, DOC, and other ions were not significantly related to the percentage of total wetland area in the Constable Pond subwatersheds, except that lower SO_4^{2-} concentrations at Constable 1 and 6 (Table V) were presumably due to high rates of SO_4^{2-} reduction in relatively large wetland areas. The significant inverse relationships

Table VII. Soil characteristics of Grass Pond subwatersheds 3 and 6 (Grass 3 and 6)[a]

	Units	Grass 3, site 104 mean						Grass 6, site 102 mean			
Grain size											
Sand	%	68·8						38·1			
Silt	%	29·5						57·5			
Clay	%	0·4						3·6			
Gravel	%	1·3						1·0			
Soil chemistry											
Soil horizon		O	A1	E	B2	B3	C	A1	E	B2	B3
Al	meq/100 g	1.5	4·3	0·8	5·1	1·4	0·6	3·0	1·8	9·5	4·0
H	meq/100 g	4.4	4·9	0·9	1·1	0·0	0·0	6·4	0·8	2·5	1·0
Ca	meq/100 g	NA	0·2	0·2	0·1	0·03	0·03	16·7	0·1	1·3	0·1
Mg	meq/100 g	NA	0·1	0·1	0·1	0·02	0·02	1·8	0·04	0·2	0·04
Na	meq/100 g	NA	0·06	0·1	0·04	0·04	0·04	0·2	0·04	0·1	0·1
K	meq/100 g	NA	0·4	0·04	0·1	0·02	0·02	0·5	0·04	0·2	0·03
Sum of base cations	meq/100 g	NA	0·6	0·3	0·4	0·1	0·1	19·2	0·3	1·8	0·2
Cation exchange capacity	cmol kg^{-1}	NA	9·8	0·9	6·6	1·4	0·5	28·6	2·9	13·7	5·3
Base saturation	%	NA	6·4	13·2	6·3	8·1	24·6	67·1	9·1	12·2	4·4

[a] NA: data are not available.

between SO_4^{2-} and the percentage of total wetland area (Table VI) may be due to losses of SO_4^{2-} from dissimilatory SO_4^{2-} reduction under anaerobic conditions (Giblin and Wieder, 1992).

For shrub wetlands, both DON and DOC increased with increasing proportion of shrub wetland area in the Constable Pond subwatersheds, but only the relationship with DOC was significant ($r^2 = 0\cdot64$, $p = 0\cdot03$). No significant relationship with shrub wetland area was present for the Grass Pond watershed, probably due to the very small wetland area in the Grass Pond watershed. For the same reason, the relationships with forested wetland area were similar to the relationships with total wetland area in the Grass Pond watershed. The stronger relationship of wetland area with DOC than DON has also been reported in other studies (Chapman *et al.*, 2001; Ito *et al.*, 2005), and suggests the importance of factors other than the presence of wetlands in regulating DON, compared with DOC.

Although the relationships with wetland area were stronger for DOC than for DON, the concentrations of DON and DOC appeared to be positively related (Figure 6). The relationship between DON and DOC was stronger at the Constable Pond inlets than at the Grass Pond inlets (Table VI) and the DOC/DON ratios were higher at Constable Pond inlets (Table III) due to much higher DOC concentrations. The DON and DOC concentrations were more closely correlated in 2000, the year with higher precipitation and discharge, suggesting a more pronounced effect of wetlands during wetter conditions and the lesser importance of the contribution of glacial till groundwater inputs to surface waters.

To evaluate the influence of wetlands on the strength of the relationship between DON and DOC, the r^2 values of the monthly DON versus DOC relationships in each subwatershed were compared with the percentage of wetland area in the subwatersheds. In both the Grass Pond and Constable Pond subwatersheds, the r^2 values of the relationship between DON and DOC in each subwatershed increased with increasing percentage of total wetland area ($r^2 = 0\cdot74$, $p = 0\cdot01$ and $r^2 = 0\cdot83$, $p = 0\cdot007$ in the Grass Pond and Constable Pond watersheds respectively). The DOC/DON ratios were not significantly related to the percentage of total, shrub, or forested wetland area. These results suggest that, as the percentage of wetland area increases, the DOC/DON ratio approaches the value found in the wetland waters.

