



# Nitrogen biogeochemistry in the Adirondack Mountains of New York: hardwood ecosystems and associated surface waters

Myron J. Mitchell<sup>a,\*</sup>, Charles T. Driscoll<sup>b</sup>, Shreeram Inamdar<sup>c</sup>, Greg G. McGee<sup>a</sup>,  
Monday O. Mbila<sup>d</sup>, Dudley J. Raynal<sup>a</sup>

<sup>a</sup>SUNY-ESF, 1 Forestry Drive, Syracuse, NY 13210, USA

<sup>b</sup>Syracuse University, Dept. Civil and Envir. Engin., Syracuse, NY 13244, USA

<sup>c</sup>SUNY College at Buffalo, Buffalo, NY 14222, USA

<sup>d</sup>Alabama A&M University, Normal, AL 35762, USA

Received 25 September 2001; accepted 26 July 2002

**“Capsule”:** *Factors that regulate the fate of atmospherically deposited nitrogen to hardwood forests and subsequent transport to surface waters in the Adirondack region of New York are described.*

## Abstract

Studies on the nitrogen (N) biogeochemistry in Adirondack northern hardwood ecosystems were summarized. Specific focus was placed on results at the Huntington Forest (HFS), Pancake-Hall Creek (PHC), Woods Lake (WL), Ampersand (AMO), Catlin Lake (CLO) and Hennessy Mountain (HM). Nitrogen deposition generally decreased from west to east in the Adirondacks, and there have been no marked temporal changes in N deposition from 1978 through 1998. Second-growth western sites (WL, PHC) had higher soil solution  $\text{NO}_3^-$  concentrations and fluxes than the HFS site in the central Adirondacks. Of the two old-growth sites (AMO and CLO), AMO had substantially higher  $\text{NO}_3^-$  concentrations due to the relative dominance of sugar maple that produced litter with high N mineralization and nitrification rates. The importance of vegetation in affecting N losses was also shown for N-fixing alders in wetlands. The Adirondack Manipulation and Modeling Project (AMMP) included separate experimental N additions of  $(\text{NH}_4)_2\text{SO}_4$  at WL, PHC and HFS and  $\text{HNO}_3$  at WL and HFS. Patterns of N loss varied with site and form of N addition and most of the N input was retained. For 16 lake/watersheds no consistent changes in  $\text{NO}_3^-$  concentrations were found from 1982 to 1997. Simulations suggested that marked  $\text{NO}_3^-$  loss will only be manifested over extended periods. Studies at the Arbutus Watershed provided information on the role of biogeochemical and hydrological factors in affecting the spatial and temporal patterns of  $\text{NO}_3^-$  concentrations. The heterogeneous topography in the Adirondacks has generated diverse landscape features and patterns of connectivity that are especially important in regulating the temporal and spatial patterns of  $\text{NO}_3^-$  concentrations in surface waters.

© 2003 Elsevier Science Ltd. All rights reserved.

**Keywords:** Acidic deposition; Forests; Hydrology; Water quality; Watersheds

## 1. Introduction

Considerable attention has been placed on evaluating nitrogen (N) biogeochemistry in ecosystems. Understanding of relationships between atmospheric N deposition and forest ecosystem biogeochemistry is critical in assessing the effects of elevated N inputs. Elevated levels of N in ecosystems due to anthropogenic activities

impacts biotic diversity, N cycling and result in increased leaching losses (Vitousek et al., 1997) and possibly even altered forest productivity (Aber et al., 1998). Evaluating the role of N biogeochemistry in the Adirondack Mountains of New York State is particularly important since the surface waters of the region have only shown limited response in acid-base chemistry to changes in atmospheric inputs of acidic deposition including N constituents (NAPAP, 1998; Stoddard et al., 1999). The absence of significant increases in surface water pH and acid neutralizing capacity (ANC), and depletion of the labile pool of soil base cations have

\* Corresponding author. Tel.: +1-315-470-6765; fax: +1-315-470-6996.

E-mail address: [mitchell@syr.edu](mailto:mitchell@syr.edu) (M.J. Mitchell).

been attributed to concomitant changes in base cation status and the increasing contribution of N in both precipitation and surface water chemistry (Driscoll et al., 1998). Recently attention has focused on evaluating the “N saturation” status of forest ecosystems (Aber et al., 1998; Fenn et al., 1998) and resultant increases in nitrate ( $\text{NO}_3^-$ ) in surface waters that can contribute to freshwater acidification (Stoddard, 1994) and coastal eutrophication (Howarth et al., 1996; Paerl, 1997). In the Adirondack region, elevated  $\text{NO}_3^-$  concentrations have been found in surface waters and this may have contributed to their limited recovery from the effects of acidic deposition (Driscoll et al., 1998; Kretser et al., 1989; Mitchell et al., 2001a). The drainage losses of  $\text{NO}_3^-$  in conjunction with other mobile anions especially sulfate ( $\text{SO}_4^{2-}$ ) also may influence the losses and concentrations of nutrient base and potentially toxic hydrogen ( $\text{H}^+$ ) and aluminum ( $\text{Al}^{n+}$ ) ions (Reuss and Johnson, 1986). It is clearly recognized that a variety of factors including N deposition (Driscoll et al., 1998), land use history (Aber and Driscoll, 1997), vegetation composition (Lovett et al., 2000) and hydrological flow paths (Burns et al., 1998; Mitchell, 2001) can influence spatial and temporal patterns of N solutes in forest watersheds.

