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## *Element Cycling in Upland/ Peatland Watersheds*

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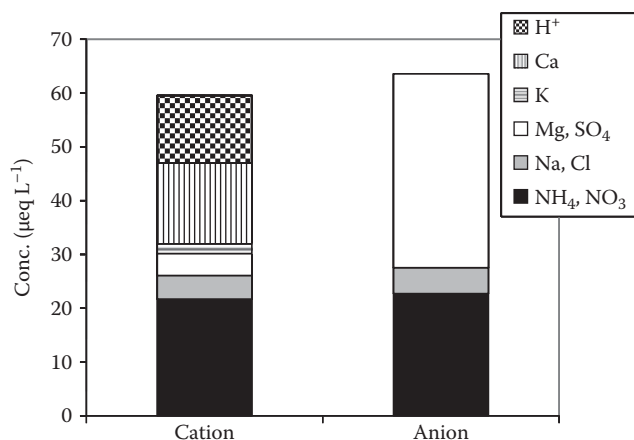
### Introduction

Studies at the Marcell Experimental Forest (MEF) have measured the pools, cycling, and transport of a variety of elements in both the upland and peatland components of the landscape. Peatlands are important zones of element retention and biogeochemical reactions that greatly influence the chemistry of surface water. In this chapter, we summarize findings on nitrogen (N), sulfur (S), carbon (C), major cations, and other biogeochemically important elements in uplands and peatlands. We have organized this chapter to describe processes that affect the transport and storage of elements in watersheds. First, we address a primary route for entry into ecosystems, atmospheric deposition. We then describe compositional changes as water passes through canopies in upland forests before water and solutes infiltrate soils. We also track changes in chemistry as precipitation infiltrates organic soils in bogs, upland runoff passes into the lags that surround bogs, and groundwater

passes through fens. We then examine solute concentrations and yields as waters exit watersheds at the downstream end. Finally, we summarize the cycling of elements within the watersheds.

## Atmospheric Deposition

Monitoring of atmospheric deposition at the MEF began in the early 1970s with measurements of bulk deposition in open sites and measurement of throughfall and stemflow in forested sites (Verry and Timmons, 1977). The MEF was one of the original sites of the National Atmospheric Deposition Program (NADP). The chemistry of wet-only precipitation has been monitored continuously there since 1978. This long record of atmospheric inputs has been invaluable in formulating budgets and informing process studies. Verry (1983) was the first to summarize the solute composition of wet-only precipitation at the MEF. The dominant cations were ammonium ( $\text{NH}_4^+$ ), calcium ( $\text{Ca}^{2+}$ ), and hydrogen ion ( $\text{H}^+$ ), and the dominant anions were nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ; Figure 8.1). The mean pH from 1978 through 1980 was 4.9, and variability in  $\text{H}^+$  concentration most closely tracked variations in  $\text{NO}_3^-$  concentrations. The nearly equal concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  reflect the remote, rural location distant from both industrial and agricultural sources. Little of the  $\text{SO}_4^{2-}$  is associated with sea salt at this site, but

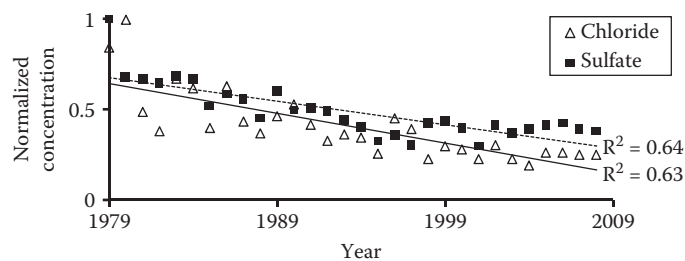


**FIGURE 8.1**

Average (volume-weighted mean) ionic composition of wet-only precipitation as measured at the MEF for 1978–1980, Verry, 1983). Concentrations are expressed as charge equivalents. The  $\text{Na}^+$  concentration reported by Verry was reduced because it was more than 50% higher than the 3-year mean of values now reported by the NADP for 1978–1980.

Verry reported that  $\text{SO}_4^{2-}$  concentrations were not correlated with  $\text{H}^+$  concentration and hence probably not derived only from sulfur dioxide ( $\text{SO}_x$ ) emissions.

There have been significant changes in precipitation chemistry during the NADP monitoring (1978 to present). Volume-weighted mean annual concentrations of  $\text{SO}_4^{2-}$  have declined, closely paralleling a decline in chloride ( $\text{Cl}^-$ ) concentrations (Figure 8.2). The pH has increased by about 0.3 units, but this decrease in  $\text{H}^+$  concentration is five times smaller than the decrease in  $\text{SO}_4^{2-}$  concentration on an equivalent basis. The decrease in  $\text{SO}_4^{2-}$  concentration is most strongly correlated with decreases in sodium ( $\text{Na}^+$ ) and  $\text{Cl}^-$  concentrations, though significant correlations are also observed among  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and magnesium ( $\text{Mg}^{2+}$ ) concentrations (Table 8.1). These correlations support the contention that soil dust is a significant source of the  $\text{SO}_4^{2-}$  deposited at



**FIGURE 8.2** Historical changes in precipitation at the MEF. Volume-weighted mean concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were normalized to the maximum value in the period of record to put both on the same scale. Solid lines show the least-squares regression; the upper line is for  $\text{SO}_4^{2-}$ , and the lower is for  $\text{Cl}^-$ . Both regressions are statistically significant ( $p < 10^{-6}$ ).

**TABLE 8.1**

Correlation Coefficients for Volume-Weighted Mean Nutrient Concentrations in Wet-Only Precipitation Collected at the MEF NADP Station (1978–2008)

	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	pH
$\text{Ca}^{2+}$	1							
$\text{Mg}^{2+}$	0.89 <sup>a</sup>	1						
$\text{K}^+$	0.68 <sup>a</sup>	0.64 <sup>a</sup>	1					
$\text{NH}_4^+$	0.38 <sup>a</sup>	0.17	0.19	1				
$\text{NO}_3^-$	0.60 <sup>a</sup>	0.45 <sup>a</sup>	0.48 <sup>a</sup>	0.43 <sup>a</sup>	1			
$\text{Cl}^-$	0.52 <sup>a</sup>	0.51 <sup>a</sup>	0.38 <sup>a</sup>	-0.06	0.71 <sup>a</sup>	1		
$\text{SO}_4^{2-}$	0.66 <sup>a</sup>	0.68 <sup>a</sup>	0.42 <sup>a</sup>	0.17	0.75 <sup>a</sup>	0.80 <sup>a</sup>	1	
pH	0.10	-0.02	0.01	0.43 <sup>a</sup>	-0.32	-0.58 <sup>a</sup>	-0.55 <sup>a</sup>	1

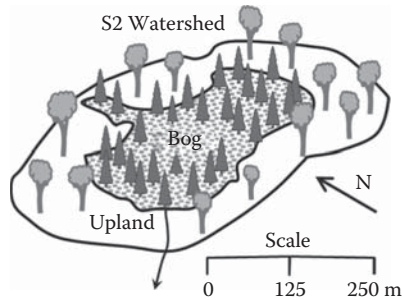
<sup>a</sup> Significant at  $p < .05$ .  $\text{Na}^+$  was excluded due to significant skew and lack of normality in the distribution.

this site (Urban et al., 1989c); agricultural lands are several hundred kilometers to the south and southwest. During this period, a trend toward decreasing deposition of  $\text{NO}_3\text{-N}$  (Figure 2.3b) at the MEF and elsewhere throughout the upper Midwest is consistent with a decrease in N oxide emissions (McDonald et al., 2010).

Comparison of bulk precipitation (wet plus dry deposition) collected in the open and below canopies of aspen on uplands and black spruce in peatland showed that some elements increased in concentration and others decreased while passing through the canopy. Inorganic N is taken up by the canopy while phosphorus (P), organic N,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  are enriched in throughfall (Verry and Timmons, 1977). Some of this enrichment results from washoff of dry deposition from the canopy, but, for  $\text{K}^+$ , the increased fluxes in throughfall represent leaching from plant foliage. For N, there may be conversion of inorganic N to organic N by epiphytic bacteria, lichens, or algae; in the black spruce stand, there was no enrichment in total N after passing through the canopy. Collection of dry deposition by foliage and subsequent washoff by precipitation has been reported for other substances, including  $\text{SO}_4^{2-}$  (Verry, 1986), mercury (Hg) (Kolka et al., 1999b), and trace metals (e.g., Lindberg et al., 1986). Because of the greater leaf area index of conifers (dominant in the peatlands), the enrichment of these substances in throughfall into the peatlands is greater than in the uplands that are characterized by hardwood (aspen) stands (Kolka et al., 1999b). That deposition of most cations increased more upon passage through the aspen canopy compared to the black spruce canopy suggests that much of the increase results from leaching from deciduous vegetation.

Atmospheric deposition of organic carbon has been poorly characterized (e.g., Willey et al., 2000). Studies at the MEF have provided some of the few measurements in the region. Results showed that wet deposition of organic carbon is about seven times less than the yield of organic carbon from the MEF watersheds. Kolka et al. (1999b) reported an organic carbon flux in bulk precipitation of  $1.2 \text{ g C m}^{-2} \text{ year}^{-1}$  for 1995. This flux is within the range ( $0.2\text{--}1.7 \text{ g C m}^{-2} \text{ year}^{-1}$ ) reported from other locations (Dillon and Molot, 1997; Willey et al., 2000). Considerable organic carbon is leached from tree canopies; the flux (throughfall and stemflow) below aspen canopies was  $7.6 \text{ g C m}^{-2} \text{ year}^{-1}$  vs.  $8.5 \text{ g C m}^{-2} \text{ year}^{-1}$  below a spruce canopy. Whether this organic matter is exported, respired, or stored within the ecosystems is not known.

The measurements of wet-only deposition and bulk deposition at the MEF provide some of the few data available to estimate atmospheric deposition of organic N (cf. Neff et al., 2002). Verry and Timmons (1977) reported bulk deposition in the open of  $0.23 \text{ g organic N m}^{-2} \text{ year}^{-1}$  for a typical year; Urban (1983) reported wet-only deposition of organic N of  $0.05 \text{ g m}^{-2} \text{ year}^{-1}$  in 1982. The discrepancy suggests that dry deposition of organic N is much larger than wet deposition, perhaps on the order of  $0.2 \text{ g N m}^{-2} \text{ year}^{-1}$ .



**FIGURE 8.3**  
Schematic of the S2 watershed. The uplands comprise two-thirds of the watershed. (Adapted from Kolka, R.K. et al., *J. Environ. Qual.*, 28, 766, 1999a.)