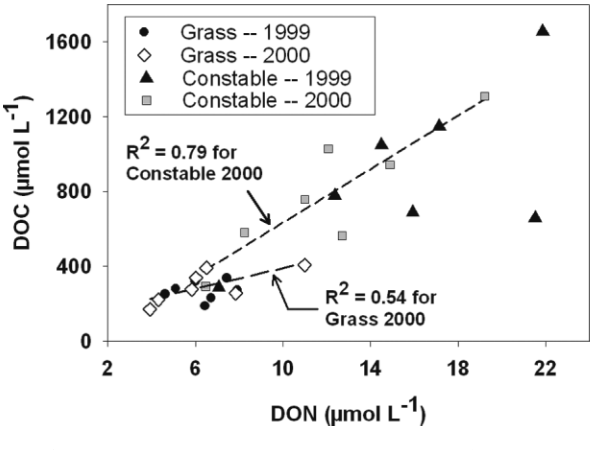


Figure 6. The relationships between the concentrations of DON and DOC at the Grass Pond and Constable Pond inlets

Other land cover types. The concentrations of DON and DOC and the DOC/DON ratios were also associated with forest type. However, the effect of forest type appears to be secondary to the influence of wetland area. Multiple regression analyses showed that the DOC/DON ratio increased with increasing percentage of coniferous forest area in the Grass Pond subwatersheds where the wetland area is very small (adjusted $r^2 = 0\cdot92$, $p = 0\cdot01$, coefficient $0\cdot98(\%)^{-1}$ in 2000), although the relationship in 1999 was not significant ($p = 0\cdot1$). In the Grass Pond watershed, forest type and its resultant effect on DOM might be expected to emerge due to the relatively small area covered by wetlands. The increasing DOC/DON ratio with coniferous forest area could be explained by the higher DOC fluxes in coniferous forests than in deciduous forests (Hope *et al.*, 1994). At the inlets of both Grass Pond and Constable Pond, the monthly DOC/DON ratios increased in October, especially in 1999. These increases might have been due to the influence of fresh litter inputs during this period.

The effect of forest type on N solutes and DOC was not particularly evident in our study. This is probably because the effects of other factors, such as the contribution of groundwater inputs or the presence of wetlands, were more predominant. In addition, the relatively coarse scale of the forest cover data (compared with the wetland data), combined with the broad classification of forest types into coniferous, mixed, and deciduous forests, limited our ability to evaluate the influences of terrestrial vegetation. It has been shown that tree species have major effects on N and C cycling and losses (Lovett *et al.*, 2004). However, a significant influence of forest type on Cl^- concentrations was observed for the Constable Pond subwatersheds (i.e. inverse relationships between deciduous forest area and Cl^- concentrations presumably associated with dry deposition), which suggests that the broad classification of forest type on a coarse scale can be also useful for examining the effect of forest type.

Other terrestrial processes influencing nitrate

In the Constable Pond subwatersheds, the absence of thick glacial till and the lack of relationships between dissolved Si and Ca^{2+} and between dissolved Si and NO_3^- all suggest a smaller contribution of glacial till groundwater inputs than in the Grass Pond subwatersheds. Nevertheless, as found for the Grass Pond inlets, NO_3^- also increased with increasing Ca^{2+} and pH, although the relationships at Grass Pond inlets were stronger (Table VI). These patterns could not be explained by the NO_3^--induced leaching of Ca^{2+} that would be accompanied by high stream NO_3^- concentrations (Lovett *et al.*, 2000), because the correlations with Ca^{2+} were also observed for low NO_3^- and no relationship with Ca^{2+} existed for SO_4^{2-} in our study sites. Rather, the positive relationships between NO_3^- and pH and between NO_3^- and Ca^{2+} may be attributed to enhanced N mineralization and nitrification at higher soil pH (Ste-Marie and Paré, 1999) and base cation levels (Ohrui *et al*., 1999). Soils under red maple have been found to have higher Ca and Mg contents (van Breemen *et al*., 1997), and potential nitrification was observed to be greater in maple stands than in beech stands (Lovett and Rueth, 1999; Lovett and Mitchell, 2004). Although the information on tree species was available only for the wetlands, the forested wetlands in the Grass Pond watershed are predominantly covered by red maple (50%), whereas forested wetlands in the Constable Pond watershed are dominated by balsam fir and red or black spruce (100%). The tree species in the Grass Pond watershed might also be associated with elevated base cation concentrations and increased NO_3^- production, as seen in other Adirondack watersheds (Christopher *et al*., 2006).

At the Constable Pond inlets, NO_3^- concentrations decreased with increasing DON and DOC concentrations (Table VI). Devito *et al.* (2000) suggested that the presence of DOC as an electron donor enhanced denitrification, thereby controlling NO_3^- attenuation. The anoxic conditions under which denitrification occurs may have also been suitable for the production of DON and DOC. The absence of these inverse relationships between NO_3^- and DON or DOC at the Grass Pond inlets again suggests that the contribution of groundwater inputs to NO_3^- concentrations is important. The DOM level could be also influenced by groundwater (Saunders *et al*., 1980; Hagedorn *et al*., 2000).

