Biogeochemical cycling and chemical fluxes in a managed northern forested wetland, Michigan, USA

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ABSTRACT

Forest harvesting and subsequent regeneration treatments may cause changes in soil and solution chemistry that adversely affect forest productivity and environmental quality. The objective of this study was to assess soil carbon (C), nitrogen (N), and base cation pools and fluxes, and to construct a hydrogen ion (H$^+$) mass balance to identify major processes controlling acidity production and consumption 14 years following whole-tree harvesting and regeneration in a northern forested wetland with underlying mineral soils derived from calcareous glacial drift. Results for soil elemental and nutrient pools in the harvested/regenerated stand were compared to an adjacent non-harvested stand and a riparian zone. The riparian zone had the highest soil total C, total N, and exchangeable calcium (Ca) and magnesium (Mg) pools; however, no difference in exchangeable potassium (K) was evident among stand types. Moreover, no differences between the harvested/regenerated and uncut stands were evident in any of the soil chemical pools.

Net export of base cations was minimal and the H$^+$ mass balance indicated that net cation exchange was not a significant process in H$^+$ production or consumption in either the uncut or harvested/regenerated stands. The most striking differences in the H$^+$ mass balance were (1) eight times the H$^+$ consumption from sulfate (SO$_4^{2-}$) reduction in the harvested/regenerated stand compared to that in the uncut condition and (2) nearly twice the H$^+$ production due to N immobilization in the harvested/regenerated stand. However, both stand types were net H$^+$ sinks and increases in H$^+$ export due to whole-tree harvesting were not evident.

The riparian zone was a net exporter of base cations. This finding was attributed to a combination of base cation exchange and carbonate mineral weathering; data suggested the importance of the latter. More research, however, is required to isolate the contributions of cation exchange and carbonate weathering on base cation export from the riparian zone. Stream chemistry was consistent with that of the riparian zone, indicating a strong linkage between the riparian zone stream chemistry, and whole-tree harvesting had no intermediate term (i.e., 14 years) effects on stream acidification in this managed northern wetland ecosystem.

1. Introduction

Forested wetlands are recognized for their importance in maintaining the environmental quality of a landscape, yet they are also an important economic timber base in the Upper Great Lakes Region of the United States (National Wetlands Policy Forum, 1988). In Michigan alone, over 20% of the commercial forest lands have been classified as wetlands (Smith and Kahn, 1987). In the Upper Great Lakes Region, wetlands with a mineral subsoil have been heavily used as a timber resource because of their greater pro-

ductive capacity and commercial operability during winter months compared to peatlands.

The common management technique for forested wetlands with a mineral subsoil in the Upper Great Lakes Region is whole-tree harvesting followed by intensive mechanical site preparation, such as bedding or disc trenching. We have shown that site preparation bedding and trenching increased jack pine (*Pinus banksiana* Lamb.) seedling growth compared to whole-tree harvesting only (Gale et al., 1998). Increased growth is achieved through improvement in soil aeration along with mixing of forest floor and surface mineral soil material, thereby increasing nutrient mineralization from organic matter. However, relative cover of herbaceous species was lower and graminoid species higher in the harvested treatments relative to an uncut reference stand five years after treatments

regardless of site preparation type (Gale et al., 1998); graminoid vegetation was still higher in the treated areas 12 years later (Anderson et al., 2007). A shift in bryophyte communities also occurred, where feathermosses were common in the treatments and Sphagnum mosses dominant in the reference stand 12 years following treatment installations (Anderson et al., 2007). Faster growth of jack pine and altered understory vegetation communities may influence hydrologic and biogeochemical properties as regenerating vegetation grows (e.g., Jones and Post, 2004), but the associated ramifications have not been fully explored.

Hydrology and biogeochemical cycling in forested wetlands differ from that in upland forests. For example, up to 70% of water and base cation fluxes in a forested watershed can come from lowland forests (e.g., forested wetlands) that moderate stream acidification (Johnson et al., 2000). Forested wetlands also reduce dissolved organic carbon (DOC) flux from forests to streams through DOC sorption to metal oxides and uptake by soil microorganisms (Kalbitz et al., 2000), thereby partially regulating energy fluxes within streams. For example, DOC retention depends on hydrologic pathways, with water flow occurring through zones where DOC adsorption or microbial uptake can occur. In histic-mineral wetlands, the thickness of the organic layer is thin (5–15 cm) and the water table generally quite low (McLaughlin et al., 1996), so that, under summer conditions, some DOC-rich surface water will be adsorbed as it passes through the mineral soil (Dalva and Moore, 1991; McLaughlin et al., 1994). This might not be the case if the organic layers were thicker or the water table higher (e.g., Webster and McLaughlin, 2010). Because of the important biogeochemical role of forested wetlands in the landscape, we need to develop a thorough understanding of the effects of silvicultural practices on nutrient cycling and long-term sustainability of that forest type.

Many ecosystem physical, chemical, and biological properties interact to determine sustainability of forested wetlands. Whole-tree harvesting and mechanical site preparation can contribute to nitrogen (N), carbon (C), and base cation depletion and subsequent decreases in soil productivity and increased surface water acidification (Likens et al., 1970; Weetman and Webber, 1972; Boyle et al., 1973; Malkonen, 1976; Kimmins, 1977). However, results for C and base cation responses to whole-tree harvesting reported in the literature are inconsistent, ranging from net losses (Olsson et al., 1996a) and net increases (Johnson et al., 1997; Yanai et al., 1999; McLaughlin and Phillips, 2006) to no net change (Piirainen et al., 2004). This makes generalizations and predictions of whole-tree harvesting and site preparation effects on nutrient and C cycling and water quality difficult.

Riparian zones are recognized as important control points regulating water quality and aquatic productivity and efforts to develop riparian management policies for those ecosystems are increasing (Verry and Dolloff, 2000). Riparian zones account for only a small part of a forested landscape (Naiman and Decamps, 1997), but are critical to water, C, alkalinity, and base cation [calcium ions (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+)] ion transfer from terrestrial to aquatic ecosystems (Fiebig et al., 1990; Hornbeck and Kochenderfer, 2000). However, few studies have addressed biogeochemical cycling in riparian zones and the role these systems play in acid–base dynamics (e.g., McLaughlin, 2009; McLaughlin and Webster, 2010).

We have been investigating whole-tree harvesting and site preparation effects on the structure and function of a forested wetland with a mineral subsoil in the Lake Michigan Drainage Basin since 1988 (Trettin et al., 1996a,b, 1997; McLaughlin et al., 1994, 1996, 2000; Gale et al., 1998; Anderson et al., 2007). Previous research showed that site preparation bedding and trenching stimulated soil organic matter decomposition (Trettin et al., 1996a). These increases were positively related to site disturbance; greatest decomposition occurred on the bedded treatment, followed by the

trenched and whole-tree harvest only treatments. An initial mineral soil C loss of 38% occurred within the first 18 months following harvesting and site preparation and was associated with faster organic matter decomposition (Trettin et al., 1996b). Five years later, however, the bedded treatment suffered the least amount of soil organic matter loss, with the organic matter content in the mineral soil of the bedded treatment recovering to reference levels (McLaughlin et al., 1996). Soil organic matter returned to reference levels in all silvicultural prescriptions 11 years after treatments (Trettin et al., submitted for publication).

We also reported alterations in dissolved organic carbon (DOC) chemistry in the soil solution and shallow groundwater five years following harvesting and site preparation (McLaughlin et al., 1996). The harvest-only and bedded silvicultural prescriptions resulted in more humic characteristic of DOC than that observed under reference conditions. Moreover, elevated nitrate (NO_3^-), ammonium (NH_4^+), and dissolved organic N (DON) concentrations occurred in both the soil solution and shallow groundwater in the bedded treatment five years after installation (Trettin et al., 1997). In addition, 35% of the total N in soil solution occurred as NH_4^+ and NO_3^- in the treatments, but only 18% occurred as inorganic N in the reference stand (Trettin et al., 1997). These results indicate alterations in organic matter decomposition and N mineralization remained at this site five years after whole-tree harvesting and mechanical site preparation. Also, soil solution and water table base cation concentrations were elevated as much as three-fold within 18 months following harvesting and site preparation, with concentrations highest for the most disturbed treatments (Trettin, 1992).

We also found that N and phosphorus (P) additions, alone and in combination, stimulated organic matter decomposition by 15–44% regardless of site preparation treatment (McLaughlin et al., 2000). Moreover, site preparation bedding stimulated net N mineralization, but N and P additions inhibited mineralization by 10–25%. In contrast, N immobilization dominated N cycling in the harvest-only and trenched treatments, which was further stimulated by 25–60% through N and P additions (McLaughlin et al., 2000).