In this paper, we will report on studies of N biogeochemistry in Adirondack northern hardwood ecosystems. The locations of the study sites that will be highlighted are provided in Fig. 1 with brief site descriptions in Table 1. The most intensively studied northern hardwood site in the Adirondacks is a second-growth stand at the Huntington Forest (HFS) in the central Adirondacks. Investigations at this site began in

the early 1980s (e.g. Mollitor and Raynal, 1982, 1983) and later this site became part of the Integrated Forest Study (IFS) that evaluated the impacts of acidic deposition on forested ecosystems (Johnson and Lindberg, 1992; Mitchell et al., 1992a). The IFS site is adjacent to the Arbutus Watershed which has also been extensively studied for almost 20 years (e.g. Mitchell et al., 2001a). The IFS site, in addition to two other second-growth, northern hardwood sites in the southwestern Adirondacks (Pancake-Hall Creek, PHC and Woods Lake, WL), were part of the Adirondack Manipulation and Modeling Project (AMMP) (Mitchell et al., 1994, 2001b). Most recently three additional sites have also been studied including two old-growth stands (Amper-sand and Catlin Lake) the latter of which is also in the Huntington Forest and another second-growth forest near Hennessy Mountain (McGee et al., 2003). In this paper we will synthesize results of our previous studies on N biogeochemistry for these sites and also include some regional analyses of the Adirondacks. We will show how the spatial and temporal patterns of N cycling in northern hardwood ecosystems are influenced by variations in atmospheric deposition, disturbance history, vegetation, and topographically regulated hydrologic flow paths.

## 2. Regional differences in the Adirondacks

### 2.1. Atmospheric deposition

Using an empirical modeling approach Ito et al. (2002) found that N inputs generally decrease from west

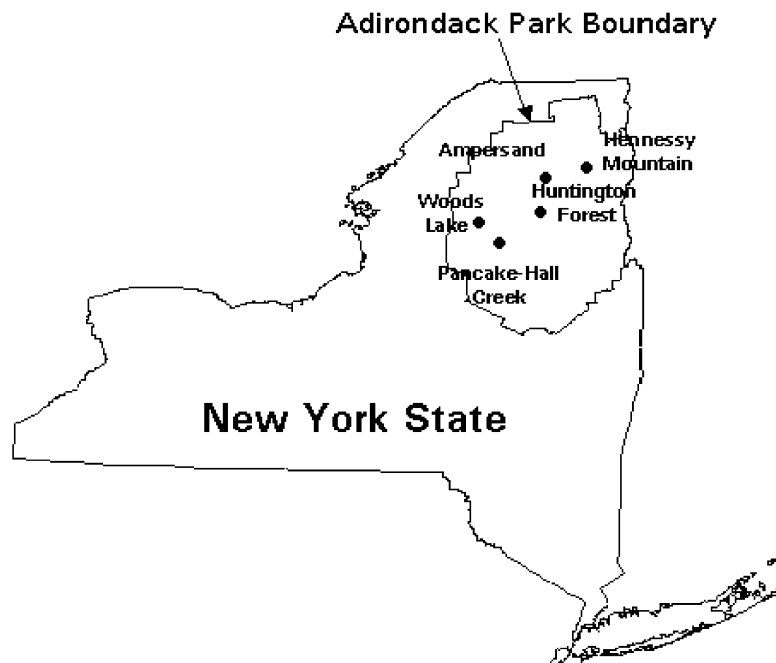


Fig. 1. Hardwood study sites in the Adirondack Park of New York State.

Table 1  
Study sites in Adirondack Mountains of New York State

Site	Abbreviation	Location (longitude and latitude)	Elevation (m)	Dominant overstory vegetation	Soil type
IFS Site at Huntington Forest	HFS	43°59' N 74°14' W	530	<i>Fagus grandifolia</i> <i>Acer saccharum</i> <i>A. rubrum</i>	Typic Haplorthod Becket-Mundal Association
Catlin Lake at Huntington Forest	CLO	44°01' N 74°17' W	560	<i>F. grandifolia</i> <i>A. saccharum</i>	Typic Haplorthod
Arbutus Watershed at Huntington Forest	Arbutus Watershed	43°59' N 74°14' W	513–701	<i>F. grandifolia</i> <i>A. saccharum</i> <i>A. rubrum</i> <i>Betula alleghaniensis</i> <i>Tsuga canadensis</i>	Uplands—Becket-Mundal series Wetlands—Greenwood Mucky peats
Woods Lake	WL	43°53' N 74°57' W	678	<i>B. alleghaniensis</i> <i>A. rubrum</i>	Typic Haplorthod Lyman Series
Pancake-Hall Creek	PHC	43°50' N 74°51' W	635	<i>A. saccharum</i> <i>Picea rubens</i> <i>F. grandifolia</i>	Typic Haplorthod Adams Series
Hennessy Mountain	HES	44°18' N 74°02' W	550	<i>F. grandifolia</i> <i>A. saccharum</i> <i>A. pennsylvanicum</i>	Typic Haplorthod
Ampersand	AMO	44°15' N 74°14' W	490	<i>A. saccharum</i> <i>F. grandifolia</i>	Typic Haplorthod

to east in the Adirondacks (Fig. 2). Other studies that have evaluated  $\text{NO}_3^-$  and  $\text{NH}_4^+$  inputs from wet deposition have also found higher values at western sites (e.g. Woods Lake and Pancake-Hall Creek) than at HFS and another monitoring site in the eastern Adirondacks (Mitchell et al., 2001b). Ammonium deposition is about one-third of total wet N deposition in the region (Mitchell et al., 2001b). We have not found any compelling evidence for recent temporal changes in N

deposition in the Adirondacks. Although a small decrease in wet  $\text{NO}_3^-$  deposition was found from 1978 to 1994 at the HFS (Driscoll et al., 1995), decreases in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and DIN (total dissolved inorganic nitrogen) deposition were not significant when measurements up to 1998 were included (Fig. 3; Mitchell et al., 2001a). Total dry N deposition was similar at the HFS from 1986 to 1988 ( $2.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) as from 1992 to 1993 ( $2.6 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) (Mitchell et al., 2001b).

