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Hydrogeochemistry Studies in the Oil Sands Region to Investigate the Role of Terrain Connectivity in Nitrogen Critical Loads

John J. Gibson [1,2,*], Sandra Jean Birks [1,3], Michael C. Moncur [1], Amy Vallarino [1], Caren Kusel [1] and Mikaela Cherry [1]

1 Department of Geography, University of Victoria, Victoria, BC V8W 3R4, Canada; Jean.Birks@innotechalberta.ca (S.J.B.); mmoncur@gmail.com (M.C.M.); amyvallarino@gmail.com (A.V.); cbkusel@yahoo.ca (C.K.); mikaela.cherry@huskers.unl.edu (M.C.)
2 InnoTech Alberta, 3-4476 Markham Street, Victoria, BC V8Z 7X8, Canada
3 InnoTech Alberta, 3608 33 Street NW, Calgary, AB T2L 2A6, Canada
* Correspondence: jjgibson@uvic.ca

Abstract: Hydrology and geochemistry studies were conducted in the Athabasca Oil Sands region to better understand the water and nitrogen cycles at two selected sites in order to assess the potential for nitrogen transport between adjacent terrain units. A bog—poor fen—upland system was instrumented near Mariana Lakes (ML) (55.899° N, 112.090° W) and a rich fen—upland system was instrumented at JPH (57.122° N, 111.444° W), 100 km south and 45 km north of Fort McMurray, Alberta respectively. LiDAR surveys were initially conducted to delineate the watershed boundaries and topography and to select a range of specific locations for the installation of water table wells and groundwater piezometers. Field work, which included a range of physical measurements as well as water sampling for geochemical and isotopic characterization, was carried out mainly during the thaw seasons of 2011 to 2015. From analysis of the runoff response and nitrogen species abundances we estimate that nitrogen exchange between the wetlands and adjacent terrain units ranged between 2.2 and −3.1 kg/ha/year for rich fens, 0.6 to −1.1 kg/ha/year for poor fens, and between 0.6 and −2.5 kg/ha/year for bogs, predominantly via surface pathways and in the form of dissolved nitrate. A significant storage of dissolved ammonium (and also dissolved organic nitrogen) was found within the pore water of the bog-fen complex at Mariana Lakes, which we attribute to decomposition, although it is likely immobile under current hydrologic conditions, as suggested by tritium distributions. In comparison with the experimental loads of between 5 and 25 kg/ha/year, the potential nitrogen exchange with adjacent terrain units is expected to have only a minor or negligible influence, and is therefore of secondary importance for defining critical loads across the regional landscape. Climate change and development impacts may lead to significant mobilization of nitrogen storages, although more research is required to quantify the potential effects on local ecosystems.

Keywords: boreal wetlands; hydrology; geochemistry; stable isotopes; nitrogen; groundwater; surface water; connectivity

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1. Introduction

Hydrologic connectivity between uplands, fens and bogs, and their role in the transport and fate of nutrients is still a poorly understood aspect of boreal hydrology. Some studies have suggested that the large soil storage capability and transpiration demands on forested uplands results in little water available for runoff resulting in little contribution from upland areas to adjacent wetland networks [1]. However, regional studies have documented significant but variable lateral connectivity between lakes and wetlands [2]. Systematic differences in water chemistry between lakes in wetland-dominated watersheds and those in forested upland-dominated watersheds was attributed to the interaction between lakes and wetlands [3]. A study of the relationship between peatlands and adjacent water bodies has revealed that peatlands are capable of exchanging large amounts of water over short periods of time with adjacent landform units, despite being decoupled from the surrounding catchment during most of the year [4]. Collectively these studies indicate a wide range in the degree of connectivity between uplands, fens and bogs, with indications that the degree of connectivity can have both a large temporal and spatial variability.

In the absence of a good general understanding of the fluxes of water and nutrients between the different ecosystem types and with the knowledge that fluxes of N between adjacent ecosystems could represent a significant yet unaccounted source or sink of N, our research program was designed with the overall goal of characterizing and quantifying the hydrologic linkages and the associated dissolved inorganic N flow within and between targeted ecosystems. The targeted ecosystems were selected for the application of ammonium nitrate amendments to simulate increases in loading from atmospheric deposition related to regional oil sands development. Applications were made to both forested and wetland sites (see [5,6]) with plots treated at rates ranging up to 26.65 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$. In the context of the experiments, the specific task of the isotope hydrology and geochemistry investigations was to characterize the hydrologic connections between discrete terrain units and to identify the potential for nitrogen exchange between them.

Specific research questions included: How does N move between jack pine uplands, bogs and fen ecosystems within the integrated watershed? What is the long-term expected N flux and critical load from the integrated landscape? How do the various ecosystem types process nitrogen under different antecedent moisture conditions? To what extent is nitrogen mobilized during snowmelt and rain events?

2. Study Area and Methodology

2.1. Study Areas

Three ecosystems (minerotrophic fen, ombrotrophic bog and jack pine upland), considered representative of the Athabasca Oil Sands Region (AOSR), were selected for long-term nitrogen addition experiments. Bog and fen experimental plots were situated near Mariana Lakes (ML) (55.899° N, 112.090° W) located 100 km south of Fort McMurray, Alberta. Upland plots were situated at Jack Pine High (JPH) (57.122° N, 111.444° W) located 45 km north of Fort McMurray, Alberta (Figure 1). A selected jack pine upland was investigated adjacent to the wetland at ML, whereas a rich fen was monitored bordering the upland at JPH.