Hydrology is also an important factor that influences the organic matter cycling at this site. Trettin et al. (1996a) reported that in addition to disturbance, the hydrologic position within the wetland relative to the draining stream affected organic matter decomposition. McLaughlin et al. (1994) reported that hydrologic position within the wetland also had a significant effect on mineral soil C retention, with greater retention occurring in areas with a relatively deep water table than in areas where water tables were shallower.

The objective of the present study was to describe C, N, and base cation cycling and to define the importance of riparian zones in mitigating acidification of the draining stream at this site 14 years following harvesting and site preparation. Three questions were of interest: (1) what are the intermediate-term effects of whole-tree harvesting on the soil exchangeable base cation, C, and N pools and fluxes? (2) What is the role of riparian zones in protecting water quality after whole-tree harvesting? and (3) Is whole-tree harvesting a sustainable approach on this site type given its nutrient capital and cycling processes?

2. Materials and methods

2.1. Site description

The study was located in the Lake Michigan Drainage Basin in the central Upper Peninsula of Michigan (46°10′N, 86°43′W). The site is part of the Wetmore Outwash Plain, which is underlain by middle Ordovician limestone (Trenton Limestone). The drift thickness in the vicinity of the site ranges from 30 to 75 m. The site's
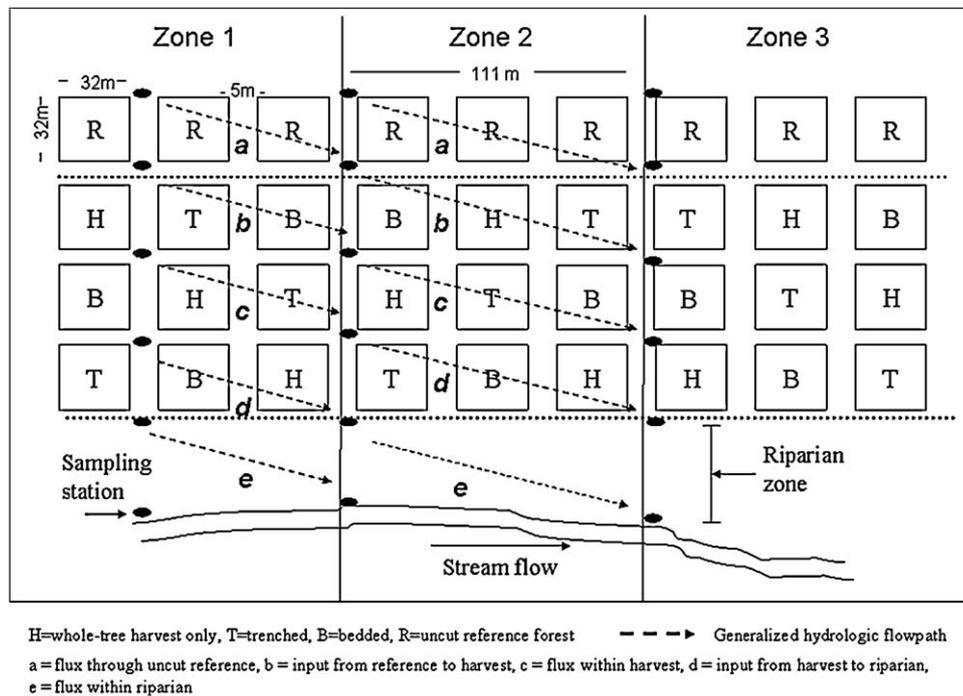
Fig. 1. Site layout for a northern forested wetland study in the Upper Peninsula of Michigan.

elevation is approximately 260 m above sea level. Mean annual temperature and precipitation at the nearest long-term climate monitoring station near Munising, Michigan (approximately 30 km from the site) are 5.0 °C and 961 mm for the period of 1979–2000, respectively.

Original (1988) overstory vegetation primarily consisted of black spruce [*Picea mariana* (Miller) BSP], tamarack [*Larix laricina* (DuRoi) K. Koch.], and jack pine [*Pinus banksiana* (Lamb.)]. The dominant species in the shrub layer were: *Vaccinium* spp., leatherleaf [*Chamaedaphne calyculata* (L.) Moench], and labrador tea [*Ledum groenlandicum* (Oeder)]. Surface vegetation was dominated by *Sphagnum* spp., with minor components of starflower [*Trientalis borealis* (Raf.)], and *Carex* spp. (Gale et al., 1998). The riparian zone overstory vegetation currently consists of red maple [*Acer rubrum* (L.)], alder [*Alnus incana* (L.) Moench ssp. *rugosa* (Du Roi)], white spruce [*Picea glauca* (Moench) Voss], and jack pine. Understory vegetation consists of alder, white birch [*Betula papyrifera*, Marsh.], black cherry [*Prunus serotina*, Ehrh.], and white spruce, with minor components of choke berry [*Aronia melanocarpa* (Michx.) Elliot] and wood fern [*Dryopteris* spp.]. Surface vegetation consists primarily of violet [*Viola* spp.], *A. melanocarpa*, bluejoint [*Calamagrostis canadensis*, (Michx.) P. Beauv.], bunchberry [*Cornus Canadensis*, L.], northern bedstraw [*Galium boreale*, L.], *T. borealis*, pondweed [*Potamogeton* spp.], dewberry [*Rubus hispidus*, L.], and goldenrod [*Solidago* spp.].

The soil on the site has been mapped as a Kinross series (sandy, mixed, frigid, Typic Endoaquod). The Kinross series is poorly drained with a fine-sand solum overlain by a 5–15 cm organic horizon composed mainly of decomposed Sphagnum. The solum is uniform to a depth of 2.5 m, acidic throughout, with generally less than 2% clay content.

2.2. Field design

The overall field layout was a randomized complete block design with three blocks located parallel to the West Branch of the Sturgeon River. Each block consisted of nine 32 m × 32 m plots with a 5 m buffer between each plot. In addition, three blocks, each containing three plots, were established in an uncut area adjacent to the cut area.

Silvicultural prescriptions were applied in July 1988. A 14.5-ha parcel of the study site was clearcut using feller bunchers. Tree bundles were skidded to a landing where trees were sorted into fiber and fuel product classes. Fuelwood was whole-tree chipped, while the fiber wood was delimbed, topped, and bucked into pulpwood bolts at the landing site. All trees greater than approximately 5 cm in diameter at breast height were removed from the site.

Three treatments were installed in three blocks in the harvested area along a gradient of geomorphic position and hydrology and consisted of (1) whole-tree harvest only, (2) harvested and bedding (bedded treatment), and (3) harvest and disc trenching; both (2) and (3) were followed by chemical (glyphosate) weed control (Fig. 1). Twelve years following harvesting and site preparation treatments, relative cover of herbaceous plants was higher, Sphagnum mosses lower, non-Sphagnum mosses (e.g., feathermosses) higher, and woody plants similar in the harvested/regenerated treatment relative to the uncut stand (Anderson et al., 2007).

For this study, three transects were extended from the undisturbed stream edge (riparian zone) through the harvested/regenerated (whole-tree harvest only) stand into the uncut forest. Two sampling stations were located in each of the riparian zone, harvested/regenerated stand, and uncut stand along each transect for a total of six sampling stations per stand type (Fig. 1).

2.3. Sampling and analyses

2.3.1. Hydrometric data

Daily precipitation for 2003 was obtained from the National Atmospheric Monitoring Network (NADP) site at the Seney National Wildlife Refuge Area located approximately 70 km from the study site (http://nadp.sws.uiuc.edu). Measurements of hydraulic head of piezometers were made monthly from June to October in 2003. For water table hydraulic head and chemical sampling, each transect consisted of six piezometer (slotted 2.5-cm diameter PVC pipe) nests (separated by 100 m), with piezometers inserted to 50 and 100 cm soil depth, extending from the stream

edge, through the harvested/regenerated stand and uncut stand (Fig. 1). At each piezometer location, hydraulic conductivity was measured using the Hvorslev water recovery method (Freeze and Cherry, 1979).

The mass flux of water from one part of the wetland to another was calculated following the methods of Waddington and Roulet (1997). The wetland was divided into three zones based on position and topography (Fig. 1). Water flow across the wetland was 45° relative to stream flow (Fig. 1). Therefore, we used the following method to calculate mass flux. The mass flux from one zone to another was computed assuming the boundaries between zones extended perpendicularly from the wetland's surface to its base. Water flux for both 50 and 100 cm depth into and out of the uncut stand was estimated for the wetland from monthly flownets along flowpaths labelled 'a' in Fig. 1. Mass flux into and out of the harvested/regenerated regenerated stand was estimated along flowpaths labelled 'c', and mass flux within the riparian zone along flowpaths labelled 'e' in Fig. 1. We also measured mass fluxes within the harvested/regenerated stand using flowpaths labelled 'b' and 'd' in Fig. 1. Discharge was converted into a unit area depth of subsurface runoff by dividing by the area of the zone from which the groundwater was received.