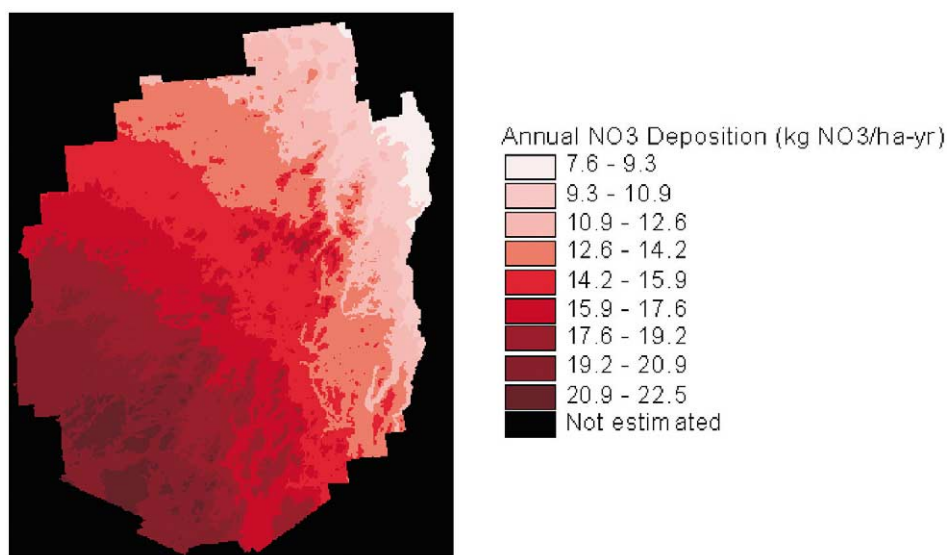


Fig. 2. Wet nitrate deposition in the Adirondack Park of New York. From Ito et al. (in press, Atmospheric Environment).

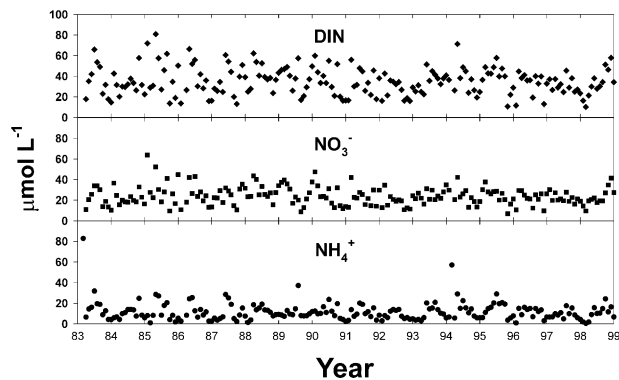


Fig. 3. Mean monthly concentrations of inorganic nitrogen solutes in wet deposition at the NADP/NTN site at the Huntington Forest (data from Mitchell et al., 2001a).

For the AMMP sites, mean  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations of throughfall (TF) were higher at WL and PHC than at HFS. The greater amounts of TF water flux at WL and PHC compared to HFS, combined with higher concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , resulted in more than twice the TF fluxes of DIN at WL ( $10.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) and PHC ( $12.0 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) compared with HFS ( $4.4 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ; Mitchell et al., 2001b). The TF fluxes at WL and PHC were also higher than for any site studied in the IFS except for a high elevation spruce site in the Smokies Mountains (Johnson and Lindberg, 1992). These TF results are consistent with the measurements of wet deposition and suggest that the western Adirondacks experience higher rates of N deposition than the central and eastern Adirondacks.

## 2.2. Spatial patterns of N cycling across the Adirondacks

Patterns in soil solution N concentrations were studied as part of the AMMP. Soil solution  $\text{NO}_3^-$  concentrations at the 15 cm depth in the reference plots were higher at PHC than at WL and HFS while at 50 cm concentrations were higher at PHC and WL than at HFS. Due to higher water fluxes at the WL and PHC sites, reference plots had higher fluxes of inorganic N than at the HFS (Fig. 4). The reference plots at the two sites (WL and PHC) with the highest atmospheric inputs of N exhibited lower N retention (53 and 33%, respectively) than HFS (68%).

As part of the AMMP, N was also experimentally added to plots as  $(\text{NH}_4)_2\text{SO}_4$  at 14 and 28  $\text{kg N ha}^{-1} \text{ year}^{-1}$  or as  $\text{HNO}_3$  at 14  $\text{kg N ha}^{-1} \text{ year}^{-1}$  (no experimental  $\text{HNO}_3$  additions were done at PHC) (Fig. 4). Details on this study including statistical analyses of response of the sites to these chemical additions are provided in Mitchell et al. (2001b). The greatest increase in DIN (predominantly  $\text{NO}_3^-$ ) loss in response to the experimental treatments occurred at HFS where the

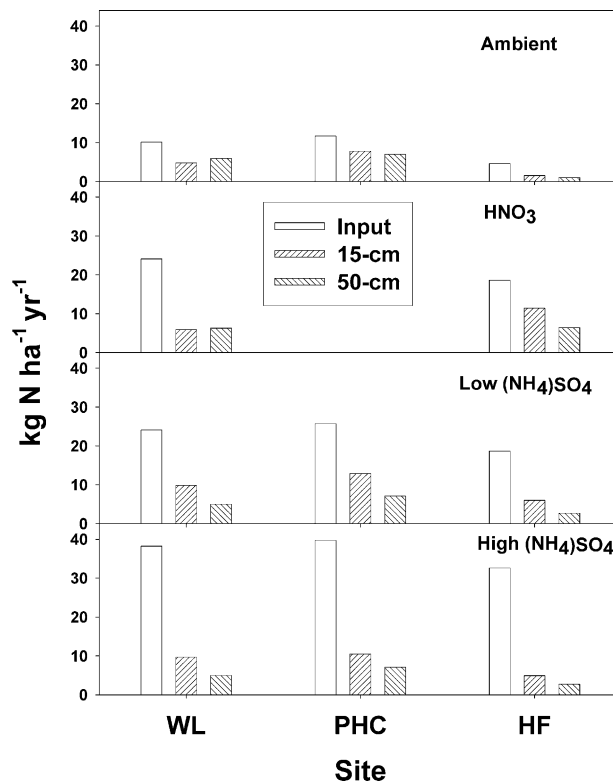


Fig. 4. Dissolved inorganic nitrogen (DIN) fluxes for the AMMP study sites (input = throughfall + experimental addition; 15 and 50 cm are DIN fluxes at 15 and 50 cm soil depths). Data from Mitchell et al. (2001b).