The ML site, which is situated at an elevation close to 700 m.a.s.l., is a 250,000 m^2 peatland complex on the Stony Mountain plateau. Upland sites are dominated by jack pine (*Pinus banksiana*) and wetlands by Sphagnum mosses (*S. angustifolium, S. magellanicum*, and *S. fuscum*). Other vegetation includes: sundews (*Drosera rotundifolia*), laurel (*Kalmia polifolia*), bog rosemary (*Andromeda glaucophylla*), and cranberries (*Vaccinium oxycoccos*). Trees in the bogs are black spruce (*Picea mariana*) and tamarack (*Larix laricina*). The wetland complex includes ombrotrophic bog and minerotrophic wet or dry, poor fen areas; the delineation of specific terrain units was based on surface vegetation and surface water chemistry indicators [7]. Glacial till (sandy outwash with some clay) is 30 to 180 m deep in the area [8] and underlain by sandstones and shales. The anisotropy of the peat and variability of the hydraulic conductivity (K_h) reflects the complexity and heterogeneity of the peatland profile. Peatland K_h ranged from 10^{-6} $m \cdot s^{-1}$ to 10^{-9} $m \cdot s^{-1}$ [9] and generally decreased rapidly with depth. Further details on regional hydrogeologic settings are provided elsewhere [9–11].

JPH, at an elevation of approximately 330 m.a.s.l., is a rich fen adjacent to a jack pine upland and situated within the Muskeg River watershed which drains into the Athabasca River. This site is approximately 700,000 m^2, and is dominated by nutrient-poor sandy soils at the surface. There is a uniform stand of jack pine (*Pinus banksiana*) trees and the forest floor vegetation is comprised of lichen (*C. mitis, C. rangiferina*, and *C. stellaris*), labrador tea

(*Rhododendron groenlandicum*), and blueberry (*Vaccinium corymbosum*). A rich minerotrophic fen runs north through the western side of the site and vegetation includes alders (*Alnus crispa*), paper birch (*Betula papyrifera*), and sedge species (*Carex*). The substrate is well-drained and of glacio-fluvial origin with average hydraulic conductivity ranging from 10^{-5} m·s^{-1} to 10^{-6} m·s^{-1} at upland and rich fen sites, respectively [12]. Soil water typically percolated vertically to the water table, situated at 1 to 1.5 m-depth and then saturated flow was directed horizontally and dependent on topography, which diverted a portion of the water to the adjacent fen.

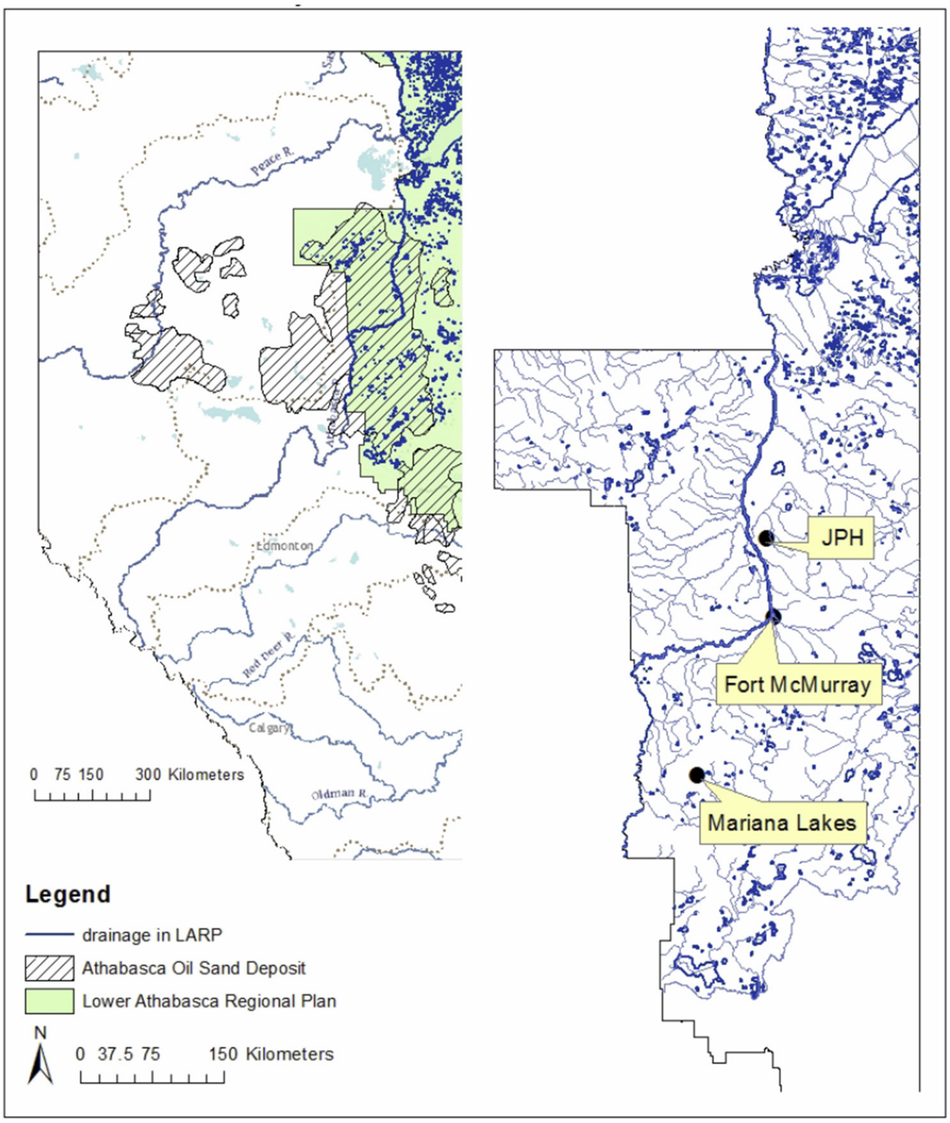


Figure 1. Map of Alberta, Canada (inset) showing location of JPH and Mariana Lakes study sites.