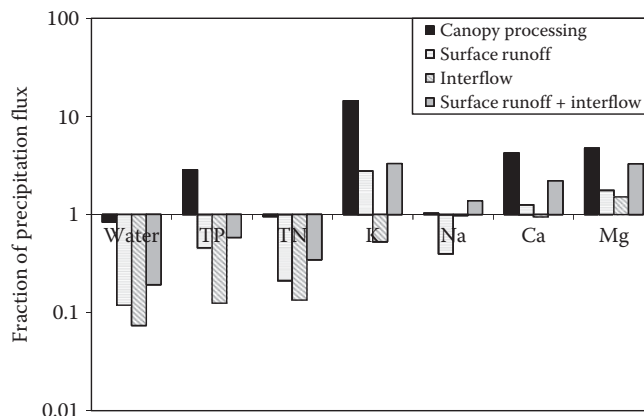
Throughfall studies generally focus on the overstory, but shrubs, herbaceous species, and bryophytes likely modify precipitation chemistry. To determine the significance of denitrification in the S2 wetland (Figure 8.3), Urban et al. (1989b) measured  $\text{NO}_3^-$  at successive depths below the moss surface. They observed that  $\text{NO}_3^-$  was essentially removed from the percolating rain water, leaving little to be denitrified in anaerobic regions of the peat.

### Processing of Elements in the Uplands of the MEF Watersheds

The bogs within the MEF are perched rather than raised, so laggs receive runoff from the surrounding mineral-soil uplands (Chapter 7). The uplands support mixed hardwood forests in various stages of succession (Chapters 2 and 12). Timmons et al. (1977) reported on water and element fluxes in runoff from the upland of the S2 watershed from 1971 to 1973. Runoff from the upland in this watershed occurs as surface runoff (primarily within the organic O horizon) and as interflow in mineral soil horizons above the less permeable B2t horizon due to clay. The composition of the runoff entering the wetlands is determined by the flow path.

Water flowpaths in the uplands vary seasonally. Surface runoff is confined largely to snowmelt. From 1971 to 1973, snowmelt accounted for 46%–68% of total annual water loss from the S2 upland, but it supplied 93%–100% of the total annual runoff. Some surface runoff occurs in response to large rain events but does not usually contribute a significant amount to the annual surface runoff.

Elements can be placed in four categories based on the manner in which they cycle within and pass through the uplands (Figure 8.4). Category 1 elements (e.g.,  $\text{Na}^+$ ) include substances that pass largely unaltered through the upland; bars showing flux ratios in Figure 8.4 are small, because the



**FIGURE 8.4**

Processing of elements within the S2 upland. The y axis shows the ratio of each flux (throughfall + stemflow, surface runoff, interflow, and surface runoff + interflow) to the flux in bulk deposition; values greater than one indicate that this flux is larger than the input to the system from atmospheric deposition (i.e., a net release of the element from the catchment occurred); values less than one indicate the element was retained in the system. The canopy processing bar includes both throughfall and stemflow. Data for interflow and surface runoff represent a 3 year average (1971–1973; Timmons, et al., 1977). Fluxes in bulk precipitation, throughfall, and stemflow are from Verry and Timmons (1977).

ratio of fluxes remains close to 1. Category 2 elements are leached from the canopy in throughfall and stemflow (large flux ratio shown by the black bar in Figure 8.4), but then are strongly retained in the soil (flux ratios less than one for remaining three bars). Total P falls into this category; the upland is a net sink for this substance. Category 3 substances (e.g., total N) are not leached from the aspen canopy (small black bar) and are also strongly retained in the soil (all other flux ratios below one), such that the upland is a stronger sink than for Category 2 elements. Category 4 elements (e.g.,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) have flux ratios greater than 1; they are highly enriched in throughfall and stemflow relative to bulk precipitation. Unlike N and P, these elements are also enriched in upland runoff relative to inputs from bulk precipitation. The uplands act as a net source for these substances. Part of the export of these substances from the uplands is a result of chemical weathering of the mineral soils. Plants augment weathering and affect the seasonality of the element export. The cations are extracted by plants from the mineral soils, and a fraction of the uptake is transported into the foliage; the cations are then leached from the canopy and flushed from the uplands upon decomposition of the leaf litter. Potassium and  $Ca^{2+}$  are flushed primarily in surface runoff, but  $Mg^{2+}$  also has a large flux in interflow. The peatlands receive significant inputs of Category 4 elements in runoff from the uplands.

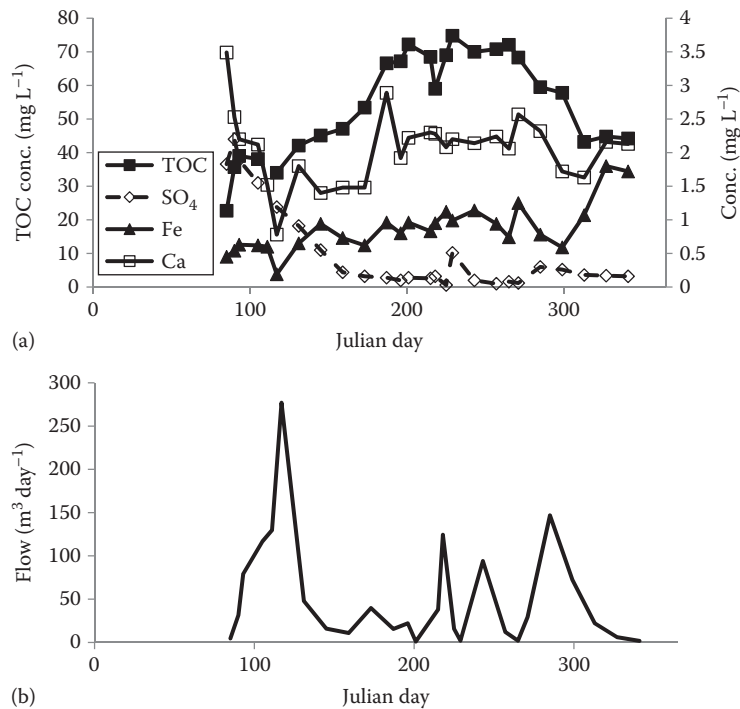
## Processing of Elements in the MEF Peatlands

### Element Export from the MEF Peatlands

#### Concentrations in Outflow

Hydrology has a major influence on seasonal patterns in element cycling. The major hydrologic event of the year at these sites is snowmelt, which generates the peak flows for the year (Julian day 125 in Figure 8.5b). During snowmelt, water retention time in the wetlands is at an annual minimum, and element uptake is correspondingly low. Although most precipitation occurs in summer months (Chapter 2), high evapotranspiration rates during these months result in little or no runoff to streams. In autumn, streamflow increases again as evapotranspiration decreases in response to plant senescence, reduced solar radiation, and falling temperatures.

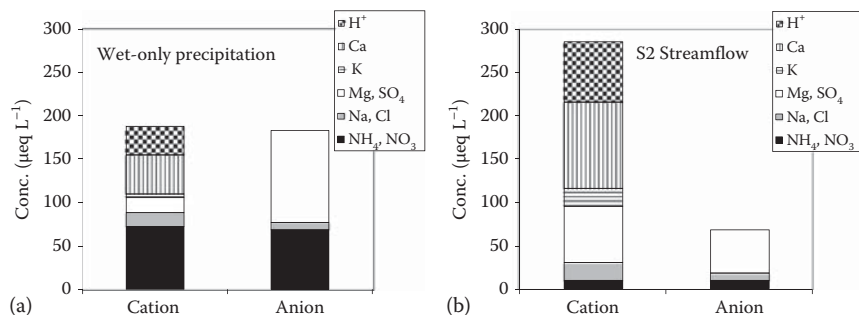
Element concentrations in the MEF streams reflect this hydrologic cycle. Biologically active substances ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) exhibit peak



**FIGURE 8.5** Concentrations for several solutes including TOC, Fe,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$ -S for 1981 (a); and seasonal cycle of water flow in 1981 (b).

concentrations during early snowmelt and minimum concentrations in summer (Figure 8.5a). Spring snowmelt generally is the only time of year when  $\text{NO}_3^-$  is measurable in the outflow from S2. Concentrations are highest in summer for substances generated by peat decomposition or bound to the dissolved organic matter (DOM) from peat decomposition (e.g., organic C, organic N, organic S, aluminum [Al], and iron [Fe]). Other substances exhibit intermediate patterns. As shown in Figure 8.5a,  $\text{Ca}^{2+}$  shows high concentrations during early snowmelt, but concentrations also increase during summer low-flow periods.

Streamflow draining the MEF watersheds reflects processes both in the uplands and in the peatlands. For instance, the increase in  $\text{Ca}^{2+}$  concentrations in autumn in the S2 stream likely reflects leaching from leaf litter in the uplands (Figure 8.5). Comparison of volume-weighted mean annual concentrations in streamflow and precipitation (Figure 8.6) shows the net effect of all processes in the watershed. Some ions ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$ ) are retained by the watershed while others ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{H}^+$ ) are “produced” within the watershed. The uptake of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  from the mineral soils into the upland plants and subsequent litterfall, leaching, and flow into the wetland was discussed previously as was the net retention of N by the upland (Timmons et al., 1977; Verry and Timmons, 1982). Figure 8.6 also indicates



**FIGURE 8.6**

Comparison of volume-weighted mean ion concentrations in atmospheric deposition and streamflow (S2) for 1981. Concentrations are expressed in charge equivalents per liter. Because much of the precipitation is evapotranspired, solute concentrations are much higher in streamflow than in precipitation even for substances with identical fluxes in precipitation and streamflow. To facilitate seeing the changes in fluxes, precipitation concentrations have been multiplied by 3.98, the quotient of annual precipitation (77.65 cm), and streamflow (19.5 cm) in 1981. Cationic charges are increased as they pass through the watershed due to the release of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  from the mineral soils and also due to the generation of free  $\text{H}^+$  in the wetland. Sodium and  $\text{Cl}^-$  pass through the watershed nearly unaltered (export/input=132% for  $\text{Na}^+$ , and 99% for  $\text{Cl}^-$ ). Measured anionic charge equivalents are greatly reduced due to retention of  $\text{NO}_3^-$  in both the upland and peatland and retention of  $\text{SO}_4^{2-}$  in the peatland. The apparent charge imbalance indicates the quantity of dissociated organic anions (humic and fulvic acid anions); organic anions protonated at the pH of the bog water (~50% of total organic anions, Urban et al., 1989a) as well as those bound to Fe and Al (~12% of total organic anions) do not appear in the charge balance shown.



the generation of free acidity ( $H^+$ ) by the peatland, and the large imbalance in ionic charge in the stream indicates the presence of high concentrations of organic anions. High concentrations of DOM generated in the peatlands and its associated acidity are important characteristics of streamflow from the MEF watersheds.

Research at the MEF has elucidated many features of the export from peatlands of DOM, which is generally measured as dissolved organic carbon (DOC). DOM is an important water-quality parameter that is intimately linked with biogeochemical cycles of several elements and with important ecosystem processes. DOM in surface waters affects light penetration (e.g., Fee et al., 1996; Jackson and Hecky, 1980), metal speciation and mobility (e.g., Lazerte, 1991), nutrient availability (e.g., Jones et al., 1988; Koenings and Hooper, 1976), alkalinity and pH (e.g., Oliver et al., 1983; Urban et al., 1989a), and toxicity and bioavailability of organic contaminants (e.g., Capel and Eisenreich, 1990). Colored organic matter is one of the primary controls on the penetration of potentially harmful UV radiation into lakes (e.g., Jerome and Bukata, 1998; Schindler et al., 1996; Smith et al., 1998). Carbon and energy are moved from terrestrial systems through surface waters in the form of DOM. Respiration of DOM in surface waters returns the carbon to the atmosphere (Cole et al., 1994; Kling et al., 1991). Many lakes are net sources of carbon dioxide to the atmosphere because of the organic carbon flow from their watersheds (Cole et al., 2000; Dillon and Molot, 1997; Schindler et al., 1997a). Concentrations of DOM derived from watersheds are high enough to cause 20%–40% of the lakes in northern Europe, eastern Canada, and the north-eastern and upper Midwest of the United States to be brown colored, with color greater than 50 platinum–cobalt units (Gorham et al., 1986; Lillie and Mason, 1983; Overton et al., 1986; Rogalla, 1986; Wright, 1983). Clearly, DOM export from the MEF watersheds is important not only within the watersheds but also for receiving waters.