$\text{HNO}_3$  additions resulted in the highest  $\text{NO}_3^-$  concentrations in soil solutions and lowest N retention. In contrast, at WL and PHC increases in soil water DIN were not evident in response to experimental N additions. In all cases, most (63–86%) of experimental + ambient inorganic N input was not leached from these forest plots. Results using enriched  $^{15}\text{N-NH}_4^+$  as a tracer at PHC suggest that most of the added N was retained within the forest floor and mineral soil (Mitchell et al., 2001b). Some N gaseous loss via denitrification was also possible although measurements at the HFS by Richey (1995) suggest that is a relatively small flux. The results suggest, that the two sites (WL and PHC) in the western Adirondacks did not respond to additional N inputs although they have experienced elevated atmospheric N inputs and higher N drainage losses in reference plots than the HFS site in the central Adirondacks. Some of these differences in site response to experimental additions of N may have been a function of stand age; the forest stands of WL and PHC were younger (24 and 33 years, respectively) than the HFS (age ~70 to 95 years).

Highest  $\text{NO}_3^-$  fluxes in the reference plots across the sites corresponded to higher  $\delta^{15}\text{N}$  values in soil and plants when the WL, PHC and HFS sites are compared. This pattern is consistent with enhanced N cycling rates in those sites with higher  $\delta^{15}\text{N}$  natural abundance values

(Mitchell et al., 2001a). An experiment at PHC used isotopically enriched  $^{15}\text{N}$ -ammonium sulfate fertilizer as part of the experimental N additions. The analyses of  $\delta^{15}\text{N}$  of various ecosystem compartments as a tracer of the ammonium addition found that the forest floor and the mineral soil were the largest sinks for added N during a 3-year study period (Mitchell et al., 2001a). These results are consistent with the mass balance analyses suggesting high rates of N retention in the forest floor and soils of these three sites. Moreover, these isotopic results suggesting that the forest floor and mineral soil are the predominant sinks for experimentally added nitrogen are consistent with findings of other studies that have used  $^{15}\text{N}$  as a tracer of experimental N additions in Europe and the United States (e.g. Emmett et al., 1998; Nadelhoffer, 1999).

The responses of surface waters in the Adirondacks have been evaluated for the period from 1982 through 1997 with respect to changes in acidic deposition using 16 lake/watershed systems that are part of the Adirondack Long-Term Monitoring (ALTM) program (Driscoll et al., 1998). Driscoll and Van Dreason (1993) had earlier reported that lakes in the western Adirondacks tended to have higher  $\text{NO}_3^-$  concentrations than other regions. However, there was no consistent change in  $\text{NO}_3^-$  concentrations from 1982 to 1997 with only one lake showing a significant increase and another lake showing a significant decrease (Driscoll et al., 1998). Nitrogen mass balances for the ALTM watersheds generally showed variation in dissolved inorganic nitrogen (DIN) retention (42–96%) but all systems showed substantial N retention. The PnET-CN simulation model (Aber and Driscoll, 1997) was used to evaluate different scenarios of N deposition and long term patterns of N biogeochemistry in the Big Moose watershed in the western Adirondacks (Driscoll et al., 1998). Simulation results suggest that N saturation has not been shown for this watershed and that it will take an extended period ( $\sim$ year 2100) when output of DIN would approach that of DIN atmospheric inputs. It was concluded that N deposition influences the N biogeochemistry in forest watersheds, but long term changes in  $\text{NO}_3^-$  loss are manifested over periods extending from decades to centuries (Driscoll et al., 1998).

The role of forest age was evaluated at four study sites (Ampersand and Catlin Lake—old-growth; Hennessey Mountain and Huntington Forest (IFS)—second-growth). The overstories at Ampersand and Catlin Lake were dominated by trees  $\sim$ 200 years old while those at Hennessey Mountain and Huntington Forest (IFS) were dominated by trees  $\sim$ 70 to 95 years old. Soil solution N (Fig. 5) and cation solute concentrations were consistently highest at Ampersand but also lowest at Catlin Lake, both of which were old-growth stands (McGee et al., 2003). These results suggest that additional factors beyond stand maturity were affecting N cycling.

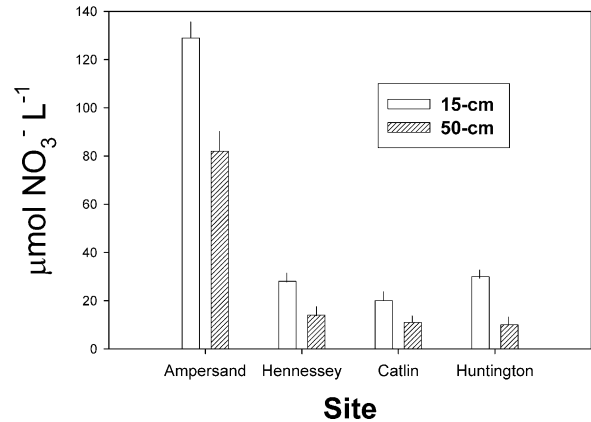


Fig. 5. Mean soil solution nitrate concentrations at four hardwood sites in the Adirondack Mountains (data from Mbila et al., in preparation).

The role of vegetation composition appears to be an important factor in affecting the N biogeochemistry of these and other sites as discussed later. Future studies that analyze concomitantly the role of forest stand composition and age are needed to evaluate the relative contributions of each of these factors to forest N cycling.

### 3. Relationships within watersheds

Studies within the Arbutus Watershed have provided information on factors controlling N biogeochemical cycling within a watershed including seasonal patterns. Discharge in the watershed is greatest at both the inlet and outlet of Arbutus Lake during snowmelt including rain on snow events. Concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were lowest at the outlet of Arbutus Lake during the summer (Fig. 6). For N solutes, there was a direct correspondence between discharge water losses and solute fluxes with lowest fluxes occurring during the later summer and early fall (August–September). In April and January, fluxes of N solutes were high not only due to the high discharge rates, but also higher solute concentrations, especially for  $\text{NO}_3^-$  at the inlet. Snow melt episodes with high  $\text{NO}_3^-$  concentrations occur in surface waters of the northeastern United States including the

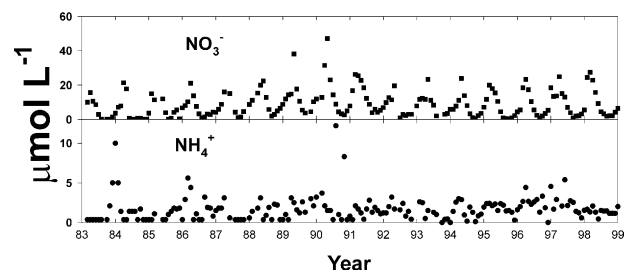


Fig. 6. Concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at the outlet of Arbutus Watershed. Details on results provided in Mitchell et al. (2001a).