2.2. Climate

Based on weather station monitoring from 2011 to 2015, we conclude that both areas have climatic conditions fairly similar to that of nearby Fort McMurray. The mean temperature for Fort McMurray ranges from −17.4 °C in January to 17.1 °C in July, and average annual precipitation is 419 mm, of which 316 mm is summer rainfall [13]. For the years of study, positive temperature departures are noted for 2011, 2012 and 2015 compared to the 1981–2010 climate normals, whereas negative departures are noted for 2013 and 2014. Positive precipitation departures are likewise noted only for 2012, with other study years ranging from 66 to 92% of normal (Table 1). Contrasting hydrological regimes were therefore observed early in the study, particularly in 2011 and 2012. Evapotranspiration commonly exceeded precipitation during the thaw season in all years, with evapotranspiration rates ranging from 2.4 to 3.2 mm·d^{-1} for bog and 2.2 to 3.6 mm·d^{-1} for fens based on meteorological measurements at the Mariana Lakes site.

Table 1. Temperature and precipitation recorded during the study compared to climate normals.

Time Period	Hydrological Regime	Mean Temperature	Temperature Anomaly	Precipitation (mm)	Precipitation % Normal
Climate Normal (1981–2010)		1.0		418.6	
2011	Dry, warm	1.5	0.5	281.6	0.67
2012	Wet, warm	1.6	0.6	425.9	1.02
2013	Dry, cool	0.77	–0.23	368.4	0.88
2014	Dry, cool	–0.02	–1.02	384.3	0.92
2015	Dry, warm	2.3	1.3	274.6	0.66

The climate in the region supports the existence and development of extensive peatlands. The hydrologic connectivity between landscape units, and thus movement of matter and the fate of N, is sensitive to the occurrence and persistence of wet periods [14], peatland depth, the underlying substrate, and the catchment area boundaries that may change depending on the hydrologic regime [1].

2.3. Experimental Design

Our approach was to quantify the hydrological connectivity in terms of both water and nutrient fluxes, using a combination of physical hydrological monitoring, biogeochemical and stable- and radio-isotope investigations. The approach included the installation of groundwater and surface water monitoring equipment, water sampling for inorganic and organic geochemistry, and isotopic analysis of water and nutrients. Early investigations focused on establishing the baseline conditions, including hydrology and geochemical setting of the two research sites, and on making preliminary assessments of water balance and surface and groundwater flow paths. Subsequent years extended these observations, but activities were augmented to include additional isotopic and geochemical tracers, including nitrogen-15 measurements to investigate the origin and fate of natural sources of nitrogen, and tritium to investigate the rates of flushing of the ML wetland. Contingencies were also made to sample and isotopically identify non-natural sources of nitrogen in the event that amendment nitrogen was found to migrate significantly off of the plots, which did not occur.

2.3.1. Instrumentation

LiDAR surveys were flown on 22 June 2011 for ML and 23 June 2011 for JPH by DigitalWorld Mapping Inc., Calgary, AB, Canada, and were used to create a Digital Elevation Model (DEM) for both sites with a horizontal resolution of 1 m^2 and a vertical resolution of $\pm$0.05 m to provide detailed information about the surface elevations to assess surface flow directions. Piezometer nests were installed in transects to traverse the different ecosystems present at each site to provide information about the vertical and horizontal hydraulic gradients between the different ecosystems. Some sampling locations were also situated nearby the experimental nitrogen addition plots without causing interference. The monitoring well network at ML consisted of 19 piezometer nests (2 or 3 wells per nest at depths of approximately 1.5 m, 3–4 m and 6–8 m) and 18 water table wells (Figure 2A). At JPH, the network consisted of 11 piezometer nests (3 wells per nest at depths of approximately 1.5 m, 3 m and 6.5 m) and 7 water table wells (Figure 2B). Piezometers, PVC or iron pipe threaded into a screened stainless steel Solinist^{TM} drivepoint (model 615), were installed into the substrate using a Pionjar^{TM} percussion hammer or driven into the peat manually (using an auger if necessary). Polyethylene tubing ran the length of the well into the drivepoint intake, and for water table wells, the PVC pipe length was slotted and covered with a Nitex mesh to screen out coarse material. The water table wells were held in place by a length of rebar driven to depth. The vertical displacement of wells was monitored relative to the deepest piezometer, and wooden platforms were installed on peat to minimize compression disturbance by field technicians during site visits. A GPR survey was also conducted in 2014/15 to improve understanding of the peat depth and stratigraphy of the wetland at ML, which confirmed peat depths averaged 8 to 12 m at its deepest point.