Awareness of water color, its association with organic compounds, and its production in wetlands predates the MEF and can be traced to at least the early nineteenth century (e.g., De Luc, 1810, cited in Garham, 1953). Early investigators had no method for measuring concentrations of DOM, and so there are few early paradigms for the factors regulating DOM concentrations in wetlands (see review in Gorham et al., 1985). De Luc (cited in Gorham, 1953) noted in 1810 that a “brown peat tint” first appeared in wetland waters at the stage when *Sphagnum* invaded. Methods for quantifying color were developed in the late nineteenth century (Hazen, 1892, 1896; Richards and Ellis, 1896), and Thompson et al. (1927) noted that the intensity of the yellow color in wetland waters increased with the stage of plant development.

Because of the disproportionate contribution of DOM by wetlands relative to their surface area, numerous authors have suggested that DOM concentrations in rivers and lakes can be predicted on the basis of the percentage of the watershed occupied by wetlands. Engstrom (1987) demonstrated that the color of Labrador lakes could be explained largely on the basis of

the area of wetland in the watershed. Similarly, DOM from wetlands was the primary contributor to color and natural acidity in Nova Scotian lakes (Gorham et al., 1986) and streams (Gorham et al., 1998). Eckhardt and Moore (1990) and Koprivnjak and Moore (1992) found that DOM concentrations in Canadian streams can be predicted based on the fraction of the watershed occupied by wetlands. Gergel et al. (1999) found that DOM concentrations in streams were predicted better by the percentage of watershed in wetlands than DOM concentrations in lakes; lakes appeared to be influenced more strongly by nearshore wetlands than by wetlands higher in the watershed. It is not known whether the predictive relationships in the individual studies can be extrapolated to larger geographic areas (cf. Aitkenhead et al., 1999) or whether the predictive capabilities can be refined by distinguishing among different types of wetlands that have different DOM concentrations (cf. Frost et al., 2006).

Work at the MEF helped document the relationship between acidity of peatland drainage and DOM. A link between peatland acidity and organic acids was hypothesized in the early 1900s (e.g., Ramaut, 1954; Skene, 1915; Thompson et al., 1927). In 1980, Hemond (1980) showed that the acidity of one bog was due to dissolved humic and fulvic acids (see also McKnight et al., 1985). The generality of this conclusion was demonstrated by Gorham et al. (1985) and Urban et al. (1987a) in a survey of North American peatlands, among which the S2 bog featured prominently. The buffering capacity and acidity of DOM have been characterized in several studies (e.g., Oliver et al., 1983; Tipping et al., 1988); titrations of waters from the S2 watershed were consistent with the model proposed by Oliver (Urban, 1987; Urban et al., 1989). The pH of individual peatlands results from the titration of the humic and fulvic acids generated in the peatlands by the bases entering peatlands from atmospheric deposition, groundwater discharge, upland runoff, or anion uptake in the peatland (Urban, 1987; Urban and Bayley, 1986; Urban et al., 1987a). Gorham et al. demonstrated the titration of organic acids that occurs across the spectrum from bogs to calcareous fens and the bimodal distribution of pH in peatlands that results from the low buffer capacity of organic acids in the pH range of 4.5–5.5 (e.g., Gorham et al., 1984, 1985; Mullen et al., 2000). In many locations, there is a large effect of wetland drainage on the alkalinity of receiving waters (e.g., Bishop et al., 2000; Driscoll and Bisogni, 1984).

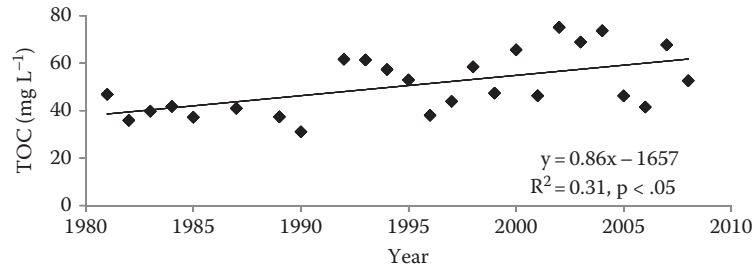
Research at the MEF documented the magnitude of DOC export from peatlands (Urban et al., 1989), systematic differences in DOM concentrations and export among different types of wetlands (Urban et al., 1989), variations in DOM composition, and geographic patterns in DOM concentrations (and associated acidity) in peatland waters (Gorham et al., 1985; Urban et al., 1987b). From 1981 to 1985, export of DOC ranged from 9 to 28 g C m<sup>-2</sup> year<sup>-1</sup> for S2 and 9 to 43 g C m<sup>-2</sup> year<sup>-1</sup> for S6 (Urban et al., 1989a). The export of DOC represents 5%–10% of net primary production in the peatlands, a significant component of the carbon budget. A similar rate of DOC export (19 g C m<sup>-2</sup> year<sup>-1</sup>)

was measured for a bog in watershed 239 of the Experimental Lakes Area (ELA) in western Ontario, Canada, and estimated for bogs across northeastern North America ranged from 5 to 20 g C m<sup>-2</sup> year<sup>-1</sup> (Urban et al., 1987a). These rates of DOC export from peatlands are large relative to export rates from upland (unsaturated soils) forests in the same area (<1–6 g C m<sup>-2</sup> year<sup>-1</sup>). The differences in the export rates among three wetlands, two at the MEF and one at ELA, reflected differences in water yields. The high carbon export rates from peatlands explain why the areal extent of wetlands is a good predictor of organic carbon loading to lakes and streams.

Concentrations of DOC in peatland waters range from 5 to more than 60 mg L<sup>-1</sup> (Gorham et al., 1985). The DOC concentrations in outflow from both the S2 (flow-weighted means of 31–75 mg L<sup>-1</sup> for 1981–2008) and S6 (flow-weighted means of 31–47 mg L<sup>-1</sup>) peatlands exceed the mean concentration reported for 28 peatlands across northeastern North America (Gorham et al., 1985). Higher DOC concentrations in midcontinental peatlands reflect the higher ratios of evapotranspiration to precipitation that result in lower water flow rates and less dilution of DOC by rain (Urban et al., 1987a). Watershed studies in Ontario have shown that droughts reduce water and DOC yields from the watersheds (D'arcy and Carignan, 1997; Moore et al., 1998; Schiff et al., 1998; Schindler et al., 1996).

Research at the MEF also has documented other effects of the export of DOM from peatlands. The high concentrations of DOM in bog waters result in a large binding capacity of bog waters for minor and trace metals. Binding sites on DOM compete with binding sites on the solid phase (peat), and can result in significant loss of trace metals from peatlands that experience significant water flow out of the system. In the S2 peatland, only about 35% of lead (Pb) inputs were retained (Urban et al., 1990). Leaching of <sup>210</sup>Pb from peat below the water table rendered <sup>210</sup>Pb-dating inaccurate at this site as well as at numerous other peatlands throughout North America (Urban et al., 1990). Aluminum in outflow from the MEF watersheds also is primarily (>85%) organically bound (Helmer et al., 1990). There are strong correlations between export of Hg and DOC from the MEF watersheds (Chapter 11; Kolka et al., 1999a, 2001), and, across the landscape, there is a correlation between the percentage of wetlands in watersheds and stream Hg concentrations (Grigal, 2002). Retention of Hg in the S2 watershed is only about 80% efficient largely due to the export of Hg bound to particulate organic matter and DOM in the outflow (Grigal et al., 2000). Enrichment of the DOM with organic S may contribute to the loss of Hg from the watershed (cf. Drexel et al., 2002; Ravichandran, 2004).

Given the importance of DOM to biogeochemical processes within the MEF watersheds as well as in receiving waters, any changes in export of DOM over time may have significant biogeochemical repercussions. Historical changes in DOC concentrations in lakes, streams, and rivers have been reported in several areas of the world and variously attributed to climate change and changes in acid deposition and land use (Hruska et al., 2009; Lepisto et al., 2008; Monteith et al., 2007; Schindler et al., 1997b). Data

**FIGURE 8.7**

Historical increase in volume-weighted concentrations of TOC in outflow from the MEF S2.

from the S2 watershed also indicate that concentrations of DOC and total organic C (TOC) in the outlet stream have increased over the past 30 years (Figure 8.7). The statistically significant trendline (linear regression,  $p < .05$ ) suggests that concentrations have increased by more than 50% ( $15\text{--}25\text{ mg L}^{-1}$ ) since 1980. Although concentrations have increased significantly, fluxes have not; the trend toward increasing fluxes over time is not statistically significant (linear regression,  $p = .14$ ), and fluxes in the most recent 10 years are not significantly different (t-test,  $p > .05$ ) than fluxes in the first 10 years of the record.

Decreasing inputs of sulfuric acid in rain probably do not cause an increase in TOC concentrations in the S2 stream. It is thought that the trend in England, Scandinavia, and northeastern North America of increasing DOC concentrations in rivers, streams, and lakes over the past 20 years (e.g., Lepisto et al., 2008; Worrall and Burt, 2004; Worrall et al., 2003) is due to a decrease in atmospheric deposition of sulfuric acid (De Wit et al., 2007; Evans et al., 2006; Monteith et al., 2007). This hypothesis reinvoles the theory of Krug and Frink (1983) that mineral acid deposition inhibits the release of organic acids into surface waters by increasing ionic strength and decreasing pH (see Evans et al., 2008). However, at the MEF, there has been no significant change in concentrations of  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$ , and pH has declined in the stream outflow over the 30 year record despite a decrease in the atmospheric deposition of both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . An increase in DOC solubility as a result of higher pH has not occurred here. Because there has been no change in  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  concentration in the outflow, the change in TOC cannot be attributed to changing ionic strength driven by declines in concentrations of acid anions. These two ions are strongly retained by the watershed; it is possible that a decrease in retention of these anions has caused a decrease in alkalinity generation within the watershed. Such a change in alkalinity generation and export, if it has occurred, is hidden in the “anion deficit” of the outflow; changes in this unmeasured concentration of organic anions could cause changes in ionic strength, but such a change has not been observed. There has been a slight increase in electrical

conductivity over the 30 year record, which suggests that ionic strength has not declined at this site, certainly not by the amount necessary to induce an increase in DOC concentrations (cf. Hruska et al., 2009). Concentrations and yields of other major ions also are buffered biogeochemically by the watershed such that changes in precipitation inputs have minor effects on the stream draining the watershed. For instance, the historical reduction in  $\text{Ca}^{2+}$  deposition in precipitation (14% decrease from 1980 to 2008) has not resulted in a decrease in concentrations or fluxes of  $\text{Ca}^{2+}$  in the S2 outflow. Atmospheric deposition of  $\text{Na}^+$  and  $\text{Cl}^-$  has declined by 60%–70% over the past 30 years; this decline would cause at most a decrease in ionic strength of 3% if it was observed in the streamflow. However, there has been no trend in streamflow concentrations and yields since 1980. The interquartile ranges in annual streamflow, TOC export, and volume-weighted mean concentrations of TOC and several major ions have increased over 30 years. Hence, it seems that acid rain is not the causative factor at this site, but it is not clear whether the increased variability and increased concentrations of TOC are a response to climate change.