Adirondacks (Wigington et al., 1996). Due to biotic processes that retain or consume  $\text{NO}_3^-$ , the losses of this solute during the summer were relatively small with 94 and 95% of  $\text{NO}_3^-$  loss occurring during the dormant season at the inlet and outlet, respectively (Mitchell et al., 2001a). The high loss rates of  $\text{NO}_3^-$  during the dormant season at the outlet of Arbutus Lake as well as for three other forest watersheds in the northeastern US were reported previously for the period from 1982 to 1994 (Mitchell et al., 1996a). The marked increase in  $\text{NO}_3^-$  concentrations and fluxes in the spring of 1990 within the Arbutus watershed has been found for other sites in the northeastern US. These elevated  $\text{NO}_3^-$  values in the spring of 1990 (Fig. 6) were attributed to a major freezing event in December 1989 (Mitchell et al., 1996b).

Dissolved organic nitrogen (DON) contributed a substantial portion of total solute N loss in the Arbutus watershed especially at the lake outlet where it constituted 47% of the total N solute fluxes (Mitchell et al., 2001a). McHale et al. (2000) reported for the period from June 1995 to May 1996 found that DON in the Arbutus lake outlet contributed 61% of total N solute fluxes. Campbell et al. (2000) found that DON was the major form of dissolved N in the drainage waters of nine forest watersheds in New England. At WL and HFS, DON in reference plots at 15 cm contributed 40 and 76% of the total dissolved nitrogen (TDN) while at PHC, DON contributed only 10% due partly to the high  $\text{NO}_3^-$  at PHC (Mitchell et al., 2001b). No effect of N additions on DON concentrations was detected at any of the AMMP study sites. Although it appears that the greatest response to soil solutions and surface waters as seen in temporal and spatial variation as well as the effects of experimental N additions is manifested mostly in  $\text{NO}_3^-$  concentrations, understanding the influence of DON is also warranted especially over extended periods.

### 3.1. Vegetation influences

Studies of biotic processes also indicate that landscape position and vegetation type can have marked effects on N processes. For example, it has been shown that speckled alder can add substantial amounts of N to wetlands due to N fixation (up to  $37 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) and these contributions could influence spatial patterns of N solutes in the surface waters of the Adirondacks especially at local scales (Hurd et al., 2001). Additionally, the presence of alders in shrub wetlands stimulates nitrification contributing to elevated stream water  $\text{NO}_3^-$  levels, especially during peak-flow conditions (Hurd and Raynal, 2003). Ohri et al. (1999) found that net N mineralization rates were less within a wetland without alder and with a coniferous overstory than an upland conifer zone and an upland hardwood zone. Net nitrification rates were higher at an upland hardwood zone than an upland conifer zone. These spatial patterns in N

processes were attributed to differences in litter types with hardwood litter components being more rapidly mineralized and nitrified.

The role of vegetation was further explored at the Ampersand old-growth sites which had higher  $\text{NO}_3^-$  concentrations than other sites within the Adirondacks (Mbila et al., in preparation). Some old-growth forests may have low net ecosystem production (including steady-state with respect to biomass accumulation) and thus their potential for N sequestration is lower than for younger, aggrading stands (Aber et al., 1998; Fenn et al., 1998). When a forest exhibits rapid growth, its demand for nutrients including N is high. As a forest matures, ecosystem N pools (e.g. biomass, forest floor and possibly the mineral soil) generally become larger and internal N cycling (e.g. litterfall inputs, mineralization, nitrification) may begin to exceed the biotic capacity for N retention. One possible factor that could affect the nutrient dynamics of mature forests is the formation of treefall gaps that can influence N pools and fluxes. Canopy gaps created by treefalls may increase light levels, soil temperatures and soil moisture all of which can influence nutrient cycles (Collins et al., 1985). These processes are also influenced by gap size and age. The role of treefall gaps in affecting N dynamics was investigated by McGee et al. (2003) at the old-growth Ampersand site. It was found that the concentrations of N solutes (dominated by  $\text{NO}_3^-$ ) at 50-cm soil depth did not vary among various disturbance zones. It was concluded that even within disturbed areas there was sufficient biotic demand to retain any additional N made available by disturbances in this old-growth site.

The influence of vegetation composition was likely responsible for the differences in  $\text{NO}_3^-$  concentrations in Catlin Lake, Hennessy Mountain, Ampersand and Huntington Forest (IFS) sites although other factors such as differences in nutrient availability among the sites could also be a contributing factor (Fig. 5). Sugar maple and American beech were the most important tree species at all four sites, but the Catlin Lake and Huntington Forest (IFS) sites had more representation of acid tolerant species (American beech, black cherry, red spruce) whereas Ampersand and Hennessy Mountain were dominated by acid intolerant species (sugar maple, eastern hophornbeam, basswood and white ash; Mbila et al., in preparation). Litter C and N concentrations did not differ among the stands but lignin:N ratios differed with Catlin Lake > Huntington Forest (IFS) > Hennessy Mountain > Ampersand. Differences in vegetation type (especially differences in the predominance of sugar maple) among the stands have likely resulted in different nutrient cycling patterns due to differences in the types of litter inputs (Fig. 7) and decomposition rates (Mbila et al., in preparation). Sugar maple with its low lignin concentration and relatively

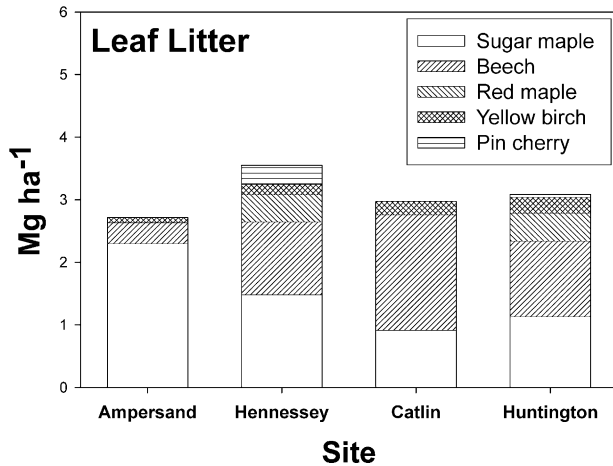


Fig. 7. Contributions of different tree species to leaf litter inputs to four hardwood sites in the Adirondack Mountains (data from Mbila et al., in preparation).