2.3.2. Soil sampling

Forest floor characteristics were measured using a 0.25 m × 0.25 m template at all sampling stations on each transect. Forest floor thickness was measured along each face from which samples were excavated, and the forest floor volume removed was estimated as the product of sample area and average thickness (McLaughlin and Phillips, 2006). Forest floor material was dried at 60 °C until constant mass; dried material was ground through a Wiley mill and analyzed for loss-on-ignition (LOI) at 550 °C, total Kjeldahl nitrogen (TKN), extractable Ca, Mg, and K using 1 M ammonium (NH_4)-acetate (pH 7). Exchangeable bases were measured using a Varian Liberty Series II ICP. Total C was measured using a LECO CR-12C Analyzer and TKN measured as liberated NH_4^+ ions using a flow injection system (TRAACS 800, Braun and Lubbe) auto analyzer.

Mineral soil was sampled by coring to 100 cm depth at each sampling station, with horizons described as per Soil Survey Staff (1992). Samples were taken for each soil horizon, returned to the laboratory, and stored at 4 °C until dried. Soil was dried at 60 °C to constant mass and passed through a 2 mm sieve. Chemical analyses were conducted as described above for the forest floor. Nutrient and elemental contents per unit area basis were estimated as the product of concentration, bulk density, and depth, with a correction for stone content. Stone volume was estimated following McLaughlin and Phillips (2006).

2.3.3. Soil solution and water table sampling

At each sampling station, soil solution was sampled monthly using tension lysimeters from June through October in 2003. After hydraulic head was measured, the water in piezometers was pumped out until the piezometer was dry or three times the piezometer volume removed. The next day, water pH was measured using an Oakton 10 Series pH/conductivity/temperature meter after which water for other chemical analyses was collected using a low-speed peristaltic pump. These samples were placed on ice and transported to the laboratory. Samples were filtered through Gelman 0.45 μm filters and analyzed for: dissolved organic (DOC) and dissolved inorganic (DIC) C using a Shimadzu TOC 5000 carbon analyzer; SO_4^{2-}, NO_3^-, and Cl^- by ion chromatography using a Dionex Ion Chromatography ICS 2000 anion system; NH_4^+ using a flow injection system (TRAACS 800, Braun and Lubbe) auto analyzer; and Ca^{2+}, Mg^{2+}, K^+, and sodium (Na^+) using a Varian Liberty Series II ICP. Soil solution pH and DIC concentrations

were used to calculate the fractional carbonate equilibrium of the DIC assuming an open system (Gower et al., 1995). Organic acid (OA^-) concentration was estimated by the charge balance approach where:

$$OA^- \, (\mu quiv \, l^{-1}) = (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$$
$$- (HCO_3^- + SO_4^{2-} + NO_3^- + Cl^-)$$

Concentrations of all cations and anions are in $\mu equiv. \, l^{-1}$.

2.3.4. Mass balances

Mass balance calculations were based on inputs to, and outputs from, each stand type. Wet atmospheric deposition from the Seney National Wildlife Refuge NADP station was combined with groundwater inputs calculated from piezometer nests at the uncut stand interface to estimate total inputs for each constituent. The flux at the bottom of the reference stand for zones 1 and 2 (Fig. 1) were used as inputs to the harvested/regenerated stand. Fluxes along flowpaths 'c' in Fig. 1 were used to calculate inputs from the harvested/regenerated stand to the riparian zone. Finally, fluxes along flowpaths 'e' served to calculated fluxes in the riparian zone.

The net flux of each constituent was used to construct an H^+ mass balance, with associated measurement errors with the calculation of the flux of each constituent, by assuming that net output of each constituent was associated with either net production or net consumption of H^+ (e.g., Steinmann and Shotyk, 1997; Cirmo et al., 2000). Specifically, carbonic acid and organic acid dissociations, S and N redox reactions, and cation exchange/carbonate mineral weathering (Table 1) were used to construct the mass balance. We acknowledge a large variation in our calculations, but the mass balances allow for a generalization of the important biogeochemical reactions contributing to H^+ generation that can serve to develop future research hypotheses.

2.4. Statistical analyses

Most of the constituent data from the soil solution, water table, and soils were not normally distributed ($P > 0.05$) based on the Shapiro–Wilk test for normality (Conover, 1980). Levene's test for homogeneity of variances indicated that the variances may ($P \leq 0.05$) or may not ($P > 0.05$) have been equal, depending on the matrix and constituent analyzed. Therefore, nonparametric statistics were used for all statistical analyses (Conover, 1980). All analyses were conducted using SAS (SAS Institute, 1992) and unless otherwise stated the 0.05 level of significance was used.

A one-way ANOVA on the ranks of the data was employed to test the hypothesis of no treatment effects on total soil (forest floor plus mineral soil) base cation and elemental content per unit area. If treatment differences occurred, nonparametric multiple comparisons were used to separate the ranks. A split-plot ANOVA on the ranks of the data was used to test the hypothesis of no treatment effects on solution chemistry. The main plot factor was stand type and the sub-plot factor was water depth (25, 50, and 100 cm below the surface). If treatment differences occurred, nonparametric multiple comparisons were used to separate the ranks. When significant differences in constituents were found based on depth, the Van der Waerden one-way analysis test was used to test the hypothesis of no depth effects on the specific constituents within either the reference or regenerating watersheds, respectively.

We also calculated minimum detectable differences (MDD) of the current design and the number of transects (e.g., experimental units) required to detect a 20% difference in the mean of the data ranks at 0.05 level of significance and power of 70% using a noncentrality parameter (Steidl and Thomas, 2001) for soil solution and water table constituents to supplement the ANOVA results.

Table 1

Hydrogen ion producing and consuming reactions used in H$^+$ mass balance calculations for a managed northern forested wetland in the Upper Peninsula of Michigan (from McLaughlin and Webster, 2010).

Reaction type	Equation	Net H$^+$ (mol)
Hydrogen-releasing reactions		
Sulfur oxidation	$H_2S + 2O_2 = SO_4^{2-} + 2H^+$	+2
Nitrification	$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$	+2
Nitrogen immobilization	$NH_4^+ + R^a\text{-COH} = R\text{-}C_2H_2O_2NH_2 + H^+$	+1
Soil cation exchange	$Ca^{2+} + H_2X^b = CaX + 2H^+$	+2
	$Mg^{2+} + H_2X = MgX + 2H^+$	+2
	$K^+ + HX = KX + H^+$	+1
	$Na^+ + HX = NaX + H^+$	+1
Calcite precipitation	$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$	+1
Organic acid dissociation[c]	$R\text{-COOH} = R\text{-COO}^- + H^+$	+1
Carbonic acid dissolution	$H_2CO_3 = HCO_3^- + H^+$	+1
Hydrogen-consuming reactions		
Sulfate reduction	$SO_4^{2-} + 2CH_2O + 2H^+ = H_2S + 2CO_2 + H_2O$	−2
Denitrification	$NO_3^- + 1.25CH_2O + H^+ = 1.25CO_2 + 0.5N_2 + 1.75H_2O$	−1
Soil cation exchange	$CaX + 2H^+ = Ca^{2+} + H_2X$	−2
	$MgX + H^+ = Mg^{2+} + H_2X$	−1
	$KX + H^+ = K^+ + HX$	−1
	$NaX + H^+ = Na^+ + HX$	−1
Calcite dissolution	$CaCO_3 + CO_2 + H_2O = Ca^{2+} + CO_3^{2-}; CO_3^{2-} + H^+ = HCO_3^-$	−1

[a] R denotes rest of organic compound.
[b] X denotes peat cation exchange site.
[c] Assuming monoprotic acid.

3. Results

3.1. Hydrometric data

Total annual precipitation reported at the Seney National Wildlife Refuge NADP station for 2003 was 958 mm, which was similar to the 21-year average (1979–2000) of 961 mm for nearby Munising, MI. However, June through October precipitation was 574 mm, which was 25% higher than the 21-year average of 433 mm for Munising, MI. Mean water table depth was 43 ± 16, 52 ± 24, and 46 ± 19 cm below the surface of the riparian zone, harvested/regenerated stand, and uncut forest, respectively, and did not differ among stand types. Monthly mean water table depth patterns were generally similar among stand types, with the exception of August, when the water table was about 30% lower in the harvested/regenerated stand than in the uncut forest and the riparian zone (Fig. 2). Water table flow at 50 and 100 cm depth was 45° relative to the stream and shallow groundwater flow from transect 1 to transect 3, with upwelling discharge occurring at the riparian zone and stream interface (Fig. 3); and no seasonal changes in flowpaths were observed in this study.

3.2. Soil and solution chemistry

3.2.1. Soil pools

Total soil (forest floor and mineral soil) pools of C, N, Ca, and Mg were highest in the riparian zone (Table 2). No differences in the K pool was evident among stand types. In addition no differences for soil pools of any measured constituent were found between the uncut and harvested/regenerated stands.