### ***Variations among Wetland Types***

Studies at the MEF have helped clarify the dependence of dissolved solute composition on water flowpaths. There is a large difference in the water chemistry of streams draining the two types of wetlands (perched bogs and groundwater fens) in the gaged watersheds at the MEF. Although both uplands and wetlands comprise the watersheds, streamflow is generated primarily from the wetland portions of the watersheds (Verry and Kolka, 2003). The relative contributions of peatlands and uplands to the solutes in the streamflow vary by solute (e.g., Kolka et al., 2001; Verry and Timmons, 1982).

A major distinction among the watersheds is that the groundwater fen (S3) has high concentrations of solutes derived from mineral dissolution (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and Si) relative to the perched bogs (S1, S2, S4, S5, and S6). A longer contact time of the groundwater with soil minerals allows greater dissolution than occurs in the upland runoff into the perched bogs. The bogs have higher concentrations of organically bound solutes (e.g., DOC, dissolved organic N [DON], dissolved organic phosphorus, Al, Fe, and Hg) as a result of lower water flow rates (less dilution of substances released from the peat) and lower ash content of the peat in the bogs. Higher ash content in fen peat implies higher concentrations of base cations, iron oxides, and aluminum oxides that would limit the release of organic matter into fen waters. The higher concentrations of inorganic ions in fen waters lead to higher conductivity while the higher organic-matter content of bog waters leads to higher color and lower pH. This contrast is illustrated in [Table 8.2](#) with data from Verry (1975) and Kolka et al. (1999a).

TABLE 8.2

Comparison of Fen and Bog Water Solute Concentrations<sup>a</sup>

Solute Category or Source	Solute Perched Bog Streamflow	Groundwater Fen Streamflow	Fen:Bog
Mineral dissolution			
Ca <sup>2+</sup>	2.4 mg L <sup>-1</sup>	16.6 mg L <sup>-1</sup>	6.9
Mg <sup>2+</sup>	0.97 mg L <sup>-1</sup>	2.88 mg L <sup>-1</sup>	3.0
Alkalinity	~0	54.2 mg L <sup>-1</sup> as CaCO <sub>3</sub>	>54
Si	2.7 mg L <sup>-1</sup>	4.9 mg L <sup>-1</sup>	1.8
Specific conductance	51 μS cm <sup>-1</sup> (25°C)	125 μS cm <sup>-1</sup> (25°C)	2.45
Organically bound			
DOC <sup>b</sup>	46.6 mg L <sup>-1</sup>	4.2 mg L <sup>-1</sup>	0.09
	0.69 mg L <sup>-1</sup>	0.33 mg L <sup>-1</sup>	0.48
TDP <sup>c</sup>	0.19 mg L <sup>-1</sup>	0.09 mg L <sup>-1</sup>	0.47
Al	0.79 mg L <sup>-1</sup>	0.16 mg L <sup>-1</sup>	0.20
Fe	1.35 mg L <sup>-1</sup>	0.98 mg L <sup>-1</sup>	0.72
Hg <sup>b</sup>	11.6 ng L <sup>-1</sup>	1.4 ng L <sup>-1</sup>	0.12
pH	3.6	6.5	
Color	303	100	
Atmospherically derived			
SO <sub>4</sub> <sup>2-</sup>	4.6 mg L <sup>-1</sup>	6.0 mg L <sup>-1</sup>	1.30
NO <sub>3</sub> <sup>-</sup>	0.20 mg L <sup>-1</sup>	0.10 mg L <sup>-1</sup>	0.50
Cl <sup>-</sup>	0.7 mg L <sup>-1</sup>	0.4 mg L <sup>-1</sup>	0.57

<sup>a</sup> All data except DOC and Hg are from Verry (1975). Values represent means of concentrations measured from 1968–1972.

<sup>b</sup> Data from Kolka et al. (1999a) includes the bogs at S1, S2, S4, and S5, and the S3 fen. Mean of the volume-weighted means for 1994 and 1995.

<sup>c</sup> TDP, total dissolved phosphorus.

### Element Budgets

Element budgets have been measured and reported multiple times for the MEF watersheds (e.g., Urban and Bayley, 1986; Urban and Eisenreich, 1988; Urban et al., 1989c, 1990, 1995; Verry, 1975; Verry and Timmons, 1982; Verry and Urban, 1992). Budgets for the S2 watershed for the four major cations S, P, N, and C are summarized in Table 8.3. Most of these data were collected from 1971 to 1973 and from 1981 to 1984. Here, the areal basis for these budgets is the wetland (bog plus lagg) portion of the watershed. Inputs include atmospheric deposition (bulk deposition or separate estimates of wet and dry) and upland runoff; streamflow is the only output considered. These budgets differ from those of Verry and Urban (1992), who used throughfall plus stemflow as the measure of atmospheric deposition. For elements not leached from foliage, throughfall may provide a



TABLE 8.3

Element Budgets for the S2 Watershed ( $\text{g m}^{-2} \text{Year}^{-1}$ ). Accounting for Gas Emissions Leads to Lower Retention of C and N (in Parentheses)

	Atmospheric Deposition <sup>a</sup> ( $\text{g m}^{-2} \text{Year}^{-1}$ )	Surface Runoff ( $\text{g m}^{-2} \text{Year}^{-1}$ )	Interflow ( $\text{g m}^{-2} \text{Year}^{-1}$ )	Outflow ( $\text{g m}^{-2} \text{Year}^{-1}$ )	% Retention ( $\text{g m}^{-2} \text{Year}^{-1}$ )
Carbon <sup>b</sup>	1.2	0.49	1.75	33.6	-879% (25%)
Nitrogen <sup>c</sup>	1.04	0.16	0.17	0.6	56% (38%)
Phosphorus	0.048	0.022	0.004	0.046	38%
Sulfur	0.49 <sup>d</sup>		0.3	0.46	42%
Calcium	0.44 <sup>d</sup>	0.88	0.44	0.91	48%
Magnesium	0.08 <sup>d</sup>	0.25	0.14	0.38	19%
Sodium	0.20 <sup>d</sup>	0.09	0.14	0.24	45%
Potassium	0.18 <sup>d</sup>	0.6	0.08	0.61	28%

<sup>a</sup> Bulk deposition from Verry and Timmons (1977).

<sup>b</sup> Values from Kolka et al. (1999a) for 1993–1995.

<sup>c</sup> Values from table 9 in Urban and Eisenreich (1988).

<sup>d</sup> Values from Urban et al. (1995) for years 1971–1973 and 1981–1984.

better estimate of dry deposition than bulk deposition. For elements with gas exchange (C and N), this budget is incomplete and the second value in parentheses for percent retention accounts for gas fluxes (Chapter 10) into and out of the wetland.

The major conclusion to be drawn from comparison of the element budgets is that retention of many of the elements (N, P, S,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$ ) is similar (40%–50%), but retention of  $\text{K}^+$  and  $\text{Mg}^{2+}$  is lower by 20%–30%. The macronutrients N, P, and S are all similarly conserved (~40%) while gas emissions of C lead to lower retention (25%). Differences among elements are not due to the differing importance of inputs from the upland as large interannual differences in upland inputs cause little change in the magnitude of element export (Urban et al., 1995). The major mechanism for retention of all the elements is burial of partially decomposed vegetation and, to a lesser extent, retention within an aggrading vegetation compartment; differences among elements likely reflect differential decomposition rates of different components of the organic matter. Greater incorporation of Ca into wood and slower decomposition of wood may explain the greater retention of  $\text{Ca}^{2+}$  relative to  $\text{Mg}^{2+}$ . Magnesium exhibits a net export during the summer months of some years (Urban et al., 1995), which is further evidence of low  $\text{Mg}^{2+}$  retention in vegetation. The greater retention of  $\text{Na}^+$  relative to  $\text{K}^+$  may reflect the rapid release and recycling of  $\text{K}^+$  within the wetland (Buttleman and Grigal, 1985); the pool of  $\text{K}^+$  in living vegetation represents more than 100 years of atmospheric inputs while the amount of  $\text{Na}^+$  in vegetation represents only 2 years of atmospheric deposition.

## Element Cycling within the MEF Peatlands

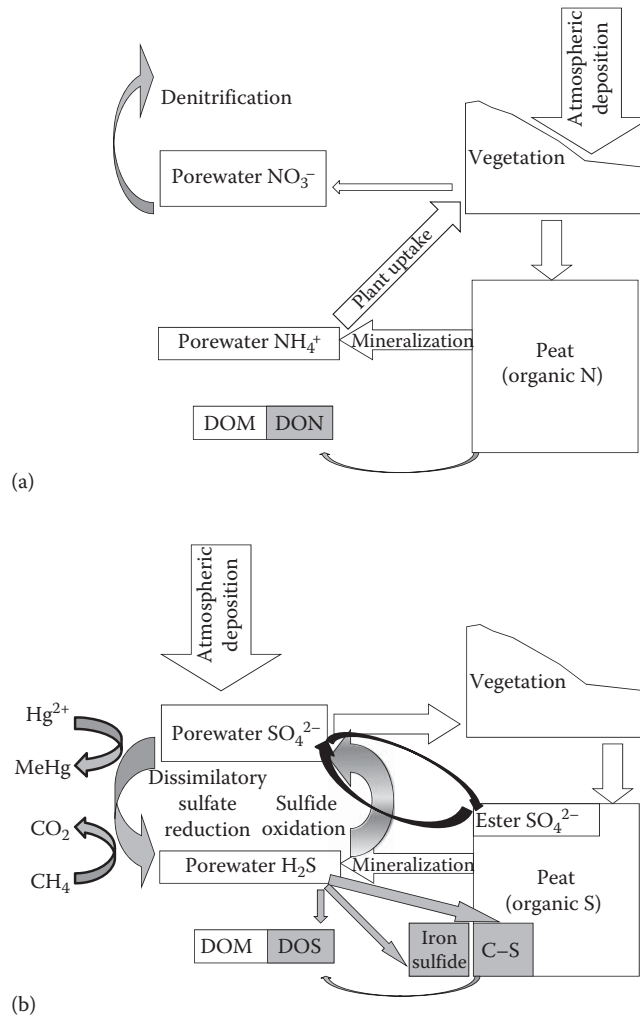
### *Nitrogen*

One of the major strengths of the MEF is the length of the historical record. This strength is apparent in the 30 year record of atmospheric deposition of N. Data from this site document the decrease in atmospheric deposition of  $\text{NO}_3^-$  that has occurred over this 30 year period. Deposition of  $\text{NO}_3^-$  has decreased at a rate of about 1% per year or 30% over the period of record. The decline observed at the MEF (Figure 2.3b) is consistent with that observed throughout the upper Midwest (McDonald et al., 2010) and results from the decrease in emissions of N oxides over this period (U.S. Environmental Protection Agency, 2000). The 30% decrease in wet deposition of  $\text{NO}_3^-$  has resulted in about a 7% decrease in the total N deposition.