high N concentrations decomposes more rapidly than other litter types especially American beech with its relatively high lignin concentrations (Melillo et al., 1982; Mitchell et al., 1992b). The importance of vegetation type was previously shown in a comparison of a site in Turkey Lakes (Ontario, Canada) and the Huntington Forest (IFS) sites where the former site was almost exclusively sugar maple while the latter site had significant vegetation component of American beech (Mitchell et al., 1992b). The importance of vegetation type was also shown by Lovett et al. (2000) working in the Catskill Mountains of New York where watersheds with higher proportions of red oak that produces litter with high lignin content had lower  $\text{NO}_3^-$  concentrations in stream waters than watersheds dominated by other hardwood species.

### 3.2. Landscape influences

McHale et al. (in press) developed a conceptual model of stream flow generation and watershed  $\text{NO}_3^-$  release in the Arbutus watershed and suggested that hillslope hollows were the principal zones of water mixing and that till groundwater was the principal source of surface water  $\text{NO}_3^-$ . Inamdar et al. (2000, 2003a,b) used hydrograph separation techniques and TOPMODEL simulations to study the storm-event evolution of water and solutes from the Arbutus watershed. The intent was to investigate how landscape units such as hillslopes, variable source areas, and valley-bottom wetlands influenced the mixing and eventual expression of event (new) and pre-event (old) waters from the catchment. Using storm-event new and old water signatures and  $\text{NO}_3^-$  and DOC concentrations, Inamdar et al. (in preparation a,b) proceeded to establish an implicit linkage between water sources and solute concentrations.

Tracer-based hydrograph separations showed that old water contributions were highest on the initial portion of the rising limb of the hydrograph. In contrast, new water contribution peaked after the discharge peak and continued through hydrograph recession. Inamdar et al. (in preparation-a) attributed this lag in new water to the disconnectedness of variable source areas or surface-saturated in the watershed. The high old water contributions on the hydrograph rising limb were attributed to the displacement of till water by infiltrating rainwater. The release of glacial till water at spring-heads allowed for its early expression in streamflow.

Nitrate and DOC concentrations associated with summer storm-events followed patterns similar to the old and new water trajectories. Nitrate concentrations were found to peak early on the rising limb, with DOC concentrations reaching a peak value after maximum discharge. Solute concentrations measured in precipitation, throughfall, soilwater, and ground/till indicated till water and near-surface soil water as the controlling end-members for  $\text{NO}_3^-$  and DOC, respectively. Inamdar et al. (2003a,b) reconciled these observations on solute and new-old water signatures via a conceptual model (Fig. 8). The early expression of nitrate was attributed to the displacement of nitrate-rich glacial till water, whereas the lag in DOC expression was attributed to the delayed surface runoff from disconnected surface saturated areas.

These studies suggest that landscape patterns of connectivity may be especially important in affecting the spatial and temporal patterns of solutes in surface waters. In regions such as the Adirondacks where climate, glaciation, and slow soil development have generated a unique spatial mosaic of hillslopes, hollows, isolated saturated areas with thin soil mantle, and valley bottom wetlands the role of water connectivity may play a particularly important role within each watershed in affecting patterns of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and DON concentrations and fluxes. The degree of connectivity over time is strongly influence by antecedent moisture conditions and storm events, with high connectivity being only found during high moisture conditions (Inamdar et al., 2003a,b).

The importance of water sources in affecting  $\text{NO}_3^-$  concentrations was also emphasized by investigations in other regions (Mitchell, 2001). For example, Creed and Band (1998) working at the Turkey Lake watershed used a modeling approach that linked hydrological and biogeochemical processes and showed how topographic features can be used to explain much of the variability in  $\text{NO}_3^-$  export among small watersheds. Burns et al. (1998) have suggested for Catskill Mountain watersheds that groundwaters with high concentrations of  $\text{NO}_3^-$  may be an especially important source of N to streams during baseflow.