3.2.2. Solution chemistry

The riparian zone had the highest soil solution and water table Ca^{2+}, Mg^{2+}, and HCO$_3^-$ and lowest H$^+$, Na$^+$, and SO$_4^{2-}$ concentrations (Table 3). The only differences occurring in the soil solution at 25 cm depth between the uncut and harvested/regenerated stands
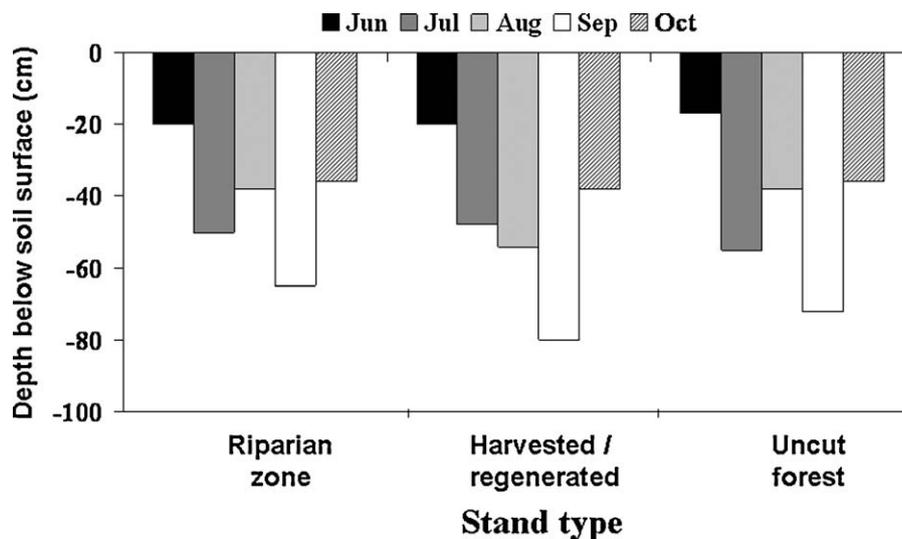

Fig. 2. Depth to the water table (cm below surface) for a riparian zone, 14-year-old regenerating stand, and an uncut stand in a managed forested wetland in the Upper Peninsula of Michigan.

Table 2

Total nutrient and elemental pools in a managed northern forested wetland in the Upper Peninsula of Michigan.

Stand type	Total C (t ha^{-1})	Total N (t ha^{-1})	Exchangeable Ca (kg ha^{-1})	Exchangeable Mg (kg ha^{-1})	Exchangeable K (kg ha^{-1})
Uncut forest	127 [b*]	5.9 [b]	684 [b]	161 [b]	299
Harvested/regenerated	116 [b]	5.6 [b]	816 [b]	164 [b]	366
Riparian zone	589 [a]	25.3 [a]	6174 [a]	357 [a]	436

[*] Numbers within columns followed by different lower case letters differ among stand types at $P \leq 0.05$.
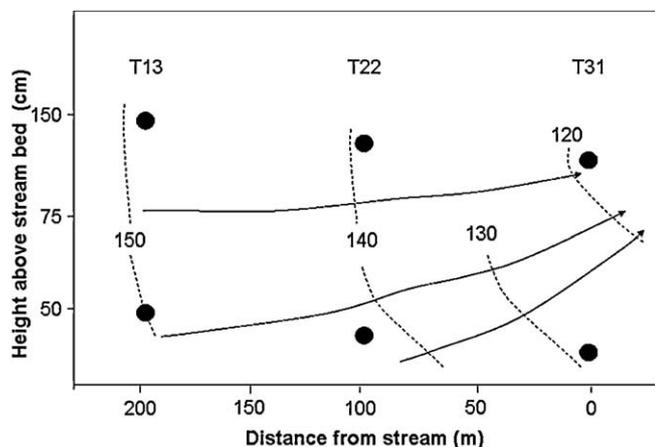
Fig. 3. Flownet diagram of shallow groundwater flow in a managed northern forested wetland in the Upper Peninsula of Michigan (T13 = transect 1, sample station, 3; T23 = transect 2, sample station, 3; T31 = transect 3, sample station 1, as per Fig. 1).

were higher SO_4^{2-} and lower HCO_3^- concentrations in the uncut forest (Table 3) and higher OA$^-$ (100 cm) and DOC (50 and 100 cm) in the harvested/regenerated stand.

Calcium ions accounted for 34 to 66% of the total cation charge across stand types and depths, whereas Mg^{2+} accounted for 25–31% of the total cation charge in the riparian zone across depths but only 13–17% of that in the harvested/regenerated and uncut stands (Table 3). Sodium ions accounted for 25–33% of the cation charge in the uncut and harvested/regenerated stands, but less than 10% of that in the riparian zone. Soil solution and water table Mg^{2+}:Ca^{2+} ratios varied from 0.29 to 0.55 across stand types. Moreover, the ratio of $(Mg^{2+} + Ca^{2+})$:HCO_3^- was near 1.0 across depths in the riparian zone, near 3.0 in the soil solution, and near 1.0 in both water table depths of the uncut stand.

No differences in K$^+$ or NH$_4^+$ concentration were found among stand types, while NO_3^- was higher only in the 50 cm water table of the riparian zone and SO_4^{2-} was higher in the uncut and harvested/regenerated stand soil solution than in the riparian zone (Table 3). The contribution of H$^+$, K$^+$, and NH$_4^+$ to cation charge accounted for no more than 10% each across stand types and depths. Solution pH was highest across depths in the riparian zone and did not differ between the harvested/regenerated and uncut stands.

Bicarbonate concentrations ranged from 4 to 10 times higher in the soil solution and water table of the riparian zone compared to that in the uncut and harvested/regenerated stands (Table 3). Bicarbonate also dominated the anion charge balance of the soil solution and water table of the riparian zone, where it contributed about 90% to the anion charge across depths. In contrast, HCO_3^- accounted for only 44–51% of the anion charge in the harvested/regenerated and between 19 and 64% of that in the uncut stands (Table 3). Sulfate concentration decreased progressively with depth across stand types and contributed 26–37% of the anion charge in the harvested/regenerated and uncut conditions in the soil solution, but <10% at the deeper water table levels (Table 3). Sulfate contributed <10% to the anion charge of the riparian zone soil solution and water table. Organic acids accounted for 24–44% of the anion charge in the uncut and harvested/regenerated stands, but <10% of that in the riparian zone.

Monthly patterns in the charge balance of the soil solution in the uncut stand were highly variable, with Ca^{2+} plus Mg^{2+} accounting for 49–76% of the cation charge (Fig. 4A). Moreover, HCO_3^- was a minor component of the anion charge and SO_4^{2-} and OA$^-$ dominated the anion balance (Fig. 4A). However, the proportion of the anion charge attributed to HCO_3^- increased to at least 50% at the two water table depths. In contrast to the uncut stand, Ca^{2+} plus Mg^{2+} consistently accounted for about 75% of the cation charge in the harvested/regenerated stand (Fig. 4B). Bicarbonate ions accounted for approximately one-third of the total anion charge in the soil solution, with SO_4^{2-} and OA$^-$ equally contributing

Table 3

Mean (and standard deviation) solution chemistry in a managed northern forested wetland in the Upper Peninsula of Michigan.

Constituent	Stand type (μequiv. l^{-1})									Stream
	Uncut forest			Harvested/regenerated stand			Riparian zone			
	25[c]	50[c]	100[c]	25[c]	50[c]	100[c]	25[c]	50[c]	100[c]	
H$^+$	35 [a*] (25)	5.6 [A**] (7.4)	3.6 [1***] (5.5)	22 [b] (21)	4.9 [A] (8.0)	3.7 [1] (0.4)	5.5 [c] (12.1)	0.3 [B] (0.3)	0.3 [2] (7.5)	0.9 (0.5)
Ca^{2+}	115 [b] (227)	122 [B] (98)	106 [2] (85)	160 [b] (61)	157 [B] (98)	190 [2] (117)	411 [a] (425)	655 [A] (458)	674 [1] (409)	619 (199)
Mg^{2+}	65 [b] (169)	51 [B] (35)	43 [2] (75)	46 [b] (30)	49 [B] (20)	59 [2] (30)	227 [a] (347)	240 [A] (309)	266 [1] (310)	213 (194)
K$^+$	19 (8)	19 (6)	24 (8)	17 (7)	20 (9)	20 (7)	24 (16)	20 (11)	19 (8)	16 (12)
Na$^+$	80 [a] (22)	90 [A] (19)	88 [1] (29)	81 [a] (32)	85 [A] (34)	83 [1] (24)	48 [b] (13)	43 [B] (11)	58 [2] (11)	53 (23)
NH$_4^+$	22 (50)	10 (16)	21 (55)	20 (50)	6.9 (11)	13 (17)	7.8 (9.0)	6.0 (7.3)	21 (49)	1.6 (2.4)
NO$_3^-$	16 (10)	13 (8)	7.8 (5.8)	13 (9)	8.2 (6.3)	8.0 (4.0)	6.2 (9.4)	12 (13)	3.5 (6.0)	7.1 (12.9)
HCO$_3^-$	63 [c] (113)	192 [B] (320)	165 [2] (194)	151 [b] (311)	158 [B] (177)	186 [2] (261)	640 [a] (924)	879 [A] (447)	946 [1] (621)	817 (222)
SO$_4^{2-}$	123 [a] (23)	31 (21)	10 (15)	90 [a] (36)	34 (25)	24 (15)	52 [b] (26)	13 (14)	10 (12)	63 (22)
Cl$^-$	11 (6)	11 (8)	10 (3)	8 (6)	9 (6)	10 (6)	10 (5)	9 (5)	9 (6)	5 (0.4)
OA$^-$	136 [a] (23)	71 [AB] (19)	96 [1,2] (22)	94 [a] (13)	119 [A] (31)	146 [1] (24)	15 [b] (9)	45 [B] (22)	48 [2] (10)	12 (15)
DOC (μmol l^{-1})	3806 (2252)	1680 [B] (1441)	1492 [2] (725)	4021 (1514)	3176 [A] (1265)	2443 [1] (904)	3647 (2024)	1776 [B] (850)	1672 [2] (452)	1285 (342)
pH	4.6 [b] (0.5)	5.5 [B] (0.7)	5.8 [2] (0.6)	4.9 [b] (0.6)	5.7 [B] (0.7)	5.8 [2] (0.6)	5.7[a] (0.7)	6.9 [A] (0.6)	6.8 [1] (0.6)	7.5 (0.3)