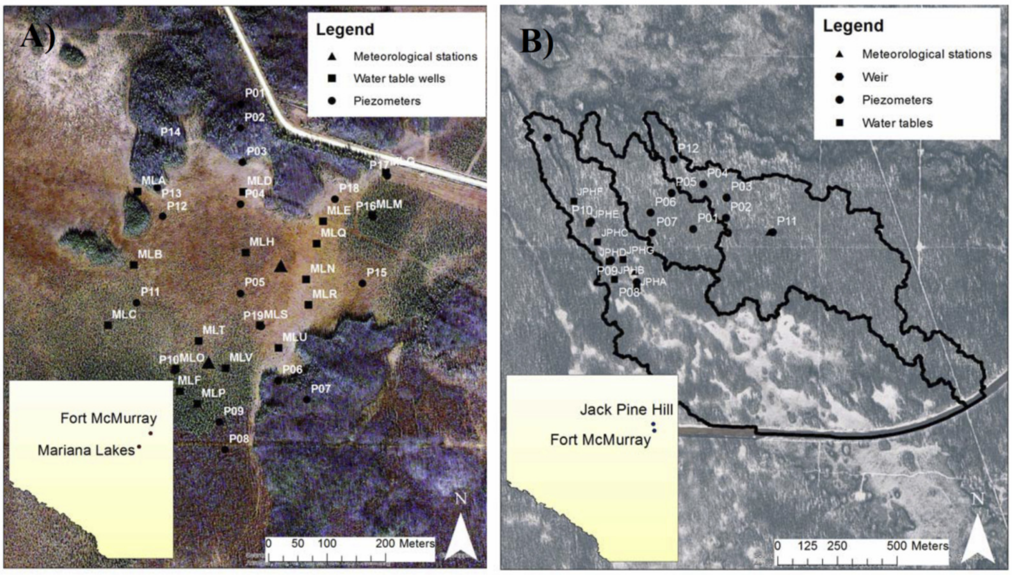


Figure 2. Location of instrumentation installed at (**A**) ML and (**B**) JPH. Note the scale differences in (**A**,**B**). Colours at ML depict uplands (purple), bogs (green), and fens (brown). Outlines at JPH depict delineated drainage areas including the rich fen (unit located to the southwest) and upland terrain units.

The depth to a static water level in a piezometer can be used to calculate the hydraulic head elevation at the depth of the intake. Where hydraulic head measurements are available for different depths at a given location the vertical hydraulic gradient and direction of vertical flow can be determined. The horizontal distribution of hydraulic head measurements can then be used to determine the horizontal direction of groundwater flow. The elevations of each of these wells were surveyed in, and water level measurements were made periodically throughout the 2011 to 2015 field seasons. Falling and rising head permeability tests were also conducted on selected piezometers so that estimates of hydraulic conductivity could be determined. A network of shallow water table wells (1 m deep) were installed across the wetlands at both sites and instrumented with pressure transducers to provide continuous measurements of the water table elevations. Each of these water table wells was anchored to lengths of pipe drilled into the mineral soil to account for potential fluctuations of the peat surface. As shallow water table wells are best suited for wetland monitoring, where the water table is close to the surface, we installed more of these devices at the ML site where the proportion of wetland area was greatest. Slug or bail tests (following [15,16]) were conducted during two campaigns at a subset of wells to determine the hydraulic conductivity values at different depths for each landscape unit [9].

Meteorological stations were installed at a bog and fen location at the ML site. Since a TEEM meteorological station was already located at JPH, an additional station was not installed in 2011. Two meteorological stations were installed at JPH in 2012—at an upland and a fen site. The meteorological data collected includes air/water/soil temperatures, relative humidity, precipitation, wind direction, net radiation and other meteorological parameters necessary to estimate evapotranspiration by the Priestley-Taylor method and to perform vertical water budget calculations (i.e., runoff potential) by the method described in [17]. Precipitation collectors for isotopic analyses were installed during the 2011 and 2012 seasons to characterize the geochemistry and isotopic composition of the precipitation.

Weirs were installed to gauge the discharge in outflow streams at JPH and ML, the latter which only became channelized significantly downstream of the monitored wetland near the culvert under Highway 63. Unfortunately, beaver activity at JPH and high runoff at ML rendered both installations inoperative during the majority of the study.

2.3.2. Water Sampling and Analysis

Water samples were collected from all piezometers and water table wells after flushing using a peristaltic pump. Grab samples were also collected from streams, precipitation collectors, depression storage, and snowmelt. Sampling campaigns were undertaken in June and August 2011, May, July/August, and September 2012, June 2013, June and September 2014, and July 2015. The timing of field work was often dependent on weather and/or logistical constraints, but our strategy was effective overall in obtaining samples at a range of antecedent moisture conditions throughout the thaw season and to a lesser extent during the melt period. A flow-through cell was used to minimize contact with the atmosphere during field measurement of pH, temperature, electrical conductivity and Eh (redox potential) using a portable hand-held meter (Thermo Scientific Orion Star^{TM}, Waltham, MA, USA). The alkalinity was determined by digital titration after filtration within a day of sample collection at the field camp. Field measurements of some major ions were determined by colorimetry after filtration including nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+). Samples were also collected for oxygen-18, deuterium and tritium in water ($\delta^{18}O_{H20}$, δ^2H_{H2O}, $^3H_{H20}$, respectively), carbon-13 in dissolved inorganic carbon and particulate matter ($\delta^{13}C_{DIC}$, $^{13}C_{PM}$, respectively) and nitrogen-15 in nitrate ($^{15}N_{N03}$) analyses. Samples for major and minor analyses were inline or vacuum-filtered (2011 only) at 0.45 um within 48 h. Inline filtration reduced sampling handling and allowed samples to be split at the time of sampling. Samples for ^{15}N analyses were frozen in the field. All other samples were stored in tightly sealed HDPE bottles that were filled to minimize headspace and stored at 4 °C. Samples for cation analyses were acidified with 16 M of nitric acid, and samples for DOC were kept in opaque vials.