Inverse relationships between N or NO_3^- and the C/N ratio observed in streams (Campbell *et al*., 2000) or soils and soil solutions (Gundersen *et al*., 1998) have led to a discussion on using the C/N ratio as an indicator of N status associated with N saturation (Campbell *et al*., 2000). In the present study, the DOC/DON ratio appeared to decrease with increasing NO_3^- at the inlets of the two lakes ($r^2 = 0{\cdot}53$, $p = 0{\cdot}06$ in 1999 at the Grass Pond inlets; $r^2 = 0{\cdot}18$, $p = 0{\cdot}06$ for all data points; Table VI; Figure 7). However, the DOC/DON ratio also decreased with increasing pH and Ca^{2+} (Table VI). Nitrate was also positively correlated with pH and Ca^{2+}. Strong relationships between NO_3^- leaching, nitrification, and the C/N ratio were reported to exist in a regional analysis along an N deposition gradient (Currie, 1999). In our study sites, with the minimal difference in wet N deposition, the inverse relationships between NO_3^- and DOC/DON are not associated with an N deposition gradient, but may be also attributable to enhanced N mineralization and nitrification rates at higher soil pH and base cation levels. Some environmental and physical factors have been shown to influence N mineralization and/or nitrification rates in similar ecosystems, such as tree species (which would be related to N mineralization and nitrification rates; Finzi *et al*., 1998; Lovett and Rueth, 1999) and soil pH, elemental composition, and texture (which have been found to influence nitrification rates; van Breemen *et al*., 1997). Regardless of the specific causes, our results suggest those relationships must be interpreted with caution.

CONCLUSIONS

Water samples from seven lake inlets and an outlet from each of two lake-watersheds located only ~26 km apart were used to examine the influences of various physical factors on N solutes and DOC. NO_3^- was the major N solute at two of the Grass Pond inlets, reflecting the contribution of groundwater inputs flowing through thick glacial till. The concentrations of the likely weathering products, dissolved Si, Ca^{2+}, Mg^{2+}, and Na^+, as well as ANC and pH, were also higher at these two Grass Pond inlets than at the other Grass Pond inlets and the Constable Pond inlets. The contribution of groundwater at the Grass Pond inlets appeared to be predominant and might have masked the possible effects of other terrestrial factors. In the Constable Pond watershed, underlain by thin glacial till, DON was the major N solute at the lake inlets. The DON and DOC concentrations were higher at the Constable Pond inlets than at the Grass Pond inlets, probably due to a larger proportion of wetland area in the Constable Pond watershed. The DOC/DON ratios were also higher at the Constable Pond inlets, which might have been due to a larger proportion of coniferous forest area. Although DON and DOC were strongly correlated, the stronger relationship of the proportion of wetland area with DOC than with DON suggests the importance of factors other than the presence of wetlands in regulating DON. Despite the distinctive differences in inlet N chemistry between the two lakes, NO_3^- or DON concentrations at the outlets of the two lakes were similar. The similarity in NO_3^- or DON at the lake outlets, together with lower DOC/DON ratios at the lake outlets and at the inlets having upstream ponds in their subwatersheds, suggests the importance of the sources and processing within the lakes.

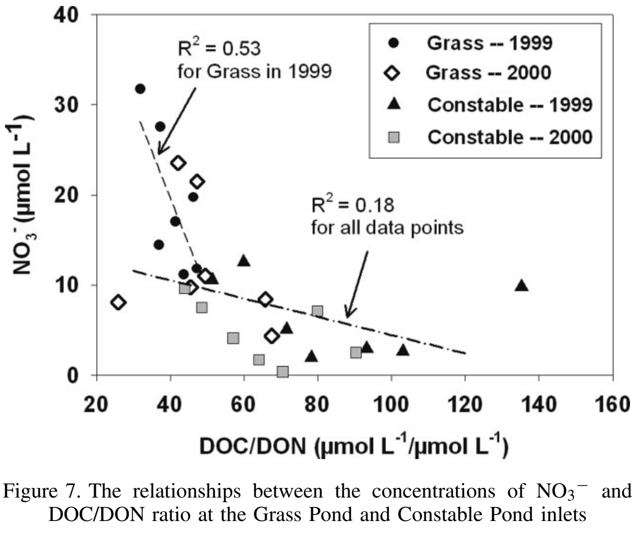


Figure 7. The relationships between the concentrations of NO_3^- and DOC/DON ratio at the Grass Pond and Constable Pond inlets

The NO_3^- concentrations at the Grass Pond outlet in particular did not show the influence of groundwater inputs, which was found in the inlet chemistry, or the effects of other terrestrial processes that occurred in the subwatersheds. For DOC, the higher concentrations at the Constable Pond outlet than at the Grass Pond outlet might have been the result of much higher DOC concentrations at the Constable Pond inlets than at the Grass Pond inlets, suggesting the importance of the influences of terrestrial processes (such as those associated with wetlands and/or forest type) on lake outlet DOC. The pattern of decreasing NO_3^- with increasing DOC/DON ratio in the sites with similar wet N deposition suggests that such relationships may not solely be a function of N deposition. Our results suggest the particular importance of groundwater contribution and in-lake processing in regulating N solutes in our study sites.

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