[*] Numbers within rows followed by different lower case letters differ among stand types for 25 cm depth at $P \leq 0.05$.

[**] Numbers within rows followed by different upper case letters differ among stand types for 50 cm depth at $P \leq 0.05$.

[***] Numbers within rows followed by different numbers differ among stand types for 100 cm depth at $P \leq 0.05$.
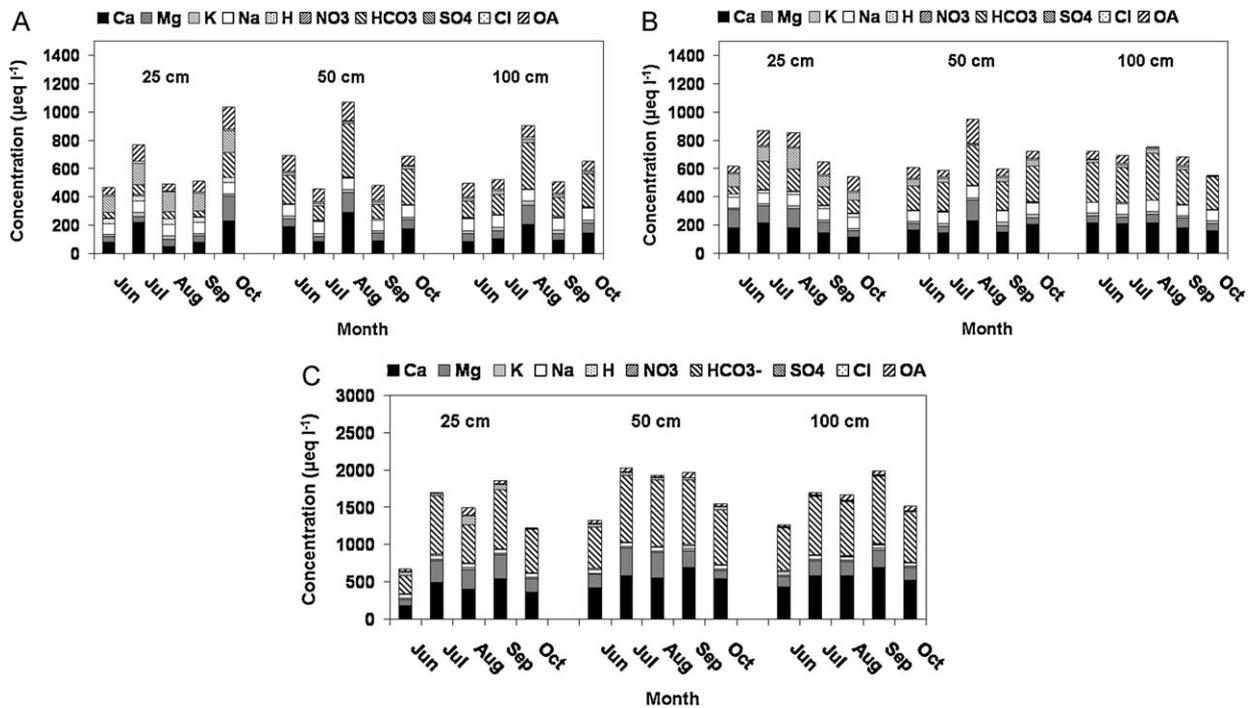
[c] Depth below surface (cm).

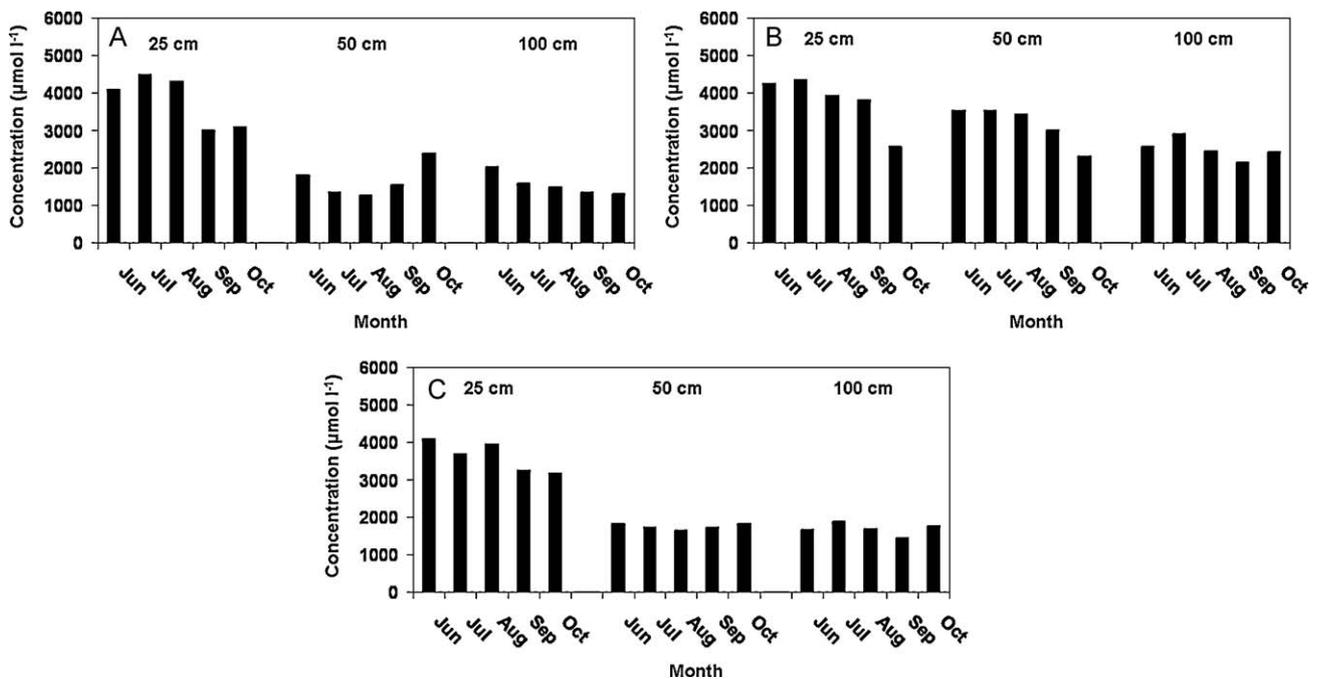**Fig. 4.** Monthly mean cation and anion balances for soil solution at 25 cm and water table at 50 and 100 cm for (A) an uncut stand, (B) 14-year-old regenerating stand, and (C) riparian zone in a managed northern forested wetland in the Upper Peninsula of Michigan (OA⁻ = organic acids).

most of the remaining anion charge of the harvested/regenerated stand soil solution (Fig. 4B). Bicarbonate also accounted for one-half to greater than two-thirds of the anion charge at 50 and 100 cm in the harvested/regenerated stand (Fig. 4B). Monthly patterns in the charge balance were also consistent in the riparian zone, with Ca^{2+} and Mg^{2+} accounting for most of the cation charge and HCO_3^- accounting for >90% of the anion charge (Fig. 4C).

Dissolved organic C concentration in the soil solution (i.e., at 25 cm) did not differ among stand types (Table 3; Fig. 5A–C).