The geochemical analysis of nutrients and dissolved organic carbon (DOC) was conducted by InnoTech Alberta, Vegreville (segmented flow analysis—acid digestion then persulfate UV digestion, followed by color loss measurement) and other geochemical analyses were conducted by Earth and Environmental Sciences, University of Waterloo (on ICP-MS X or ICP-OES iCAP 6500 and IC-OH or IC-CO3 systems respectively). Stable isotopes were analyzed at InnoTech, Victoria (on Delta V Advantage dual inlet), with results reported in delta (δ) notation and expressed in per mil (‰) relative to international standards: Vienna Standard Mean Ocean Water (VSMOW) for water isotopes and Vienna Pee Dee Belemnite (VPDB) for carbon isotopes. Field sampling and laboratory analysis methods were consistent with those used in other regional investigations [9,18]. Duplicate samples and field blanks were routinely submitted to other laboratories to assess accuracy and reliability. Conductivity data were corrected for pH as described by Sjors [19], to account for the conductivity contributed by the presence of hydrogen ions. Charge balance errors (following [20]) were found to increase from near zero for waters in contact with mineral soils to as much as 95% for very dilute or organic-rich, peat porewaters. Average errors were less than 25%. A propensity for an ion deficit is attributed to the negative charge carried by organic matter, which is an unknown entity in the charge balance calculation (for example, [21]).

2.3.3. Amendment Experiments

Amendment experiments were performed on fen and bog plots situated at the ML wetland and on upland jack pine forest plots situated at JPH. Detailed protocols are described by [5] and Watmough et al. [6], respectively. At ML, 1 m^2 plots were treated with an ammonium nitrate solution at the rates of 0, 5, 10, 15, 20, and 25 kg $N{\cdot}ha^{-1}{\cdot}yr^{-1}$, each with three replicates. Tap water used to prepare the solutions for both sites was found to contain an additional 1.13 kg of $N{\cdot}ha^{-1}{\cdot}yr^{-1}$. Bulk atmospheric deposition of ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic N (DON) was also monitored during the experiment using resin samplers, and was found to be 1.65 kg of N/ha/year (R.K. Wieder, pers. Comm.). Control plots without solution were also maintained. Monitoring of the peat porewater was carried out 24 h after each of 5 to 8 nitrogen additions per season using peepers located at 5 depths ranging from surface to 1 m depth. Decomposition, mineralization, growth response of sphagnum (i.e., *Sphagnum* NPP, *Sphagnum* N, capitula response), and growth response of vascular plants (vascular NPP, vascular N) were also monitored to characterize potential vegetation effects. The main results of the addition of nitrogen are that (i) *Sphagnum fuscum* capitula are becoming smaller, which allows excess N inputs to move to the rooting zone where they are more available to vascular plants; (ii) the growth of vascular plants is being stimulated; and (iii) vascular plant litter decomposes at a much higher rate which will affect the overall rate of ecosystem decomposition as plant composition shifts to more vascular plants [5].

Similar applications were made to the upland plots at JPH, although the presence of a sparse tree canopy and understory necessitated the use of larger plots (20 m × 80 m) and required the use of a helicopter for the application of the ammonium nitrate solution. The experiment included additions of 5, 10, 15, 20, and 25 kg of $N{\cdot}ha^{-1}{\cdot}yr^{-1}$, with one control plot. A water control was not used. All plots included three 10 m^2 destructive sampling subplots, three 10 m^2 non-destructive tree monitoring subplots, and thirty 1 m^2 non-destructive vegetation monitoring subplots. Sampling included a zero-tension lysimeter for soil water, throughflow collectors, stem-flow collectors, nitrogen mineralization bags and litter-fall collectors. The jack pine experiments reveal that roughly two-thirds of N applied above the canopy reaches the ground following application, with the majority of N entering biotic tissues (non-vascular and vascular plants). There is also evidence of N transformations occurring in the canopy, whereby organic N is increased in throughfall at higher application rates and ammonium is preferentially retained in the canopy over nitrate. Nitrate concentrations in water leaving the rooting zone were found to be low and there was no significant difference among treatments apart from slightly more leaching. No change was observed in soil pH or other measured analytes suggesting that soil acidification is not occurring [6].

3. Results and Discussion

3.1. Physical Hydrology

Surface and subsurface flow pathways were mapped at both sites based on LiDAR elevations, water table elevations, and piezometric head data. Spatial flow patterns were constructed from hydraulic heads at different times of the year for both JPH and ML (Figure 3). For JPH, similar trends were seen in shallow, intermediate and deep piezometers, and suggest flow generally towards the northwest or west, depending on the season and antecedent moisture conditions. Major drainage controls include incised channels infilled with rich fen vegetation, evident as dark strands trending to the northwest in Figure 3. For ML, seasonal trends in the flow pattern are also evident. After the spring melt period, shallow groundwater flows from uplands into the peatland complex and feeds the interior of the fen, which then flows toward the northeast. Complex flow patterns with seasonal reversals of flow towards the southwest are also noted for some late summer intervals when hydraulic gradients are reduced and the uplands are poorly connected.

However, water still continues to flow towards the northeast to the natural basin outlet; however, this exit is largely blocked due to the AltaGas road, which results in significant ponding of water in the roadside culvert.