Earlier studies on N cycling in the MEF watersheds (David et al., 1988; Grigal, 1991; Urban and Eisenreich, 1988) allowed predictions of the likely effects of this decrease in N deposition. Given that the MEF peatlands are N-limited (Bridgham et al., 2001; Urban and Eisenreich, 1988), a decrease in N inputs likely leads to a decrease in primary production, litter quality, and overall rates of N cycling through these systems. Surveys of peatlands across gradients of increasing N deposition have shown these responses to changes in N inputs (Turunen et al., 2004). Elevated rates of atmospheric deposition of N tend to favor growth of vascular plants over that of bryophytes (Berendse et al., 2001; Heijmans et al., 2002a,b; Limpens et al., 2003; Monique et al., 2001). High rates of nitric acid deposition in British moors are thought to have contributed to the loss of bryophytes, acidification of the moors, and inhibition of microbial enzymes (Lee and Stewart, 1978; Lee and Tallis, 1973; Lee et al., 1987). There is some evidence that high N deposition rates may threaten the survival of some of the carnivorous plant species characteristic of peatlands (Gotelli and Ellison, 2002). Large inputs of the limiting nutrient may cause supplies of other nutrients to become inadequate and to switch the limiting nutrient from N to either P or K (Hoosbeek et al., 2002). Nitrogen deposition never was high enough to observe many of these effects at the MEF; maximum historical rates were about  $1 \text{ g N m}^{-2} \text{ year}^{-1}$ . It is not known whether the composition of vegetation at the MEF is changing in response to decreased N inputs.

Studies at the MEF showed that  $\text{NO}_3^-$  inputs are unlikely to be denitrified and, therefore, are unlikely to affect rates of other forms of anaerobic respiration. In bogs receiving low rates of N deposition,  $\text{NO}_3^-$  is quickly taken up by the vegetation and does not reach anaerobic strata where it might be denitrified (Heijmans et al., 2002a; Nykanen et al., 2002; Urban and Eisenreich, 1988; Urban et al., 1989b). Consequently, there is no evidence of inhibition of methane emissions or of  $\text{SO}_4^{2-}$  reduction by elevated inputs of  $\text{NO}_3^-$  (Dise and Verry, 2001); in contrast, N inputs appear to stimulate methane emissions from some wetlands (Aerts and De Caluwe, 1999; Nykanen et al., 2002). The low pH in bogs inhibits nitrification (Bridgham et al., 2001), and hence the internal cycling of N is largely as  $\text{NH}_4^+$  (Figure 8.8a). The internal cycling



**FIGURE 8.8**

Comparison of N (a) and S (b) cycles in the S2 peatland at the MEF. Both elements are similar in having large fluxes into the vegetation, passage of this material to the upper layers of peat, and subsequent mineralization of the peat. Because of the inhibition of nitrification at the low pH of the bog, N is cycled back to the vegetation in the reduced form while S is first reoxidized to  $\text{SO}_4^{2-}$ . Because the vegetation is very efficient at capturing  $\text{NO}_3^-$  inputs to the bog, very little denitrification occurs. By contrast,  $\text{SO}_4^{2-}$  reduction is considerable. Sulfide generated via microbial  $\text{SO}_4^{2-}$  reduction or mineralization of organic matter is reoxidized, precipitated with Fe, or reacted with organic matter. Sulfate reduction inhibits the release of methane, but, in the presence of Hg, promotes Hg methylation.

of  $\text{NH}_4^+$  in the S2 bog is about eight times larger than the N input from atmospheric deposition (Figure 8.8a). The absence of nitrification and low rates of denitrification in bogs suggests that  $\text{N}_2\text{O}$  emissions from these ecosystems should be low; this hypothesis is supported by measurements by Huttunen et al. (2002), Nykanen et al. (2002), and Regina et al. (1996).

Work in the MEF watersheds suggests that peatlands are not unique in rates of cycling of N but are unique in exporting considerable organic N. Although the high C:N ratios of the peat might be expected to limit N mobility in peatlands (e.g., Fenn et al., 1998; Lovett et al., 2002), the S2 bog is inefficient at retaining N. Recent studies have suggested that N retention in ecosystems can be predicted on the basis of the soil C:N ratio (e.g., Lovett et al., 2002). The high C:N ratios in bog peat (30–60, e.g., Malmer and Holm 1984; Urban and Eisenreich, 1988) lead to efficient retention of inorganic N; retention of inorganic N is more than 90% in the S2 watershed. However, the low rates of microbial activity in acidic peat may limit the extent to which  $\text{NH}_4^+$  may be immobilized, and the loss of DOM engendered by anaerobic decomposition results in a total N retention efficiency of only 45% in the S2 bog. In bogs with adequate water flow, the export of organic N in the DOM offsets the high efficiency with which inorganic N is retained. Export of DON by peatlands is important at both the landscape and watershed scales. As has been widely reported for DOC (e.g., Engstrom, 1987; Frost et al., 2006; Koprivnjak and Moore, 1992), DON concentrations in rivers and streams in New England were strongly correlated with the areal extent of wetlands in the watershed (Pellerin et al., 2004).

Comparison of the MEF peatland watersheds with raised bogs on the extensive blanket peatlands in Minnesota suggests that the perched bogs in the MEF are less nutrient stressed than nearby raised bogs (Grigal, 1991). The fraction of plant N uptake supplied by atmospheric deposition was higher (12% vs. 15%) on raised than on perched bogs. The fraction of plant N uptake supplied by mineralization in the acrotelm was correspondingly lower in the raised bogs, but the fraction of N mineralized in the acrotelm of each type of peatland was similar (1.5% year<sup>-1</sup>). The turnover time of N in the vegetation, about 25% shorter (3.8 vs. 4.8 years) in the raised bogs, is further evidence of the greater nutrient stress in these systems.

### Sulfur

Studies of the biogeochemistry of S in peatlands at the MEF have provided important insights into its cycling and interactions with other elements. Sulfur is a macronutrient and the S cycle within peatlands is similar to cycling of N in many respects (Figure 8.8b). Research on the characterization of S cycling through the vegetation of the S2 watershed (Urban et al., 1989c) is among the most thorough for any peatland. Atmospheric deposition (0.4–0.5 g S m<sup>-2</sup> year<sup>-1</sup>) is less than the annual uptake of S by the vegetation (~1.3 g S m<sup>-2</sup> year<sup>-1</sup>) at this site. Thus, there is a large internal cycle of S within the S2

wetland. In part because of the large uptake and recycling by the vegetation, there is a net retention of S within peatlands; in the S2 peatland, about 40% of inputs is retained on an annual basis. Uptake of  $\text{SO}_4^{2-}$  by the vegetation is not as rapid as uptake of  $\text{NO}_3^-$  (Urban and Bayley, 1986; Urban et al., 1989b); accordingly, retention of inorganic S inputs (~60%) is not as efficient as retention of inorganic N (>90%). Export of atmospherically deposited  $\text{SO}_4^{2-}$  also has been observed in other peatlands (Novak et al., 2005b). Because a fraction of the organic matter is not decomposed but buried in peat, there is a large burial of organic S within peatlands. However, because of significant mineralization of organic S and uptake of this mineralized S by vegetation, there is significant vertical mobility of S within peat, and accumulation rate profiles of S in peat cannot be interpreted as historical records of atmospheric S deposition (Novak et al., 2003, 2005a; Urban et al., 1989c). Also, S inventories in peat are not proportional to S loadings to the peatland (Novak et al., 2003).

A second cycle of S through the vegetation and shallow peat (Figure 8.8b) occurs concurrently with the cycle described previously. As for N, any  $\text{SO}_4^{2-}$  in precipitation that is not taken up by the vegetation may be used as an electron acceptor for anaerobic respiration (dissimilatory  $\text{SO}_4^{2-}$  reduction). Unlike N, substantial quantities of inorganic sulfur ( $\text{SO}_4^{2-}$ ) penetrate through the vegetation to the water table and are available to be reduced via dissimilatory  $\text{SO}_4^{2-}$  reduction in the S2 bog (Urban and Bayley, 1986). In many peatlands, high rates of microbial  $\text{SO}_4^{2-}$  reduction have been measured by the addition of  $\text{SO}_4^{2-}$  or radiolabeled  $^{35}\text{SO}_4^{2-}$  (Bayley et al., 1987; Chapman and Davidson, 2001; Keller and Bridgham, 2007; Novak et al., 2003; Vile et al., 2003; Wieder and Lang, 1988; Wieder et al., 1987), including  $\text{SO}_4^{2-}$  additions to the S6 wetland at the MEF (Jeremiason et al., 2006). Sulfate reduction can account for 0%–25% of the anaerobic oxidation of organic matter in peatlands (Keller and Bridgham, 2007; Vile et al., 2003). The fate of the microbially produced  $\text{H}_2\text{S}$  varies among peatlands. In minerotrophic peatlands or those rich in iron, formation of acid-volatile sulfide (FeS) and pyrite ( $\text{FeS}_2$ ) is considerable (Novak and Wieder, 1992; Novak et al., 2003; Wieder and Lang, 1986, 1988). In peatlands, low in iron, most of the  $\text{H}_2\text{S}$  reacts with the peat and DOM to form C-bonded S (Brown, 1986; Keller and Bridgham, 2007; Novak et al., 1994; Urban et al., 1989c). Rates of  $\text{SO}_4^{2-}$  reduction greater than the annual deposition of  $\text{SO}_4^{2-}$  to peat bogs have been documented (Novak et al., 2005b); rates of oxidation of sulfide are substantial in peatlands (Bayley et al., 1986; Bottrell et al., 2007; Heitmann and Blodau, 2006; Novak et al., 2005b), allowing an internal cycle (Figure 8.8) to play a significant role in C oxidation (Keller and Bridgham, 2007; Vile et al., 2003). The factors controlling the rates and pathways for the reoxidation of sulfide in peatlands are poorly documented. Internal cycling of S does not appear to be as significant in upland mineral soil systems (Eimers et al., 2004).

A third cycle of S within peatlands about which relatively little is known entails the formation and hydrolysis of ester sulfates (Figure 8.8b). Formation of ester sulfates upon addition of  $^{35}\text{SO}_4^{2-}$  to peat has been documented

(Chapman and Davidson, 2001; Novak et al., 2003), and sulfate esters have contributed 6%–30% of total S in peat profiles (Novak et al., 2003; Prietzel et al., 2007). Aryl sulfatase activity in peat was lower in English peatlands receiving high rates of acid and pollutant deposition (Press et al., 1985). Research is needed to determine whether this cycle is quantitatively important in most peatlands.

Work at the MEF documented the significance of the export of organic S from peatlands. DOM in the S2 stream was enriched in S in summer months; C:S dropped from 300 in spring to 100 in summer (Urban et al., 1989c). Export of organic S accounted for one third of the S exported from the S2 watershed. The abiotic formation of dissolved organic S by reaction of H<sub>2</sub>S with DOC in peatlands was documented by Heitmann and Blodau (2006). Spectroscopic studies have shown oxidation states of –2 to +6 for S in humic acids from peatlands (Morra et al., 1997; Prietzel et al., 2007). Organic S may be important for the binding and transport of trace metals including Hg in bog waters (Qian et al., 2002; Xia et al., 1999; Yoon et al., 2005).