However, DOC concentrations were only 20% lower in the water table at 50 cm compared to those at 25 cm depth in the harvested/regenerated stand, but 51% and 55% lower in the riparian zone and uncut stands, respectively. DOC concentrations did not decrease between 50 and 100 cm depths in any stand type. Stream chemistry was similar to that in the riparian zone soil solution and water table chemistry, emphasizing the strong linkage between the riparian zone and stream chemistry (Table 3).

Fig. 5. Monthly mean dissolved organic carbon concentrations for soil solution at 25 cm and water table at 50 and 100 cm for (A) an uncut stand, (B) 14-year-old regenerating stand and (C) riparian zone in a managed northern forested wetland in the Upper Peninsula of Michigan.

Table 4
Pooled mean ± standard error from ANOVA tests, minimum detectable difference, and required sample size to detect 20% difference in concentrations at the 0.05 level of significance and a power of 70% for soil solution chemistry between a whole-tree harvested and mechanically prepared and an uncut reference northern forested wetland sampled in 2003.

Constituent	Pooled mean ± standard error of the actual data and ranks		Minimum detectable difference based on ANOVA of the ranks		Required number of transects to detect 20% difference at 0.05 level of significance and power of 0.70 based on ANOVA of the ranks	
	Non-ranked data (μequiv.l^{-1})	Ranks	Non-ranked data (μequiv.l^{-})	Ranks	Non-ranked data	Ranks
25 cm						
Ca^{2+}	119 ± 51	45 ± 8	151	23	13	7
Mg^{2+}	63 ± 40	44 ± 10	119	29	89	11
K^+	18 ± 1	44 ± 4	2.2	12	2	2
NH_4^+	21 ± 19	48 ± 15	17	45	200	22
HCO_3^-	141 ± 116	30 ± 6	345	17	150	9
NO_3^-	3.3 ± 0.4	48 ± 3	1.2	9	3	2
SO_4^{2-}	107 ± 32	44 ± 12	95	36	23	16
DOC (μMl^{-1})	3934 ± 1457	30 ± 13	4340	40	30	41
50 cm						
Ca^{2+}	144 ± 22	47 ± 5	65	14	5	3
Mg^{2+}	50 ± 10	47 ± 8	30	24	9	6
K^+	20 ± 2	47 ± 9	7.2	27	3	8
NH_4^+	8.4 ± 6.0	48 ± 17	21	50	110	29
HCO_3^-	167 ± 67	48 ± 11	200	27	36	13
NO_3^-	2.8 ± 1.4	48 ± 8	4.2	24	46	7
SO_4^{2-}	32 ± 24	48 ± 10	71	30	124	10
DOC (μMl^{-1})	2409 ± 421	48 ± 11	1251	32	7	12
100 cm						
Ca^{2+}	214 ± 6	48 ± 1	16	3.0	2	2
Mg^{2+}	72 ± 24	48 ± 1	71	2.7	26	2
K^+	22 ± 2	48 ± 4	5	12	2	2
NH_4^+	17 ± 12	48 ± 8	35	24	104	6
HCO_3^-	170 ± 56	48 ± 6	167	18	24	3
NO_3^-	3.5 ± 1.1	48 ± 6	3.3	18	22	3
SO_4^{2-}	31 ± 21	44 ± 8	63	24	220	6
DOC (μMl^{-1})	1964 ± 193	48 ± 6	572	6	2	3

3.2.3. Variability in measurements

For the uncut and harvested/regenerated stands, the general pattern of variability in the measured constituents was generally greater for non-ranked data than their ranks (Table 4). For most constituents in the soil solution and 50 cm water table, the required number of transects to detect a 20% difference in the ranks of the concentrations between the uncut and harvested/regenerated stands was generally much more than the three transects used in this current study, ranging from two transects for NO_3^- and K^+ to 41 transects for DOC (Table 4). However, with the exception of NH_4^+ and SO_4^{2-}, the number of transects used in the current study was adequate to detect a 20% difference in the ranks at 100 cm water table. Because of large P (0.29–0.94) values produced from the ANOVA, we believe that Type II errors are minimized for the constituents that did not significantly differ among stands.

3.3. Mass balances

The uncut and harvested/regenerated stands were near equilibrium in terms of net base cation inputs and outputs (Table 5). In contrast, those two stand types consumed 95% of H^+, 63% (uncut) and 77% (harvested/regenerated) of NH_4^+, and >95% of NO_3^- entering the uncut and harvested/regenerated stands, although variability was high. Twice as much HCO_3^- left the harvested/regenerated stand as entered, while 70% of the HCO_3^- entering the uncut stand was consumed (Table 5). However, variation around the mean HCO_3^- flux was the widest of the measured constituents (Table 6). Therefore, we suspect HCO_3^- net flux did not differ between the uncut and harvested/regenerated stands. The harvested/regenerated stand was a stronger SO_4^{2-} sink compared to the uncut stand, where 75% of the SO_4^{2-} entering the harvested/regenerated stand was consumed compared to nearly

balanced input and output for the uncut forest. Two- and three times as much Ca^{2+} and Mg^{2+} and four times as much HCO_3^- left the riparian zone as entered (Table 5). The stoichiometry of Ca^{2+}, Mg^{2+}, and HCO_3^- in the riparian zone suggests relatively equal contributions of calcite and dolomite to Ca^{2+}, Mg^{2+}, and HCO_3^- export. However, because the riparian zone mineral soil exchangeable Ca and Mg pools were also elevated over those in the uncut and harvest/regenerated stands (Table 2), more in depth studies of base cation exchange and carbonate mineral weathering are needed to confidently assign contributions of both processes to base cation losses from the riparian zone. As with the uncut and harvested/regenerated stands, K^+ and Na^+ net balances were near zero and about 95% of the NH_4^+ and NO_3^- and 85% of the SO_4^{2-} that entered the riparian zone was consumed (Table 5).

Using the stoichiometric balances for H^+ production and consumption (Table 1), N immobilization (24–32% of the H^+ production) was a consistent H^+ producing reaction across stand types (Table 6). In addition, SO_4^{2-} reduction (10–55% of H^+ consumption) and denitrification (20–45% H^+ consumption) were consistent H^+ consuming reactions across stand types. The largest discrepancies in reactions were carbonic acid (H_2CO_3) dissociation and base cation exchange/carbonate dissolution, which differed only between the riparian zone and the two forested stands. The H^+ mass balance generally followed the porewater cation/anion balance and base cation, SO_4^{2-}, and HCO_3^- export (Tables 3 and 4, Fig. 4).

4. Discussion

4.1. Uncut and harvested/regenerated stands

4.1.1. Soil carbon and nutrient pools

No depletion of soil C, N, or base cation pools in response to harvesting occurred at this site. The likely base cation source is

Table 5
June through October chemical inputs, outputs, and net change in a managed northern forested wetland in the Upper Peninsula of Michigan.

Constituent	Input (precipitation + groundwater) (equiv. ha^{-1})	Output (equiv. ha^{-1})	Net (input–output) (equiv. ha^{-1})
Uncut forest			
H^+	201 ± 32	11 ± 9	190 ± 75
Ca^{2+}	108 ± 72	122 ± 66	-14 ± 69
Mg^{2+}	65 ± 30	75 ± 39	-10 ± 34
K^+	19 ± 10	21 ± 13	-11 ± 12
Na^+	61 ± 5	102 ± 19	-41 ± 15
NH_4^+	200 ± 98	75 ± 33	125 ± 74
NO_3^-	203 ± 63	10 ± 8	193 ± 52
HCO_3^-	162 ± 190	50 ± 43	112 ± 106
SO_4^{2-}	250 ± 79	208 ± 110	42 ± 87
Cl^-	24 ± 6	28 ± 3	-4 ± 5
OA^-	5 ± 12	108 ± 65	-103 ± 92
Σ Cations	645	406	239
Σ Anions	644	404	240
Cation–anion	1	2	-1
DOC (m ha^{-1})	2991 ± 1241	2484 ± 1310	507 ± 621
Harvested/regenerated stand			
H^+	211 ± 39	10 ± 15	201 ± 20
Ca^{2+}	213 ± 83	137 ± 69	76 ± 72
Mg^{2+}	96 ± 50	45 ± 23	51 ± 34
K^+	26 ± 4	15 ± 3	11 ± 4
Na^+	112 ± 12	100 ± 15	12 ± 14
NH_4^+	270 ± 105	63 ± 44	207 ± 82
NO_3^-	230 ± 182	9 ± 7	221 ± 84
HCO_3^-	75 ± 60	150 ± 105	-75 ± 82
SO_4^{2-}	446 ± 124	110 ± 58	336 ± 74
Cl^-	42 ± 7	18 ± 5	24 ± 5
OA^-	120 ± 53	70 ± 22	50 ± 34
Σ Cations	928	370	558
Σ Anions	913	357	556
Cation–anion	15	13	2
DOC (m ha^{-1})	3360 ± 1484	1960 ± 1231	1400 ± 742
Riparian zone			
H^+	210 ± 23	1 ± 3	209 ± 16
Ca^{2+}	228 ± 65	512 ± 109	-284 ± 73
Mg^{2+}	66 ± 22	230 ± 91	-164 ± 69
K^+	20 ± 9	32 ± 10	-12 ± 9
Na^+	110 ± 17	123 ± 6	-13 ± 14
NH_4^+	259 ± 68	13 ± 12	246 ± 40
NO_3^-	229 ± 73	17 ± 20	212 ± 62
HCO_3^-	175 ± 49	759 ± 193	-584 ± 107
SO_4^{2-}	348 ± 69	54 ± 23	294 ± 60
Cl^-	32 ± 4	26 ± 5	6 ± 4
OA^-	82 ± 23	41 ± 21	41 ± 23
Σ Cations	893	911	-18
Σ Anions	866	897	-31
Cation–anion	27	14	13
DOC (m ha^{-1})	3034 ± 1851	1517 ± 777	1517 ± 973

input from the shallow groundwater, while the N source could not be determined it likely includes N-fixation, groundwater, and N deposition inputs. These factors are discussed in more detail by Trettin et al. (submitted for publication). Therefore, we focus this discussion on solution chemistry and fluxes and associated controls and variability.