Overall, the flow mapping was used to better understand where potential down gradient impacts from nitrogen additions might occur. As noted previously, no nitrogen amendment N is believed to have migrated from the plots to influence the natural background chemistry as monitored at either site.

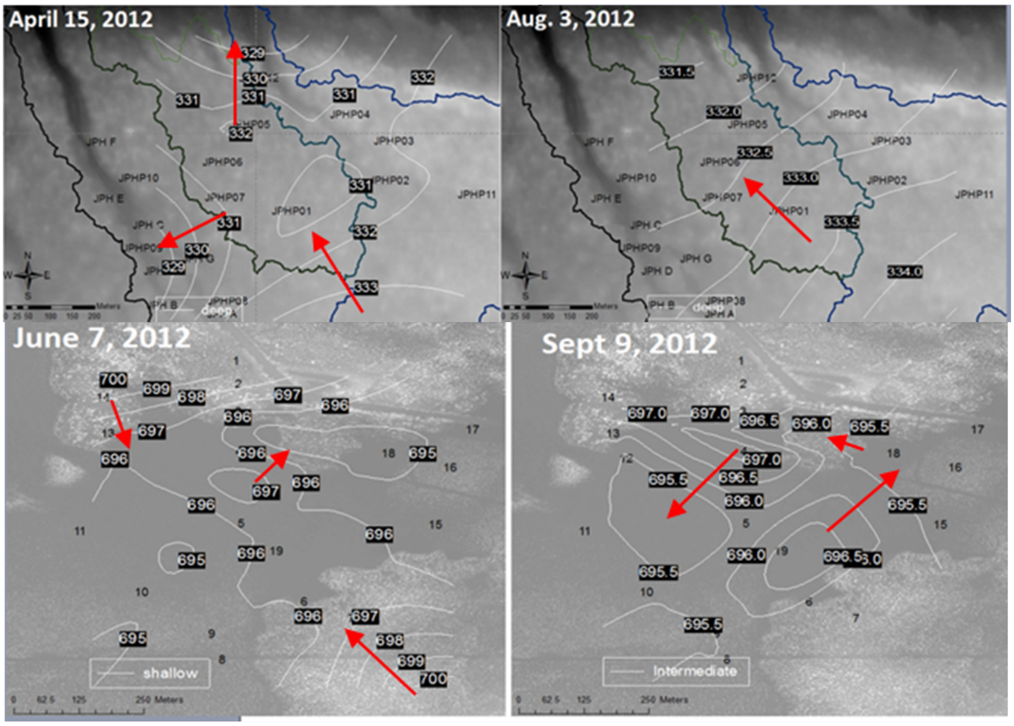


Figure 3. Maps showing hydraulic head elevations and inferred flow directions: for JPH (**top left**) April 2012, (**top right**) August 2012; and, for ML (**bottom left**) une 2012, and (**bottom right**) September 2012.

Due to the inability to effectively gauge runoff using weirs, a vertical water balance approach as developed by Tattrie [14] was used. The method relies on daily total measurements of precipitation, evaporation, change in storage, and estimates of peat porosity to predict the amount of potential runoff over time. Note that depression storage is accounted for by subtracting a 15 mm threshold, which was determined based on the depression storage capacity for wetland terrain in the area. This method allowed the temporal tracking of runoff. As shown in Figure 4, more frequent and stronger runoff events occurred in a relatively wet year, 2012, as compared to a relatively dry year, 2011 (Figure 4). At ML, on average, bogs were found to have more variable water levels than poor (wet or dry) fens. The rich fen (JPH) was subjected to higher fluctuations in water levels due to antecedent moisture conditions and/or beaver activity. The role of antecedent moisture in controlling water level fluctuations and in determining runoff was discussed in more detail by Vallarino [12].

Runoff potential for the study years was found to range from -380 to 271 mm·yr^{-1} for rich fen, -266 to 60 mm·yr^{-1} for bog, -213 to 60 mm·yr^{-1} for wet fen, and -197 to 67 mm·yr^{-1} for dry fen. Higher values were observed for wet years such as 2012, whereas lower values were found for dry years (2011, 2013 to 2015).