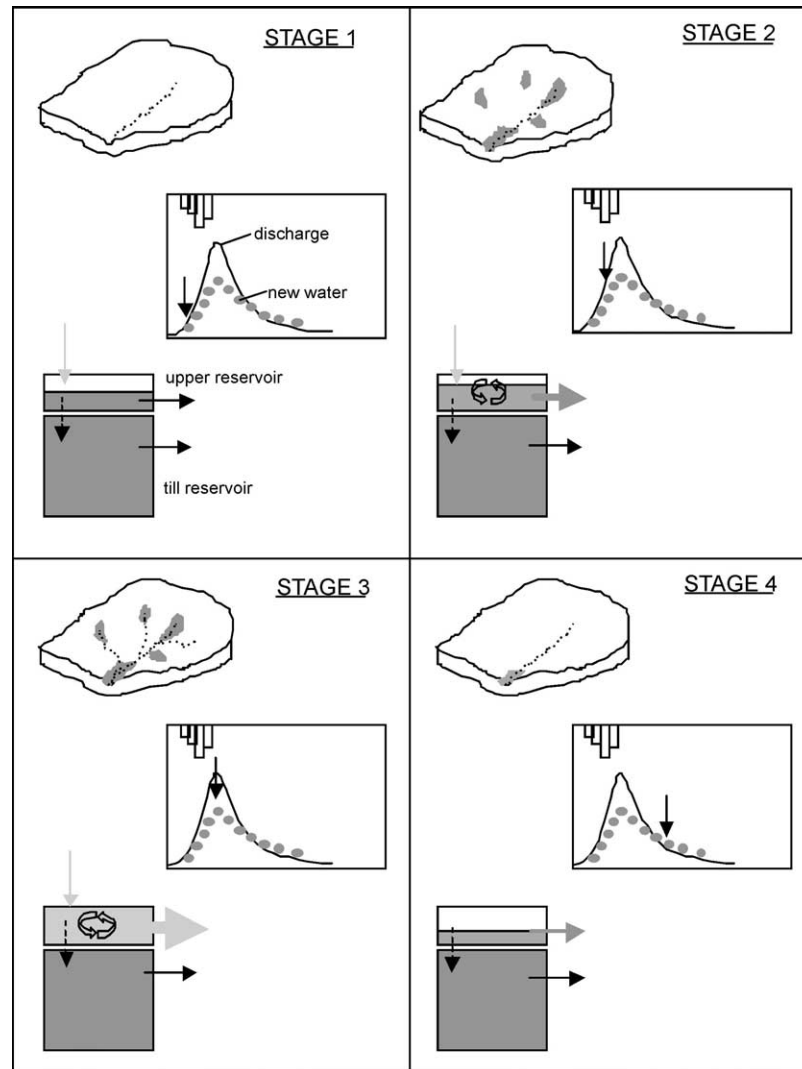


Fig. 8. Conceptual model for new water evolution at Archer Creek Catchment in the Arbutus Watershed considering the: (a) spatial distribution and connectivity of saturated areas; and (b) vertical mixing of waters. Note: arrow on the hydrograph (inset) indicates the stage during the event (from Inamdar et al., in preparation a).

#### 4. Conclusions

Studies of N biogeochemistry in the Adirondacks have shown that there are strong spatial patterns of N inputs from atmospheric deposition that result in some forest stands and watersheds having elevated  $\text{NO}_3^-$  concentrations in soil and surface waters. However, within the Adirondacks there is considerable heterogeneity in landscape types including differences in vegetation composition and the relative importance of uplands and wetlands. We have shown the role of this heterogeneity in affecting N cycling for a range of hardwood forests and watersheds in the region. Studies on forest stands have shown that vegetation composition has a major influence on soil solution  $\text{NO}_3^-$  concentrations. Studies within the Arbutus watershed have shown that topographical features can have a major influence on the contribution of different water sources to surface water

chemistry including  $\text{NO}_3^-$ . These topographical features are especially important in affecting the temporal patterns of  $\text{NO}_3^-$  concentrations in surface waters as functions of antecedent moisture conditions, connectivity of water sources and responses to storm events. Understanding how these spatial features are integrated and influence both short term and long term temporal patterns of N loss or retention within the Adirondacks will be critical in evaluating how changes in N atmospheric inputs will affect water quality, including recovery from acidification.

#### Acknowledgements

This research was funded by the New York State Energy Research and Development Authority (NYSERDA). This research was also supported by the

National Science Foundation and the USDA-Cooperative State Research Education and Extension Service. We also thank Sheila Christopher, Linda Galloway, Todd Hurd, Mari Ito, Michael McHale, Pat McHale and Ben Tabor. The staff at the Adirondack Ecological Center also contributed by providing facilities for some of this research. The comments of Gary Lovett on this manuscript were appreciated.