4.1.2. Solution chemistry
4.1.2.1. Dissolved organic carbon.
Transport of DOC from the forest floor to the mineral soil, where DOC is precipitated onto iron (Fe) and aluminum (Al) oxide exchange sites, is an important process in forest mineral soil C storage, contributing 19 to 50% of total mineral soil organic C pools in temperate and boreal forests (Neff and Asner, 2001; Kalbitz and Kaiser, 2008). Transport of DOC from the forest floor and its precipitation in mineral soils has also been proposed as an important mechanism for retaining soil C pools following whole-tree harvesting (Olsson et al., 1996b; Kalbitz et al., 2004). However, results from coniferous forests have been inconsistent. For example, at the current site, DOC sorption between 25 and 50 cm was limited in the harvested/regenerated stand relative to that in the uncut forest, although DOC concentrations in the soil solution and water table were an order of magnitude higher than that reported for upland soils (e.g., Johnson et al., 2000; Kalbitz et al., 2000). This pattern was not evident five years post-harvest (McLaughlin et al., 1996, 2000).

Adsorption of DOC in the mineral soil at the current site is much lower than in other conifer forests in eastern North America (e.g., Moore et al., 1992) because the coarse-textured soil at this site has low Fe and Al oxide contents (McLaughlin et al., 1994). Iron oxidation–reduction (redox) reactions are important to DOC sorption and desorption in soils and shifts in water table position partially control DOC concentrations in solution through Fe redox reactions (Dalva and Moore, 1991; McLaughlin et al., 1994). However, differences in water table depth between the harvested/regenerated and uncut stand were not evident in this study. Also, the net input/output balance of DOC was highly variable (Table 5), making it difficult to generalize patterns at this site. Therefore, more research is required to identify DOC sorption/desorption patterns in this forested wetland.

Table 6
Hydrogen ion (H$^+$) net production and consumption mass balance in a managed northern forested wetland in the Upper Peninsula of Michigan.

Process	Net H$^+$ production (equiv. ha^{-1})
Uncut forest	
Input	201 ± 75
Nitrogen immobilization	125 ± 74
Carbonic acid dissociation	-112 ± 67
Organic acid dissociation	103 ± 92
Sulfur oxidation	0 ± 0
Base cation exchange/calcite dissolution	-76 ± 49
Sulfate reduction	-42 ± 87
Denitrification	-193 ± 52
Balance	6
Harvested/regenerated stand	
Input	211 ± 20
Nitrogen immobilization	207 ± 84
Carbonic acid dissociation	75 ± 60
Organic acid dissociation	-50 ± 34
Sulfur oxidation	0 ± 0
Base cation exchange/calcite dissolution	150 ± 74
Sulfate reduction	-336 ± 4
Denitrification	-221 ± 82
Balance	36
Riparian zone	
Input	210 ± 16
Nitrogen immobilization	246 ± 89
Carbonic acid dissociation	584 ± 107
Organic acid dissociation	-41 ± 23
Sulfur oxidation	0 ± 0
Base cation exchange/calcite dissolution	-473 ± 71
Sulfate reduction	-294 ± 60
Denitrification	-212 ± 62
Balance	20

4.1.2.2. Inorganic nitrogen. Soil solution NH_4^+ and NO_3^- concentrations did not differ between the uncut and harvested/regenerated stands (Table 3). Moreover, little variability occurred in monthly mean NH_4^+ and NO_3^- concentrations (Fig. 4). In addition, NH_4^+ and NO_3^- concentrations were similar to those of the uncut stand at the time of harvesting (1988) and five years (1993) later (Trettin et al., 1997), which was likely due to low N mineralization and high N immobilization rates at this site (McLaughlin et al., 2000).

We assumed net NO_3^- consumption (Tables 5 and 6) in the uncut and harvested/regenerated stands was 100% due to denitrification because most N cycling research in northern wetlands indicates NO_3^- uptake is predominately through denitrification (e.g., Hedin et al., 1998; Cirmo et al., 2000). Given this assumption, N immobilization and denitrification were approximately balanced in terms of H$^+$ production and consumption in both the uncut and harvested/regenerated stands (Table 6). However, Trettin et al. (submitted for publication) reported N accrual rates between 17 and 30 kg ha^{-1} year^{-1} for aboveground biomass and 100–160 kg ha^{-1} year^{-1} for the forest floor 11 years following treatment implementation. They failed to account for the N source other than atmospheric N deposition, but suggested the source may be shallow groundwater and N fixation.

The input/output balance calculated in the current study is consistent with aboveground biomass N accrual, with inorganic N (NH_4^+-N and NO_3^--N) supplying approximately 7 kg N ha^{-1} during the 2003 growing season, albeit with large variation. Shallow groundwater contributed approximately 80% of the inorganic N relative to precipitation during this particular growing season. We did not measure N fixation, and its rates reported for northern wetlands are highly variable, ranging from 0.3 to 32 kg N ha^{-1} year^{-1} in bogs and 5–119 kg N ha^{-1} year^{-1} in fens; no comparable results were available for forested histic-mineral soil wetlands (Bowden, 1987). However, it is conceivable that the shallow groundwater and N fixa-

tion provide additional N to vegetation (i.e., Trettin et al., submitted for publication).

The fate of NO_3^- requires further evaluation at this site. For example, NO_3^- uptake by vegetation conserves N in the ecosystem, with the N returned to the forest floor through litterfall, where it is mineralized and again assimilated by vegetation (Vitousek et al., 1982). This internal cycling of N (plant uptake and mineralization) generally exceeds measured N inputs across a variety of wetland types (Bowden, 1987). Assuming denitrification is the dominant N cycling pathway, however, a loss of approximately 3 kg N ha^{-1} from the wetland would occur due to N_2O and N_2 emissions. This would reduce N availability to vegetation by about 40% during this particular year. The 3 kg N ha^{-1} lost through denitrification is on the high end of that reported in palustrine wetlands (0.02–1.1 kg ha^{-1} year^{-1}) in Wisconsin (Goodroad and Keeney, 1984). Therefore, more in-depth studies on denitrification and vegetation uptake of NO_3^- are needed at the current site.

4.1.2.3. Base cations. No differences in base cation concentrations were found in the soil solution or water table between the uncut and harvested/regenerated stands (Table 3). Soil solution and water table base cation concentrations were also similar to those reported for the uncut forest during 1988 and 1989 although, 18 months after treatment installation, base cation concentrations were elevated as much as threefold (Trettin, 1992). Monthly patterns for cations and anions in the soil solution and water table were more variable in the uncut than in the harvested/regenerated forest (Fig. 3).

The input/output balance indicated no net uptake of base cations in this forest. Trettin et al. (submitted for publication), however, reported forest floor accretion rates between 11 and 30 kg Ca ha^{-1} year^{-1} 11 years following harvesting and silvicultural treatments. Either plant roots are taking up Ca^{2+} from deeper than 1 m or, more likely, rapid cycling of Ca^{2+} occurs from the groundwater-to-litterfall-forest floor, where roots are able to capture exchangeable Ca^{2+} as described for N (Dijkstra and Smits, 2002; Dijkstra, 2003). Although the Ca^{2+} input/output calculations were highly variable, rapid Ca^{2+} cycling has been shown in various forests in eastern North America and is reported to be an important mechanism in maintaining exchangeable Ca^{2+} in the forest soils (Dijkstra, 2003; McLaughlin and Phillips, 2006). In future studies, combinations of Ca/Sr (strontium) and Sr/Ba (barium) ratios, Sr (^{87}Sr/^{86}Sr), C (^{13}C/^{12}C-HCO$_3^-$), S (^{34}S/^{32}S-SO$_4^{2-}$), N (^{15}N/^{14}N-NO$_3^-$), and oxygen (^{18}O/^{16}O) stable isotope ratios in foliage, litter, soil, soil solution, and stream water (with consideration for their limitations) may be useful to elucidate controls on base cation cycling in this forested wetland.