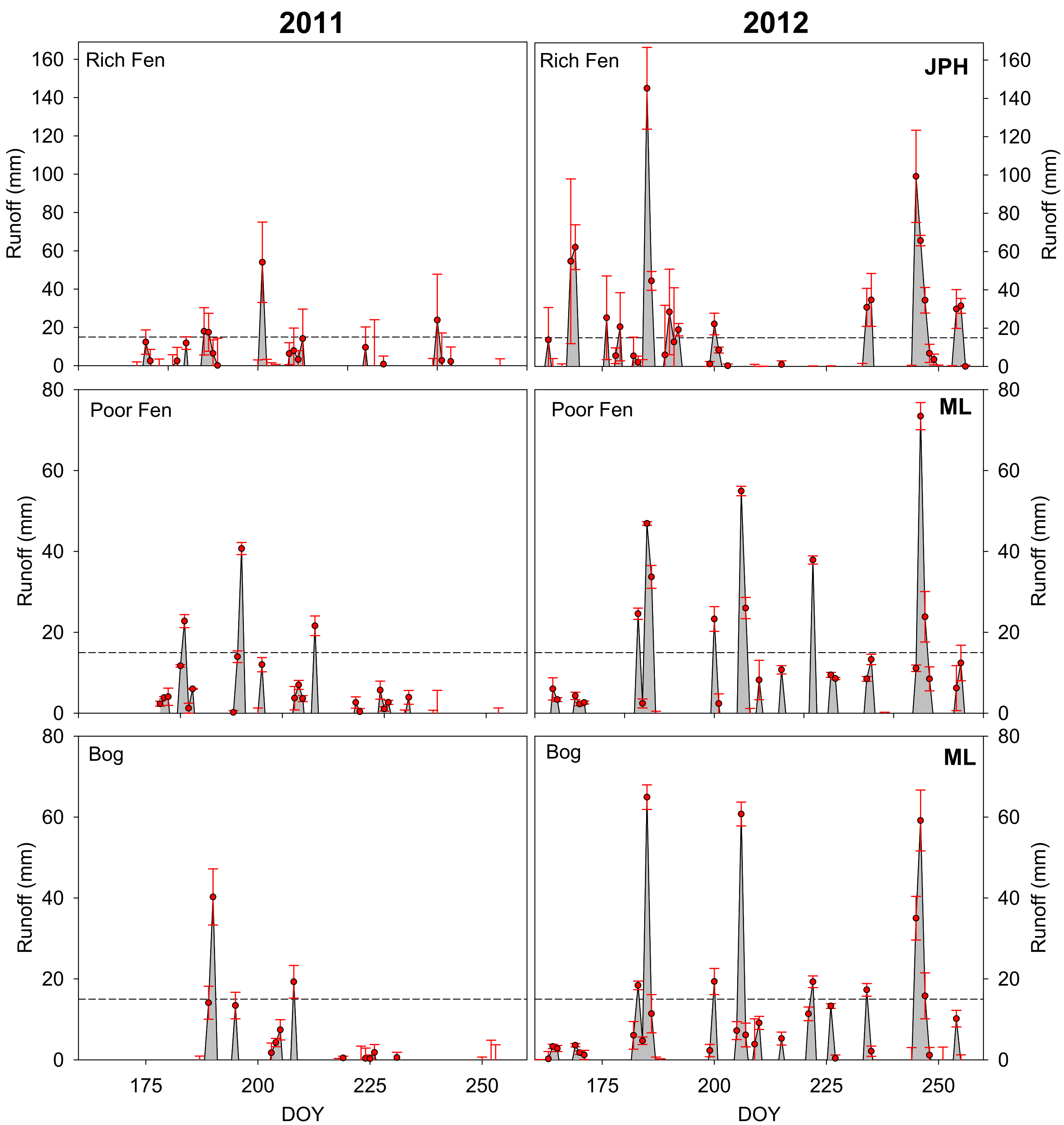


Figure 4. Time series of 2011 and 2012 runoff potential as estimated by vertical water balance for selected terrain units at ML and JPH sites. Red points denote individual daily values, error bars show 1 standard deviation of uncertainty. Dashed lines indicate detention storage capacity thresholds estimated from LiDAR surveys.

3.2. Stable Isotopes

The stable isotope composition of surface water, groundwater, and precipitation was measured at JPH and ML as a method for gaining better understanding of the water cycle at the sites including the connectivity of various terrain units. A total of 792 samples were analyzed for oxygen-18 and deuterium. In general, the isotopic composition of waters was found to be useful in labelling the origin and mixing of various waters, for determining the influence of evaporative enrichment, and for assessing upward, downward, or lateral hydraulic gradients. The isotopic composition of snow and rain were found to plot close to the global meteoric water line (GMWL; Figure 5a) with rain being enriched relative to snow. Similar patterns have been described previously in the region [2,22]. The isotopic composition of wetlands and uplands were found to plot below the GMWL, along linear trends that reveal differential influences of evaporation. Graphs showing a collection of individual isotopic data sorted by terrain type are provided in Figure S1. Average $\delta^{18}O$ and $\delta^{2}H$ measured in porewater for different terrain units at discrete depth-intervals is provided in Figure 5b,c. Depth-wise variations in $\delta^{18}O$ for individual water samples in various terrain types are shown in Figure 6. In general, depth-wise variations show wider variations in the water table and near-surface piezometers due to seasonal variations in the isotopic composition of precipitation (rain versus snow). Deeper layers in the soil are more uniform due to longer residence times and mixing and consequently are more reflective of long-term inputs. In general, downward gradients are inferred where isotopic gradients are positive (i.e., enriching with depth), whereas upward flow is inferred where isotopic gradients are negative (i.e., depleting with depth). Stagnant or lateral flow is inferred where gradients are neutral. Due to the very low hydraulic conductivity of peat it is possible that deeper layers may also inherit signals from recharge under different climatic conditions. The following specific observations are noted for the various terrain units:

- Bogs have negative or neutral isotopic profiles suggesting upward gradients (possibly driven by evaporation) or stagnancy;
- Dry fens have neutral isotopic profiles suggesting weaker flow dynamics or stagnancy;
- Wet fens have positive isotopic profiles suggesting downward gradients;
- Fen edge sites (not shown) have a negative isotopic profile suggesting upward gradients;
- Rich fens have negative isotopic profiles suggesting upward gradients;
- Uplands have positive isotopic profiles suggesting downward gradients.