## References

- Aber, J.D., Driscoll, C.T., 1997. Effects of land use, climate variation, and N deposition on N cycling and C storage in northern hardwood forests. *Global Biogeochemical Cycles* 11, 639–648.
- Aber, J.D., McDowell, W., Nadelhoffer, K., Magill, A., Bernston, G., Kamakea, M., McNulty, S., Currie, W., Rustad, L., Fernandez, I., 1998. Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. *BioScience* 48, 921–934.
- Burns, D.A., Murdoch, P.S., Lawrence, G.B., Michel, R.L., 1998. The effect of ground-water springs on  $\text{NO}_3^-$  concentrations during summer in Catskill Mountain streams. *Water Resources Research* 34, 1987–1996.
- Campbell, J.L., Hornbeck, J.W., McDowell, W.H., Buso, D.C., Shanley, J.B., Likens, G.E., 2000. Dissolved organic nitrogen budgets for upland forested ecosystems in New England. *Biogeochemistry* 49, 123–142.
- Collins, B.S., Dunne, K.P., Pickett, S.T.A., 1985. Responses of forest herbs to canopy gaps. In: Pickett, S.T.A., White, P.S. (Eds.), *The Ecology of Natural Disturbance and Patch Dynamics*. Academic Press, Orlando, Florida, USA, pp. 218–234.
- Creed, I.F., Band, L., 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. *Water Resources Research* 34, 3105–3120.
- Driscoll, C.T., Van Dreason, R., 1993. Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes. *Water, Air and Soil Pollution* 67, 319–344.
- Driscoll, C.T., Postek, K.M., Krester, W., Raynal, D.J., 1995. Long-term trends in the chemistry of precipitation and lake water in the Adirondack region of New York, USA. *Water, Air and Soil Pollution* 85, 583–588.
- Driscoll, C.T., Postek, K.M., Mateti, D., Sequeira, K., Aber, J.D., Krester, W.J., Mitchell, M.J., Raynal, D.J., 1998. The response of lake water in the Adirondack region of New York to changes in acidic deposition. *Environmental Science: International Journal of Science and Policy* 1, 185–198.
- Emmett, B.A., 1998. Kjonaas, O. J., Gundersen, P., Koopmans, C., Tietema, A., Sleep, D., Natural abundance of  $^{15}\text{N}$  in forests across a nitrogen deposition gradient. *Forest Ecology and Management* 101, 9–18.
- 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., Stottley, R., 1998. Nitrogen excess in North American Ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecological Applications* 8, 706–733.
- Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., Zhu Zhao-Liang, 1996. Regional nitrogen budgets and lotic N and P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* 35, 75–139.
- Hurd, T.M., Raynal, D.J., Schwintzer, C.R., 2001. Symbiotic  $\text{N}_2$  fixation of *Alnus incana* ssp. *rugosa* in shrub wetlands of the Adirondack Mountains, New York, USA. *Oecologia* 126, 94–103.
- Hurd, T.M., Raynal, D.J., 2003. Nitrogen solutes and surface-groundwater interactions in riparian wetlands dominated by alder shrubs or coniferous trees. *Hydrological Processes* (in preparation).
- Inamdar, S.P., Mitchell, M.J., McDonnell, J.J., 2000. Topographic and riparian controls on hydrologic and biogeochemical response of forested catchments. In: Wigington, P.J., Beschta, R.L. (Eds.), *Riparian Ecology and Management in Multi-Land Use Watersheds*. American Water Resources Association, Middleburg, Virginia, TPS, pp. 137–142.
- Inamdar, S.P., Mitchell, M.J., McDonnell, J.J., McHale, P.J., 2003a. Use of new water ratios and surface saturated area estimates to test TOPMODEL.
- Inamdar, S.P., Christopher, S.F., Mitchell, M.J., 2003b. Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes*.
- Ito, M., Mitchell, M.J., Driscoll, C.T., 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack Region of New York. *Atmospheric Environment*.
- Johnson, D.W., Lindberg, S.E., 1992. *Atmospheric Deposition and Forest Nutrient Cycling. A Synthesis of the Integrated Forest Study*. Springer Verlag, NY.
- Krester, W., Gallagher, J., Nicolette, J., 1989. Adirondack Lakes Survey, 1984-1987: an Evaluation of Fish Communities and Water Chemistry. Adirondack Lakes Survey Corp. Ray Brook, New York.
- Lovett, G.M., Weathers, K.C., Sobczak, W.V., 2000. Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. *Ecological Applications* 10, 73–84.
- McGee, G.G., Mitchell, M.J., Mbila, M.O., Leopold, D.J., Raynal, D.J., 2003. The influence of forest age and composition on elemental dynamics of Adirondack northern hardwood forests. *Ecological Applications*, submitted for publication.
- McHale, M.R., Mitchell, M.J., McDonnell, J.J., Cirno, C., 2000. Nitrogen solutes in an Adirondack forested watershed: importance of dissolved organic nitrogen. *Biogeochemistry* 48, 165–184.
- McHale, M.R., McDonnell, J.J., Mitchell, M.J., Cirno, C.P. A field based study of soil and groundwater nitrate release in an Adirondack forested watershed. *Water Resources Research* (in press).
- Melillo, J.M., Aber, J.D., Muratore, J.F., 1982. Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. *Ecology* 63, 621–626.
- Mitchell, M.J., 2001. Linkages of nitrate losses in watersheds to hydrological processes. *HPToday* 15, 3305–3307.
- Mitchell, M.J., Burke, M.K., Shepard, J.P., 1992a. Seasonal and spatial patterns of S, Ca and N dynamics of a northern hardwood forest ecosystem. *Biogeochemistry* 17, 165–189.
- Mitchell, M.J., Foster, N.W., Shepard, J.P., Morrison, I.K., 1992b. Nutrient cycling in Huntington Forest and Turkey Lakes deciduous stands: nitrogen and sulfur. *Canadian Journal of Forest Research* 22, 457–464.
- Mitchell, M.J., Driscoll, C.T., Porter, J.H., Raynal, D.J., Schaefer, D., White, E.H., 1994. The Adirondack Manipulation and Modeling Project (AMMP): Design and preliminary results. *Forest Ecology and Management* 68, 87–100.
- Mitchell, M.J., Raynal, D.J., Driscoll, C.T., 1996a. Biogeochemistry of a forested watershed in the central Adirondack Mountains: temporal changes and mass balances. *Water Air and Soil Pollution* 88, 355–369.
- Mitchell, M.J., Driscoll, C.T., Murdoch, P., Likens, G.E., Kahl, J.S., Pardo, L., 1996b. Climatic control of nitrate loss from forested watersheds in the northeast United States. *Environmental Science and Technology* 30, 2609–2612.
- Mitchell, M.J., McHale, P.J., Inamdar, S., Raynal, D.R., 2001a. Role of within lake processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack Mountains of New York State, USA. *Hydrological Processes* 15, 1951–1965.
- Mitchell, M.J., Driscoll, C.T., Owen, J., Schaefer, D., Michener, R., Raynal, D.J., 2001b. Nitrogen biogeochemistry of three hardwood

- forest ecosystems in the Adirondack Mountains. *Biogeochemistry* 56, 93–133.
- Mollitor, A.V., Raynal, D.J., 1982. Atmospheric deposition and ionic movements in Adirondack forest soils. *Soil Science Society of America Journal* 46, 1032–1036.
- Mollitor, A.V., Raynal, D.J., 1983. Atmospheric deposition and ionic input in Adirondack forests. *Journal of Air Pollution Control Association* 33, 1032–1036.
- Nadelhoffer, K.J., Emmett, B.A., Gundersen, P., Kjønaas, O.J., Koopmans, C.J., Schleppi, P., Tietema, A., Wright, R.F., 1999. Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature* 398, 145–147.
- NAPAP, 1998. National Acid Precipitation Assessment Program Biennial Report to Congress: An Integrated Assessment (1996).
- Ohuri, K., Mitchell, M.J., Bischoff, J.M., 1999. Effect of landscape position on N mineralization and nitrification in a forested watershed in the Adirondack Mountains of New York. *Canadian Journal of Forest Research* 29, 497–508.
- Paerl, H.W., 1997. Coastal eutrophication and harmful algal blooms: importance of atmospheric deposition and groundwater as “new” nitrogen and other nutrients. *Limnology and Oceanography* 42, 1154–1165.
- Reuss, J.O., Johnson, D.W., 1986. *Acid Deposition and the Acidification of Soils and Surface Waters*. Ecological Studies 59. Springer-Verlag, New York.
- Richey, D. 1995. Nitrogen Oxide and Methane Flux between Forest Soils and the Atmosphere and the Effects of Ammonium Sulfate Fertilization. MS thesis, Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York.
- 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*. Advances in Chemistry Series 237. American Chemical Society, Washington, DC, USA, pp. 223–284.
- Stoddard, J.L., Jeffries, D.S., Lukewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvale, B.L., Stainton, M.P., Traaen, T., vanDam, H., Webster, K.E., Wieting, J., Wilander, A., 1999. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* 401, 575–578.
- Vitousek, P.M., Aber, J., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, G.D., 1997. Human alteration of the global nitrogen cycle: causes and consequences. *Ecological Applications* 7, 737–750.
- Wigington Jr., P.J., DeWalle, D.R., Murdoch, P.S., Krester, W.A., Simonin, H.A., Van Sickle, J., Baker, J.P., 1996. Episodic acidification of small streams in the northeastern United States: ionic controls of episodes. *Ecological Applications* 6, 389–407.