4.1.2.4. Sulfate. The large SO_4^{2-} uptake in the harvested/regenerated relative to the uncut stand suggests that significant SO_4^{2-} reduction occurs in the disturbed stand. Other studies in conifer forests have also shown lower SO_4^{2-} output rates in harvested stands relative to uncut reference stands (McLaughlin and Phillips, 2006; Piirainen et al., 2009). Reduced S has multiple fates. For example, sulfide (S_2^-) may bind to H$^+$ forming hydrogen sulfide (H_2S) and either be lost from the soil as H_2S gas (Chapman and Davidson, 2001) or incorporated into soil organic matter (Heitmann and Blodau, 2006), and bind with Fe^{2+} forming iron-sulfide (FeS) (Ito et al., 2005). During incubation of bog peat, 87% of $^{35}SO_4^{2-}$ was incorporated into organic matter, 11% into acid-volatile H_2S, and 2% remained in the soluble pool (Brown and MacQueen, 1985). Moreover, Chapman and Davidson (2001) reported during anaerobic $^{35}SO_4^{2-}$ incubations, ^{35}S was rapidly incorporated into acid-volatile H_2S, elemental S, and chromium (Cr)-reducible S but these pools rapidly recycled. In the longer term, most of the ^{35}S was bound to organic matter. Although our site is not a peatland nor do we have soil S measurements,

the rapidly growing forest floor of the harvested/regenerated stand (Trettin et al., submitted for publication) suggests reduced S incorporation into organic matter may be important at this site. Should this be the case, H_2S bound to organic matter may be subjected to mineralization and oxidization to SO_4^{2-} during drought periods (e.g., Lazerte, 1993; Eimers et al., 2003), thereby serving as only a temporary H^+ sink and shifting to a source during drought periods (McLaughlin and Webster, 2010). Furthermore, H_2S can be incorporated into DOC in wetland ecosystems (Heitmann and Blodau, 2006) and transported to streams and lakes where, if buried in sediments, can be a long-term H^+ sink and alkalinity source (Ito et al., 2005). We also cannot dismiss this possible fate of reduced S because of the high DOC concentration at this site. Dissolved organic C is known to serve as both electron donor and acceptor, which can both oxidize and reduce S (Heitmann and Blodau, 2006). As such, more research is required to identify the fate of reduced S at this site.

4.2. Riparian zone

4.2.1. Soil carbon, nitrogen and base cation pools

The riparian zone had the largest soil C, N, and exchangeable Ca and Mg pools (Table 2), which has also been reported for other forested landscapes (Ashby et al., 1998; Clinton et al., 2010), although riparian soil base cation pool studies are limited. In forested landscapes, riparian zone soil C pools are highly variable, depending on cover type and soil type; the riparian soil C pool values for the current study were within the range of reported values. For example, the total soil C pool was $180 \, t \, C \, ha^{-1}$ for a mixed hardwood riparian zone at Coweeta, South Carolina (Knoepp and Clinton, 2009), 76 and $323 \, t \, C \, ha^{-1}$ for boreal mixedwood and Alnus shrub-dominated riparian zones, respectively, in Ontario (McLaughlin, 2009), and $523–738 \, t \, C \, ha^{-1}$ for riparian fen wetlands in Ontario (Webster and McLaughlin, 2010).

In the current study, the riparian zone also had the highest soil N pool (Table 2). In the literature, highly variable soil N results have been reported. For example, $10 \, t \, N \, ha^{-1}$ was found in the hardwood riparian zone at Coweeta (Knoepp and Clinton, 2009), compared to 4.1 and $20.3 \, t \, N \, ha^{-1}$ for mixedwood forested and Alnus riparian zones in Ontario (McLaughlin, 2009), respectively, and $28.1–33.9 \, t \, N \, ha^{-1}$ for riparian fen wetlands in Ontario (Webster and McLaughlin, 2010). The high riparian zone soil exchangeable Ca and Mg pools were similar to that reported for an Alnus-dominated riparian zone in Ontario (McLaughlin, 2009). Moreover, the high base cation pools in the riparian zone in the current study indicate a high acid-buffering capacity, which means that they likely protect the draining stream from acidification.

4.2.2. Soil solution and water table carbon, nitrogen, and base cations

Dissolved organic C concentrations at 50 cm depth were about one-half those at 25 cm. Dissolved organic C solubility is largely controlled by ionic strength, with concentration decreasing at higher ionic strength of porewater (Clark et al., 2005; Webster and McLaughlin, 2010). At the current site, Ca^{2+} and HCO_3^- from the groundwater were the main factors increasing ionic strength with depth below the soil surface and we suspect this is the result of carbonate mineral dissolution, particularly calcite, at deeper levels (e.g., McLaughlin and Webster, 2010; Webster and McLaughlin, 2010).

The H^+ mass balance in the current study also indicates that base cation exchange/carbonate dissolution was the major consumer of H^+ in the riparian zone. However, other data, such as $^{13}C/^{12}C$ ratios of HCO_3^- (e.g., Nascimento et al., 1997) and Sr ($^{87}Sr/^{86}Sr$) (Poszwa et al., 2004) are required to more effectively isolate carbonate dissolution and cation exchange. For example, McLaughlin and Webster (2010) used $^{13}C/^{12}C$ ratios of HCO_3^- to identify organic matter decomposition as an important contributor to HCO_3^- concentrations in shallow groundwater and calcite dissolution in deep groundwater. In addition, McLaughlin (2009) reported that elevated Ca^{2+} and HCO_3^- fluxes from an Alnus riparian zone compared to those in an adjacent mixedwood forest riparian zone were due to elevated calcite dissolution in the former riparian type. Given the higher Ca^{2+} and HCO_3^- concentrations in the water table compared to soil solution, we suspect similar processes to be occurring at the current study site.

Carbonic acid dissociation was the most important contributor to H^+ production in the riparian zone, and it was in close balance to base cation exchange/calcite dissolution, further indicating the importance of carbonate mineral dissolution in the riparian zone. Moreover, we suspect this significantly contributed to the elevated Ca^{2+} and Mg^{2+} fluxes from the riparian zone, where their export rates were more than twice their inputs. Therefore, the riparian zone at this site provides significant buffering capacity against acidity, similar to results reported by McLaughlin (2009) for the Alnus riparian zone in Ontario.

4.3. Forested wetlands versus upland forest acidity

Forested wetlands situated on subsurface mineral soils function differently than upland forests in terms of acidity and alkalinity production and fluxes. These differences are due to combinations of landscape position (Johnson et al., 2000; Johnston et al., 2001), precipitation amounts and temperature (Shanley et al., 2004; McLaughlin, 2009), and geological material (Ito et al., 2005). Both coniferous and deciduous upland forests situated on granitic bedrock and coarse-textured soils have rapid water infiltration rates and low acidic buffering capacity. These forests are therefore susceptible to base cation depletion from acidic deposition (Bailey et al., 1987; Likens et al., 1998) and forest harvesting (Likens et al., 1970). However, as little as 0.1% carbonate minerals contained in bedrock or surficial deposits can substantially increase soil alkalinity (i.e., HCO_3^-) and buffer H^+ production (Shanley et al., 2004).

Water residence time in forested wetlands is longer than upland soils, resulting in greater water contact time with minerals. Longer water residence time and saturated soils contribute to H^+ uptake and HCO_3^- production through denitrification and SO_4^{2-} reduction processes in soil (Hedin et al., 1998; Cirmo et al., 2000). Furthermore, at the current study site, the carbonate bedrock provides Ca^{2+}, Mg^{2+}, and HCO_3^-. As such, forest harvesting had minimal effects on stream water acidification in this managed forested wetland.

5. Summary and conclusion

No C, N, or base cation depletion occurred due to whole-tree harvesting at this site. In the uncut and harvested/regenerated stands, little net export of base cations occurred and H^+ mass balance indicated net cation exchange was not a significant process in H^+ production or consumption. The most striking differences in the H^+ mass balance were (1) eight times higher H^+ consumption from SO_4^{2-} reduction in the harvested/regenerated stand compared to the uncut condition and (2) nearly twice as much H^+ production due to N immobilization in the harvested/regenerated stand. However, both stand types were net H^+ sinks and no intermediate-term increase in H^+ export due to whole-tree harvesting was evident.

Differences in the uncut and harvested/regenerated stand occurred in DOC sorption, with about 50% less sorption occurring between 25 and 50 cm depths compared to that in the uncut stand. Additional research is required to better define (1) above- and belowground litter inputs and decomposition and (2) DOC

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