Interactions of S and Hg cycling have been well documented for the MEF wetlands. Wetlands have long been known as significant sources of total and methyl Hg to lakes and streams (Dennis et al., 2005; Hurley et al., 1999; Shanley et al., 2005). It also is widely recognized that Hg methylation occurs in association with SO<sub>4</sub><sup>2-</sup> reduction (e.g., Goulet et al., 2007; King et al., 2001). Postulating a linkage between S transformations in peatlands and Hg export, researchers at MEF demonstrated and quantified this linkage. They artificially applied SO<sub>4</sub><sup>2-</sup> to a portion of the S6 wetland and compared the concentrations of total and methyl Hg between the amended and control portions of the wetland (Jeremiason et al., 2006). Results showed that SO<sub>4</sub><sup>2-</sup> additions caused increased concentrations of methyl Hg in porewaters and an increase in export of methyl Hg following SO<sub>4</sub><sup>2-</sup> applications (Coleman-Wasik, 2008; Chapter 11).

Observations at the MEF also pointed to interactions between C and S cycling in wetlands. The potential for inhibition of methane production in wetlands due to competition for C substrates between methanogenic and SO<sub>4</sub><sup>2-</sup> reducing bacteria had been postulated by Wieder et al. (1990). This hypothesis was tested at the Bog Lake peatland, an open, nutrient-poor fen within the MEF (Dise and Verry, 2001). Application of NH<sub>4</sub>SO<sub>4</sub> to field plots lowered methane emissions by 30%. These results have since been replicated at other locations (Gauci and Chapman, 2006; Gauci et al., 2002, 2004). The mechanism behind the suppression of methane fluxes remains under investigation. Although studies have documented a stimulation of SO<sub>4</sub><sup>2-</sup> reduction in response to SO<sub>4</sub><sup>2-</sup> additions (Gauci and Chapman, 2006), laboratory studies have not always shown inhibition of methanogenesis by SO<sub>4</sub><sup>2-</sup> addition (Vile et al., 2003). Anaerobic oxidation of methane by SO<sub>4</sub><sup>2-</sup>-reducing bacteria, a phenomenon well documented in marine sediments, does not appear to be important in peat bogs (Smemo and Yavitt, 2007).

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## References

- Aerts, R. and H. De Caluwe. 1999. Nitrogen deposition effects on carbon dioxide and methane emissions from temperate peatland soils. *Oikos* 84:44–54.
- Aitkenhead, J.A., D. Hope, and M.F. Billett. 1999. The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. *Hydrological Processes* 13:1289–1302.
- Bayley, S.E., R.S. Behr, and C.A. Kelly. 1986. Retention and release of S from a freshwater wetland. *Water, Air, and Soil Pollution* 31:101–114.
- Bayley, S.E., D.H. Vitt, R.W. Newbury, K.G. Beaty, R. Behr, and C. Miller. 1987. Experimental acidification of a *Sphagnum*-dominated peatland: First year results. *Canadian Journal of Fisheries and Aquatic Science* 44:194–205.
- Berendse, F., N. Van Breeman, H. Rydin, A. Buttler, M. Heijmans, M.R. Hoosbeek, J.A. Lee et al. 2001. Raised atmospheric CO<sub>2</sub> levels and increased N deposition cause shifts in plant species composition and production in *Sphagnum* bogs. *Global Change Biology* 7:591–598.
- Bishop, K.H., H. Laudon, and S. Koehler. 2000. Separating the natural and anthropogenic components of spring flood pH decline: A method for areas that are not chronically acidified. *Water Resources Research* 36:1873–1884.
- Bottrell, S.H., R.J.G. Mortimer, M. Spence, M.D. Krom, J.M. Clark, and P.J. Chapman. 2007. Insights into redox cycling of sulfur and iron in peatlands using high-resolution diffusive equilibrium thin film (DET) gel probe sampling. *Chemical Geology* 244:409–420.
- Bridgman, S.D., K. Updegraff, and J. Pastor. 2001. A comparison of nutrient availability indices along an ombrotrophic-minerotrophic gradient in Minnesota wetlands. *Soil Science Society of America Journal* 65:259–269.
- Brown, K.A. 1986. Formation of organic sulphur in anaerobic peat. *Soil Biology and Biochemistry* 18:131–140.
- Buttleman, C.G. and D.F. Grigal. 1985. Use of the Rb/K ratio to evaluate potassium nutrition of peatlands. *Oikos* 44:253–256.
- Capel, P.D. and S.J. Eisenreich. 1990. Relationship between chlorinated hydrocarbons and organic carbon in sediment and porewater. *Journal of Great Lakes Research* 16:245–257.
- Chapman, S.J. and M.S. Davidson. 2001. <sup>35</sup>S-sulphate reduction and transformation in peat. *Soil Biology and Biochemistry* 33:593–602.
- Cole, J.J., N.F. Caraco, G.W. Kling, and T.K. Kratz. 1994. Carbon dioxide supersaturation in the surface waters of lakes. *Science* 265:1568–1570.
- Cole, J.J., M.L. Pace, S.R. Carpenter, and J.F. Kitchell. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnology and Oceanography* 45:1718–1730.
- Coleman-Wasik, J.K. 2008. Chronic effects of atmospheric sulfate deposition on mercury methylation in a boreal wetland: Replication of a global experiment. MS thesis. St. Paul, MN: University of Minnesota.
- D'arcy, P. and R. Carignan. 1997. Influence of catchment topography on water chemistry in southeastern Quebec Shield lakes. *Canadian Journal of Fisheries and Aquatic Science* 54:2215–2227.

- David, M.B., D.F. Grigal, L.F. Ohmann, and G.Z. Gertner. 1988. Sulfur, carbon, and nitrogen relationships in forest soils across the northern Great Lakes States as affected by atmospheric deposition and vegetation. *Canadian Journal Forest Research* 18:1386–1391.
- De Wit, H.A., J. Mulder, A. Hindar, and L. Hole. 2007. Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. *Environmental Science & Technology* 41:7706–7713.
- Dennis, I.F., T.A. Clair, C.T. Driscoll, N. Kamman, A. Chalmers, J. Shanley, S.A. Norton, and S. Kahl. 2005. Distribution patterns of mercury in Lakes and Rivers of north-eastern North America. *Ecotoxicology* 14:113–123.
- Dillon, P.J. and L.A. Molot. 1997. Dissolved organic and inorganic carbon mass balances in central Ontario lakes. *Biogeochemistry* 36:29–42.
- Dise, N.B. and E.S. Verry. 2001. Suppression of peatland methane emission by cumulative sulfate deposition in simulated acid rain. *Biogeochemistry* 53:143–160
- Drexel, R.T., M. Haitzer, J.N. Ryan, G.R. Aiken, and K.L. Nagy. 2002. Mercury(II) sorption to two Florida Everglades peats: Evidence for strong and weak binding and competition by dissolved organic matter released from the peat. *Environmental Science & Technology* 36:4058–4064.
- Driscoll, C.T. and J.J. Bisogni. 1984. Weak Acid/base systems in dilute acidified lakes and streams of the Adirondack region of New York State. In: *Modeling of Total Acid Precipitation Impacts*, ed. J.L. Schnoor. Boston, MA: Butterworth Publishers, pp. 53–72.
- Eckhardt, B.W. and T.R. Moore. 1990. Controls on dissolved organic carbon concentrations in streams, Southern Quebec. *Canadian Journal of Fisheries and Aquatic Science* 47:1537–1544.
- Eimers, M.C., P.J. Dillon, and S.L. Schiff. 2004. A S-isotope approach to determine the relative contribution of redox processes to net SO<sub>4</sub> export from upland, and wetland-dominated catchments. *Geochimica et Cosmochimica Acta* 68:3665–3674.
- Engstrom, D.R. 1987. Influence of vegetation and hydrology on the humus budgets of Labrador lakes. *Canadian Journal of Fisheries and Aquatic Science* 44:1306–1314.
- Evans, C.D., P.J. Chapman, J.M. Clark, D.T. Monteith, and M.S. Cresser. 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology* 12:2044–2053.
- Evans, C.D., D.T. Monteith, B. Reynolds, and J.M. Clark. 2008. Buffering of recovery from acidification by organic acids. *Science of the Total Environment* 404:316–325.
- Fee, E.J., R.E. Hecky, S.E. Kasian, and D.R. Cruikshank. 1996. Effects of lake size, water clarity and climatic variability on mixing depths in Canadian Shield lakes. *Limnology and Oceanography* 41:912–920.
- Fenn, M.E., M.A. Poth, J.D. Aber, J.S. Baron, B.T. Bormann, D.W. Johnson, A.D. Lemly, S.G. McNulty, D.F. Ryan, and R. Stottlemyer. 1998. Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. *Ecological Applications* 8:706–733.
- Frost, P.C., J.H. Larson, G.A. Lamberti, C.A. Johnston, K.C. Young, P.A. Maurice, and S.D. Bridgman. 2006. Landscape predictors of stream dissolved organic matter concentration and physicochemistry in a Lake Superior river watershed. *Aquatic Science* 68:40–51.
- Gauci, V. and S.J. Chapman. 2006. Simultaneous inhibition of CH<sub>4</sub> efflux and stimulation of sulphate reduction in peat subject to simulated acid rain. *Soil Biology and Biochemistry* 38:3506–3510.



- Gauci, V., N. Dise, and D. Fowler. 2002. Controls on suppression of methane flux from a peat bog subjected to simulated acid rain sulfate deposition. *Global Biogeochemical Cycles* 16: doi 10.1029/2000GB001370.
- Gauci, V., D. Fowler, S.J. Chapman, and N.B. Dise. 2004. Sulfate deposition and temperature controls on methane emission and sulfur forms in peat. *Biogeochemistry* 71:141–162.
- Gergel, S.E., M.G. Turner, and T.K. Kratz. 1999. Dissolved organic carbon as an indicator of the scale of watershed influence on lakes and rivers. *Ecological Applications* 9:1377–1390.
- Gorham, E. 1953. Some early ideas concerning the nature, origin and development of peatlands. *Journal of Ecology* 41:257–273.
- Gorham, E., S.E. Bayley, and D.W. Schindler. 1984. Ecological effects of acid deposition upon peatlands: A neglected field in acid-rain research. *Canadian Journal of Fisheries and Aquatic Science* 41:1256–1268.
- Gorham, E., S.J. Eisenreich, J. Ford, and M.V. Santelmann. 1985. The chemistry of bog waters. In: *Chemical Processes in Lakes*, ed. W. Stumm. New York: John Wiley & Sons, p. 339.
- Gorham, E., J.K. Underwood, F.B. Martin, and J.G. Ogden. 1986. Natural and anthropogenic causes of lake acidification in Nova Scotia. *Nature* 324:451–453.
- Gorham, E., J.K. Underwood, J.A. Janssens, B. Freedman, W. Maass, D.H. Waller, and J.G. Ogden. 1998. The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands. *Wetlands* 18: 115–132.
- Gotelli, N.J. and A.M. Ellison. 2002. Nitrogen deposition and extinction risk in the northern pitcher plant, *Sarracenia purpurea*. *Ecology* 83:2758–2765.
- Goulet, R.R., J. Holmes, B. Page, L. Poissant, S.D. Sicilliano, D.R.S. Lean, F. Wang, M. Amyot, and A. Tessier. 2007. Mercury transformations and fluxes in sediments of a riverine wetland. *Geochimica et Cosmochimica Acta* 71:3393–3406.
- Grigal, D.F. 1991. Elemental dynamics in forested bogs in northern Minnesota. *Canadian Journal of Botany* 69:539–546.
- Grigal, D.F. 2002. Inputs and outputs of mercury from terrestrial watersheds: A review. *Environmental Reviews* 10:1–39.
- Grigal, D.F., R.K. Kolka, J.A. Fleck, and E.A. Nater. 2000. Mercury budget of an upland-peatland watershed. *Biogeochemistry* 50:95–109.
- Hazen, A. 1892. A new color-standard for natural waters. *American Chemical Journal* 14:300–310.
- Hazen, A. 1896. The measurement of colors of natural waters. *Journal of the American Chemical Society* 18:264–275.
- Heijmans, M.M.P.D., H. Klees, W. De Visser, and F. Berendse. 2002a. Effects of increased nitrogen deposition on the distribution of <sup>15</sup>N-labeled nitrogen between *Sphagnum* and vascular plants. *Ecosystems* 5:500–508.
- Heijmans, M.M.P.D., H. Klees, W. De Visser, and F. Berendse. 2002b. Response of a *Sphagnum* bog plant community to elevated CO<sub>2</sub> and N supply. *Plant Ecology* 162:123–134.
- Heitmann, T. and C. Blodau. 2006. Oxidation and incorporation of hydrogen sulfide by dissolved organic matter. *Chemical Geology* 235:12–20.
- Helmer, E.H., N.R. Urban, and S.J. Eisenreich. 1990. Aluminum geochemistry in peatland waters. *Biogeochemistry* 9:247–276.

- Hemond, H.F. 1980. Biogeochemistry of Thoreau's Bog, Concord, Mass. *Ecological Monographs* 50:507–526.
- Hoosbeek, M.R., N. Van Breemen, H. Vasander, A. Buttler, and F. Berendse. 2002. Potassium limits potential growth of bog vegetation under elevated atmospheric CO<sub>2</sub> and N deposition. *Global Change Biology* 8:1130–1138.
- Hruska, J., P. Kram, W.H. McDowell, and F. Oulehle. 2009. Increased dissolved organic carbon (DOC) in Central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. *Environmental Science & Technology* 43:4320–4326.
- Hurley, J.P., J.M. Benoit, C.L. Babiarz, M.M. Shafer, A.W. Andren, J.R. Sullivan, R. Hammond, and D.A. Webb. 1999. Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environmental Science & Technology* 29:1867–1875.
- Huttunen, J.T., H. Nykanen, P.J. Martikainen, J. Turunen, and O. Nenonen. 2002. Fluxes of nitrous oxide on natural peatlands in Vuotos, an area projected for a hydroelectric reservoir in northern Finland. *Suo* 53:87–96.
- Jackson, T.A. and R.E. Hecky. 1980. Depression of primary productivity by humic matter in lake and reservoir waters of the boreal forest zone. *Canadian Journal of Fisheries and Aquatic Science* 37:2300–2317.
- Jeremiason, J.D., D.R. Engstrom, E.B. Swain, E.A. Nater, B.M. Johnson, J.E. Almendinger, B.A. Monson, and R.K. Kolka. 2006. Sulfate addition increases methylmercury production in an experimental wetland. *Environmental Science & Technology* 40:3800–3806.
- Jerome, J.H. and R.P. Bukata. 1998. Tracking the propagation of solar ultraviolet radiation: Dispersal of ultraviolet photons in inland waters. *Journal of Great Lakes Research* 24:666–680.
- Jones, R.I., K. Salonen, and H. De Haan. 1988. Phosphorus transformations in the epilimnion of humic lakes: Abiotic interactions between dissolved humic materials and phosphate. *Freshwater Biology* 19:357–369.
- Keller, J.K. and S.D. Bridgman. 2007. Pathways of anaerobic carbon cycling across an ombrotrophic-minerotrophic peatland gradient. *Limnology and Oceanography* 52:96–107.
- King, J.K., J.E. Kostka, M.E. Frischer, F.M. Saunders, and R.A. Jahnke. 2001. A quantitative relationship that demonstrates mercury methylation rates in marine sediments are based on the community composition and activity of sulfate-reducing bacteria. *Environmental Science & Technology* 35:2491–2496.
- Kling, G.W., G.W. Kipphut, and M.C. Miller. 1991. Arctic lakes and streams as gas conduits to the atmosphere: Implications for tundra carbon budgets. *Science* 251:298–301.
- Koenings, J.P. and F.F. Hooper. 1976. The influence of colloidal organic matter on iron and iron-phosphorus cycling in an acid bog lake. *Limnology and Oceanography* 21:684–696.
- Kolka, R.K., D.F. Grigal, E.S. Verry, and E.A. Nater. 1999a. Mercury and organic carbon relationships in streams draining forested upland/peatland watersheds. *Journal of Environmental Quality* 28:766–775.
- Kolka, R.K., E.A. Nater, D.F. Grigal, and E.S. Verry. 1999b. Atmospheric inputs of mercury and organic carbon into a forested upland/bog watershed. *Water, Air, and Soil Pollution* 113:273–294.



- Kolka, R.K., D.F. Grigal, E.A. Nater, and E.S. Verry. 2001. Hydrologic cycling of mercury and organic carbon in a forested upland-bog watershed. *Soil Science Society of American Journal* 65:897–905.
- Koprivnjak, J.F. and T.R. Moore. 1992. Sources, sinks and fluxes of dissolved organic carbon in subarctic fen catchments. *Arctic and Alpine Research* 24:204–210.
- Krug, E.C. and C.R. Frink. 1983. Acid rain on acid soil: A new perspective. *Science* 221:520–525.
- Lazerte, B.D. 1991. Metal transport and retention: The role of dissolved organic carbon. In: *3rd International Nordic Symposium on Humic Substances*. Finnish Humus News, pp. 71–82.
- Lee, J.A. and J.H. Tallis. 1973. Regional and historical aspects of lead pollution in Britain. *Nature* 245:216–218.
- Lee, J.A. and G.R. Stewart. 1978. Ecological aspects of nitrogen assimilation. *Advances in Botanical Research* 6:1–43.
- Lee, J.A., M.C. Press, S. Woodin, and P. Ferguson. 1987. Responses to acidic deposition in ombrotrophic mires. In: *Effects of Air Pollutants on Forests, Agriculture and Wetlands*, ed. T.C. Hutchinson and K.M. Meema. New York: Springer-Verlag, pp. 549–560.
- Lepisto, A., P. Kortelainen, and T. Mattsson. 2008. Increased organic C and N leaching in a northern boreal river basin in Finland. *Global Biogeochemical Cycles* 22:GB3029.
- Lillie, R.A. and J.W. Mason. 1983. *Limnological Characteristics of Wisconsin Lakes*. Technical Bulletin #138. Madison, WI: Wisconsin Department of Natural Resources.
- Limpens, J., F. Berendse, and H. Klees. 2003. N deposition affects N availability in interstitial water, growth of *Sphagnum* and invasion of vascular plants in bog vegetation. *New Phytologist* 157:339–347.
- Lindberg, S.E., G.M. Lovett, D.D. Richter, and E.W. Johnson. 1986. Atmospheric deposition and canopy interactions of major ions in a forest. *Science* 231:141–145.
- Lovett, G.M., K.C. Weathers, and M.A. Arthur. 2002. Control of nitrogen loss from forested watersheds by soil carbon:nitrogen ratio and tree species composition. *Ecosystems* 5:712–718.
- Malmer, N. and E. Holm. 1984. Variation in the C:N quotient of peat in relation to decomposition rate and age determination with Pb-210. *Oikos* 43:171–182.
- McDonald, C.P., N.R. Urban, and C. Casey. 2010. Modeling historical trends in Lake Superior total nitrogen concentrations. *Journal of Great Lake Research* 36(4):715–721.
- McKnight, D., E.M. Thurman, R. Wershaw, and H. Hemond. 1985. Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts. *Ecology* 66:1339–1352.
- Monique, M.P., P.D. Heijmans, F. Berendse, W.J. Arp, A.K. Masselink, H. Klees, W. De Visser, and N. Van Breeman. 2001. Effects of elevated carbon dioxide and increased nitrogen deposition on bog vegetation in the Netherlands. *Journal of Ecology* 89:268–279.
- Monteith, D.T., J.L. Stoddard, C.D. Evans, H.A. deWit, M. Forsius, T. Hogasen, A. Wilander et al. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450:537–540.
- Moore, T.R., N.T. Roulet, and J.M. Waddington. 1998. Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands. *Climatic Change* 40:229–245.

- Morra, M.J., S.E. Fendorf, and P.D. Brown. 1997. Speciation of sulfur in humic and fulvic acids using X-ray absorption near-edge structure (XANES) spectroscopy. *Geochimica et Cosmochimica Acta* 61:683–688.
- Mullen, S.F., J.A. Janssens, and E. Gorham. 2000. Acidity of and the concentrations of major and minor metals in the surface waters of bryophyte assemblages from 20 North American bogs and fens. *Canadian Journal of Botany* 78:718–727.
- Neff, J., E. Holland, F. Dentener, W. McDowell, and K. Russell. 2002. The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle? *Biogeochemistry* 57: 99–136.
- Novak, M. and R.K. Wieder. 1992. Inorganic and organic sulfur profiles in nine *Sphagnum* peat bogs in the United States and Czechoslovakia. *Water, Air, and Soil Pollution* 65:353–369.
- Novak, M., R.K. Wieder, and W.R. Schell. 1994. Sulfur during early diagenesis in *Sphagnum* peat: Insights from  $\delta^{34}\text{S}$  ratio profiles in  $^{210}\text{Pb}$ -dated peat cores. *Limnology and Oceanography* 39:1172–1185.
- Novak, M., M. Adamova, and J. Milicic. 2003. Sulfur metabolism in polluted *Sphagnum* peat bogs: A combined  $^{34}\text{S}$ - $^{35}\text{S}$ - $^{210}\text{Pb}$  study. *Water, Air, and Soil Pollution: Focus* 3:181–200.
- Novak, M., M. Adamova, R.K. Wieder, and S.H. Bottrell. 2005a. Sulfur mobility in peat. *Applied Geochemistry* 20:673–681.
- Novak, M., M. Stepanova, I. Jackova, F. Buzek, E. Prechova, M.A. Vile, S.H. Bottrell, and R.J. Newton. 2005b. Isotope systematics of sulfate-oxygen and sulfate-sulfur in six European peatlands. *Biogeochemistry* 76:187–213.
- Nykanen, H., H. Vasander, J.T. Huttunen, and P.J. Martikainen. 2002. Effect of experimental nitrogen load on methane and nitrous oxide fluxes on ombrotrophic boreal peatland. *Plant and Soil* 242:147–155.
- Oliver, B.G., E.M. Thurman, and R.L. Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochimica et Cosmochimica Acta* 47:2031–2036.
- Overton, W., P. Kanciruk, L.A. Hook, J.M. Eilers, D.H. Landers, D.F. Brakke, D.J. Blick, R.A. Linthurst, M.D. Dehaan, and J.M. Omernik. 1986. Characteristics of lakes in the eastern United States. Vol. 2, *Lakes Sampled and Descriptive Statistics for Physical and Chemical Variables*. US Environmental Protection Agency/600/4-86/0076. Washington, DC.
- Pellerin, B.A., W.M. Wollheim, C.S. Hopkinson, W.H. McDowell, M.R. Williams, C.J. Vörösmarty, and M.L. Daley. 2004. Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern U.S. rivers and streams. *Limnology and Oceanography* 49:910–918.
- Press, M.C., J. Henderson, and J.A. Lee. 1985. Arylsulphatase activity in peat in relation to atmospheric deposition. *Soil Biology & Biochemistry* 17:99–103.
- Prietzl, J., H. Knicker, J. Thieme, and M. Salome. 2007. Sulfur K-edge XANES spectroscopy reveals differences in sulfur speciation of bulk soils, humic acid, fulvic acid, and particle size separates. *Soil Biology & Biochemistry* 39: 877–890
- Qian, J., U. Skjellberg, W. Frech, W.F. Bleam, P.R. Bloom, and P.E. Petit. 2002. Bonding of methyl mercury to reduced sulfur groups in soil and stream organic matter as determined by X-ray absorption spectroscopy and binding affinity studies. *Geochimica et Cosmochimica Acta* 66:3873–3885.

- Ramaut, J. 1954. Modifications de pH apportées par la tourbe et le *Sphagnum* secs aux solutions salines et à l'eau bidistillée. *Bulletin de la Classe Des Sciences*, Bruxelles, Series 5, 40.
- Ravichandran, M. 2004. Interactions between mercury and dissolved organic matter—A review. *Chemosphere* 55:319–331.
- Regina, K., H. Nykanen, J. Silvola, and P.J. Martikainen. 1996. Fluxes of nitrous oxide from boreal peatlands as affected by peatland type, water table level and nitrification capacity. *Biogeochemistry* 35:401–418.
- Richards, E.H. and J.W. Ellis. 1896. The coloring matter of natural waters, its source, composition and quantitative measurement. *Journal of the American Chemical Society* 18:68–81.
- Rogalla, J.A. 1986. Empirical acidification modeling for Lakes in the Upper Great Lakes Region. MS thesis. St. Paul, MN: University of Minnesota.
- Schiff, S., R. Aravena, E. Mewhinney, R.J. Elgood, B. Warner, P.J. Dillon, and S.E. Trumbore. 1998. Precambrian Shield wetlands: Hydrologic control of the sources and export of dissolved organic matter. *Climatic Change* 40:167–188.
- Schindler, D.W., P.J. Curtis, B.R. Parker, and M.P. Stainton. 1996. Consequences of climate warming and lake acidification for UV-B penetration in North American boreal lakes. *Nature* 379:705–708.
- Schindler, D.E., S.R. Carpenter, J.J. Cole, J.F. Kitchell, and M.L. Pace. 1997a. Influence of food web structure on carbon exchange between lakes and the atmosphere. *Science* 277:248–251.
- Schindler, D.W., P.J. Curtis, S.E. Bayley, B.R. Parker, K.G. Beaty, and M.P. Stainton. 1997b. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. *Biogeochemistry* 36:9–28.
- Shanley, J.B., N.C. Kamman, T.A. Clair, and A. Chalmers. 2005. Physical controls on total and methylmercury concentrations in streams and lakes of the northeastern USA. *Ecotoxicology* 14:125–134.
- Skene, M. 1915. The acidity of *Sphagnum* and its relation to chalk and mineral salts. *Annals of Botany* 29:65–87.
- Smemo, K.A. and J.B. Yavitt. 2007. Evidence for anaerobic CH<sub>4</sub> oxidation in freshwater peatlands. *Geomicrobiology Journal* 24:583–597.
- Smith, R.E.H., J.A. Furgal, and D.R.S. Lean. 1998. The short-term effects of solar ultraviolet radiation on phytoplankton photosynthesis and photosynthate allocation under contrasting mixing regimes in Lake Ontario. *Journal of Great Lakes Research* 24:427–441.
- Thompson, T.G., J.R. Lorah, and G.B. Rigg. 1927. The acidity of the waters of some Puget Sound Bogs. *Journal of the American Chemistry Society* 49:2981–2988.
- Timmons, D.R., E.S. Verry, R.E. Burwell, and R.F. Holt. 1977. Nutrient transport in surface runoff and interflow from an aspen-birch forest. *Journal of Environmental Quality* 6:188–192.
- Tipping, E., C.A. Backes, and M.A. Hurley. 1988. The complexation of protons, aluminum and calcium by aquatic humic substances: A model incorporating binding-site heterogeneity and macroionic effects. *Water Research* 22:597–611.
- Turunen, J., N.T. Roulet, and T.R. Moore. 2004. Nitrogen deposition and increased carbon accumulation in ombrotrophic peatlands in eastern Canada. *Global Biogeochemical Cycles* 18:GB3002.

- U.S. Environmental Protection Agency. 2000. National air pollutant emission trends. Washington, DC: US Environmental Protection Agency.
- Urban, N.R. 1983. The nitrogen cycle in a forested bog watershed in northern Minnesota. MS thesis. St. Paul, MN: University of Minnesota.
- Urban, N.R. 1987. The nature and origins of acidity in bogs. PhD dissertation. St. Paul, MN: University of Minnesota.
- Urban, N.R. and S.E. Bayley. 1986. The acid-base balance of peatlands: A short-term perspective. *Water, Air, and Soil Pollution* 30:791–800.
- Urban, N.R. and S.J. Eisenreich. 1988. The nitrogen cycle of a *Sphagnum* bog. *Canadian Journal of Botany* 66:435–449.
- Urban, N.R., S.J. Eisenreich, and E. Gorham. 1987a. Proton cycling in bogs: Geographic variation in northeastern North America. In: *The Effects of Air Pollutants on Forests, Wetlands and Agricultural Ecosystems*, ed. T.C. Hutchison and K.M. Meema. New York: Springer-Verlag, pp. 577–598.
- Urban, N.R., S.J. Eisenreich, and E. Gorham. 1987b. Proton cycling in bogs: Geographic variation in northeastern North America. In: *The Effects of Air Pollutants on Forests, Wetlands and Agricultural Ecosystems*, ed. T.C. Hutchison and K.M. Meema. New York: Springer-Verlag, pp. 577–598.
- Urban, N.R., S.E. Bayley, and S.J. Eisenreich. 1989a. Export of dissolved organic carbon and acidity from peatlands. *Water Resources Research* 25:1619–1628.
- Urban, N.R., S.J. Eisenreich, and S.E. Bayley. 1989b. The relative importance of denitrification and nitrate assimilation in mid-continental bogs. *Limnology and Oceanography* 33:1611–1617.
- Urban, N.R., S.J. Eisenreich, and D.F. Grigal. 1989c. Sulfur cycling in a forested *Sphagnum* bog in northern Minnesota. *Biogeochemistry* 7:81–109.
- Urban, N.R., E.S. Verry, and S.J. Eisenreich. 1995. Retention and mobility of cations in a small peatland. *Water, Air, and Soil Pollution* 79:201–224.
- Urban, N.R., S.J. Eisenreich, D.F. Grigal, and K.T. Schurr. 1990. Mobility and diagenesis of Pb and Pb-210 in peat. *Geochimica et Cosmochimica Acta* 54:3329–3346.
- Verry, E.S. 1975. Streamflow chemistry and nutrient yields from upland-peatland watersheds in Minnesota. *Ecology* 56:1149–1157.
- Verry, E.S. 1983. Precipitation chemistry at the Marcell Experimental Forest in north central Minnesota. *Water Resources Research* 19:454–462.
- Verry, E.S. 1986. The fate of ions in till, granite, and organic soil landscapes in Minnesota. Grand Rapids, MN: USDA Forest Service.
- Verry, E.S. and D.R. Timmons. 1977. Precipitation nutrients in the open and under two forests in Minnesota. *Canadian Journal of Forest Research* 7:112–119.
- Verry, E.S. and D.R. Timmons. 1982. Water-borne nutrient flow through an upland-peatland watershed in Minnesota. *Ecology* 63:1456–1467.
- Verry, E.S. and N.R. Urban. 1992. Nutrient cycling at Marcell Bog, Minnesota. *Suo* 43:147–153.
- Verry, E.S. and R.K. Kolka. 2003. Importance of wetlands to streamflow generation. In: *First Interagency Conference on Research in the Watersheds*, ed. K.G. Renard, S.A. McElroy, W.J. Gburek, H.E. Caufield, and R.L. Scott. Benson, AZ: USDA, Agricultural Research Service, 126–132.
- Vile, M.A., S.D. Bridgham, and R. Kelman Wieder. 2003. Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland. *Ecological Applications* 13:720–734.

- Wieder, R.K. and G.E. Lang. 1986. Fe, Al, Mn, and S chemistry of *Sphagnum* peat in four peatlands with different metal and sulfur input. *Water, Air, and Soil Pollution* 29:309–320.
- Wieder, R.L. and G.E. Lang. 1988. Cycling of inorganic and organic sulfur in peat from Big Run Bog, West Virginia. *Biogeochemistry* 5:221–242.
- Wieder, R.K., G.E. Lang, and V.A. Granus. 1987. Sulphur transformations in *Sphagnum*-derived peat during incubation. *Soil Biology & Biochemistry* 19:101–106.
- Wieder, R.K., J.B. Yavitt, and G.E. Lang. 1990. Methane production and sulfate reduction in two Appalachian peatlands. *Biogeochemistry* 10:81–104.
- Willey, J.D., R.J. Kieber, M.S. Eyman, and G.B. Avery. 2000. Rainwater dissolved organic carbon: Concentrations and global flux. *Global Biogeochemical Cycles* 14:139–148.
- Worrall, F. and T. Burt. 2004. Time series analysis of long-term river dissolved organic carbon records. *Hydrological Processes* 18:893–911.
- Worrall, F., T. Burt, and R. Shedden. 2003. Long term records of riverine dissolved organic matter. *Biogeochemistry* 64:165–178.
- Wright, R. 1983. Predicting acidification of North American lakes. Acid Rain Research Series, Norwegian Institute for Water Research.
- Xia, K., U.L. Skyllberg, P.R. Bloom, E.A. Nater, W.F. Bleam, and P.A. Helmke. 1999. X-ray absorption spectroscopic evidence for the complexation of Hg(II) by reduced sulfur in soil humic substances. *Environmental Science & Technology* 33:257–261.
- Yoon, S.-J., L.M. Diener, W.F. Bleam, P.R. Bloom, and E.A. Nater. 2005. X-ray absorption studies of CH<sub>3</sub>Hg<sup>+</sup>-binding sites in humic substances. *Geochimica et Cosmochimica Acta* 69:1111–1121.