$\delta^{18}O$ versus $\delta^{2}H$ plots (Figure 5), showing average values for different terrain units/depths, confirm that ML waters plot along a local evaporation line with a slope close to 6.0, suggesting that evaporation loss is a major driver of enrichment. While JPH waters are offset below the GMWL and therefore record some evaporative losses, isotopic variations at the site occur predominantly along a trend subparallel to the GMWL, indicating higher rates of vertical flushing. At both sites, depth-wise trends for uplands (2) and wet fen are shown to be enriching with depth (i.e., downward gradients), whereas rich fen becomes more depleted with depth (i.e., upward gradient). Dry fen is found to be varying only slightly, whereas bog is depleting from surface to intermediate levels and then is enriching, suggesting more complex behaviour.

Hydrologic connections (groundwater flow) between adjacent upland and rich fen at JPH are consistent with observed hydraulic and isotopic gradients, and isotopic signature of deep piezometers in the rich fen are consistent with intermediate to deep sources from the upland.

Hydrologic connections (groundwater flow) from adjacent uplands to the fen edge at Mariana Lakes are consistent with observed hydraulic and isotopic gradients, and isotopic signature of the fen edge is consistent with intermediate sources from the upland. Based on the similarity in isotopic signature, hydrologic interaction between bogs and dry fens appears to occur near surface, but at intermediate to deeper levels shifts in isotopic composition may suggest that dry fens also interact with upland-type waters.

It is apparent from examining the isotopic data that the hydrologic differences in the bog—dry fen—wet fen continuum are preserved in the porewater isotopic signatures (Figure 5).

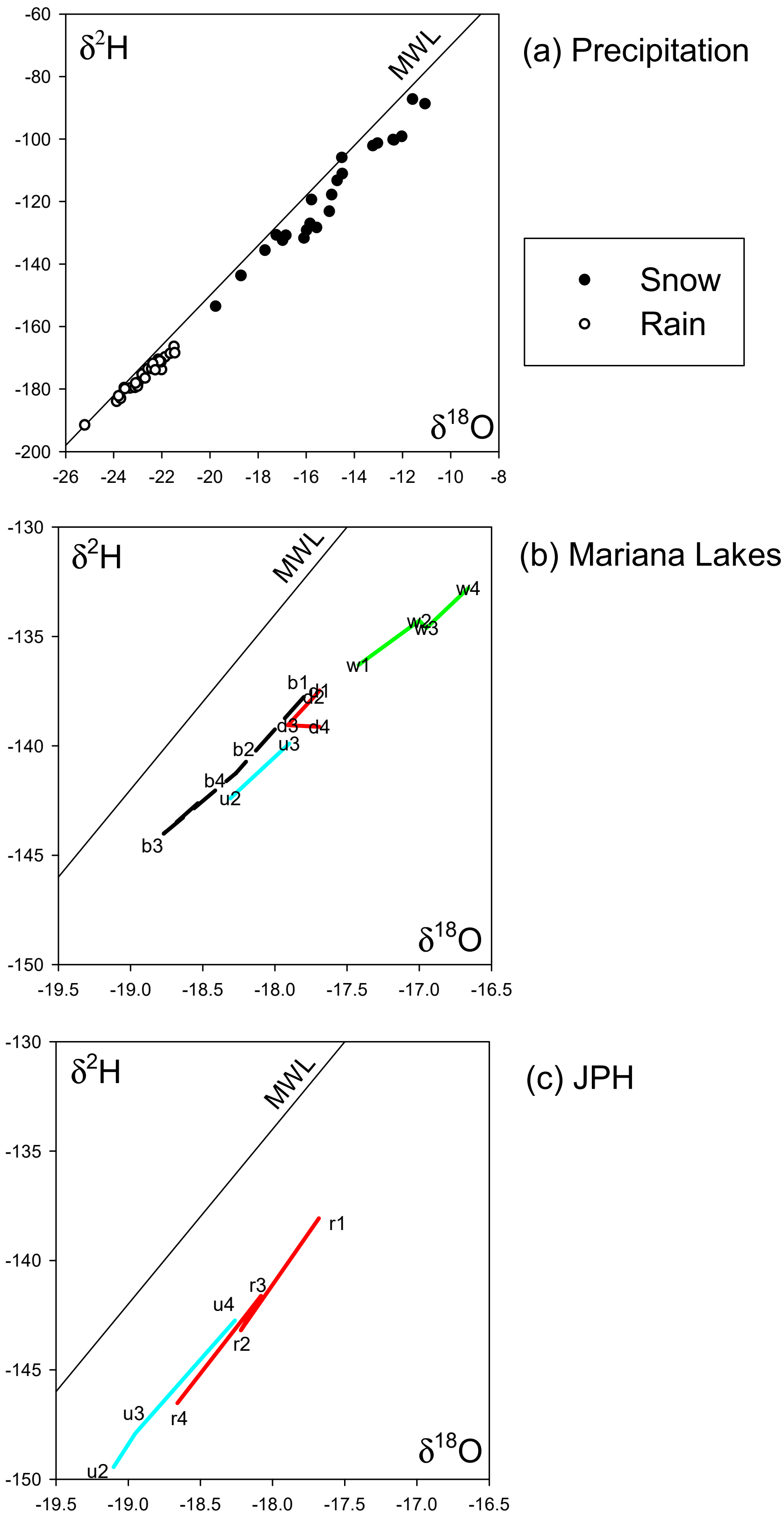


Figure 5. Isotopic composition of (**a**) precipitation (snow and rain), and average isotopic composition of water table wells, and shallow to deep piezometers (**b**) Mariana Lakes, and (**c**) Jack Pine High. Note that b—bog, d—dry fen, w—wet fen, r—rich fen, u—upland; 1—water table, 2—shallow piezometers, 3—intermediate piezometers, 4—deep piezometers.

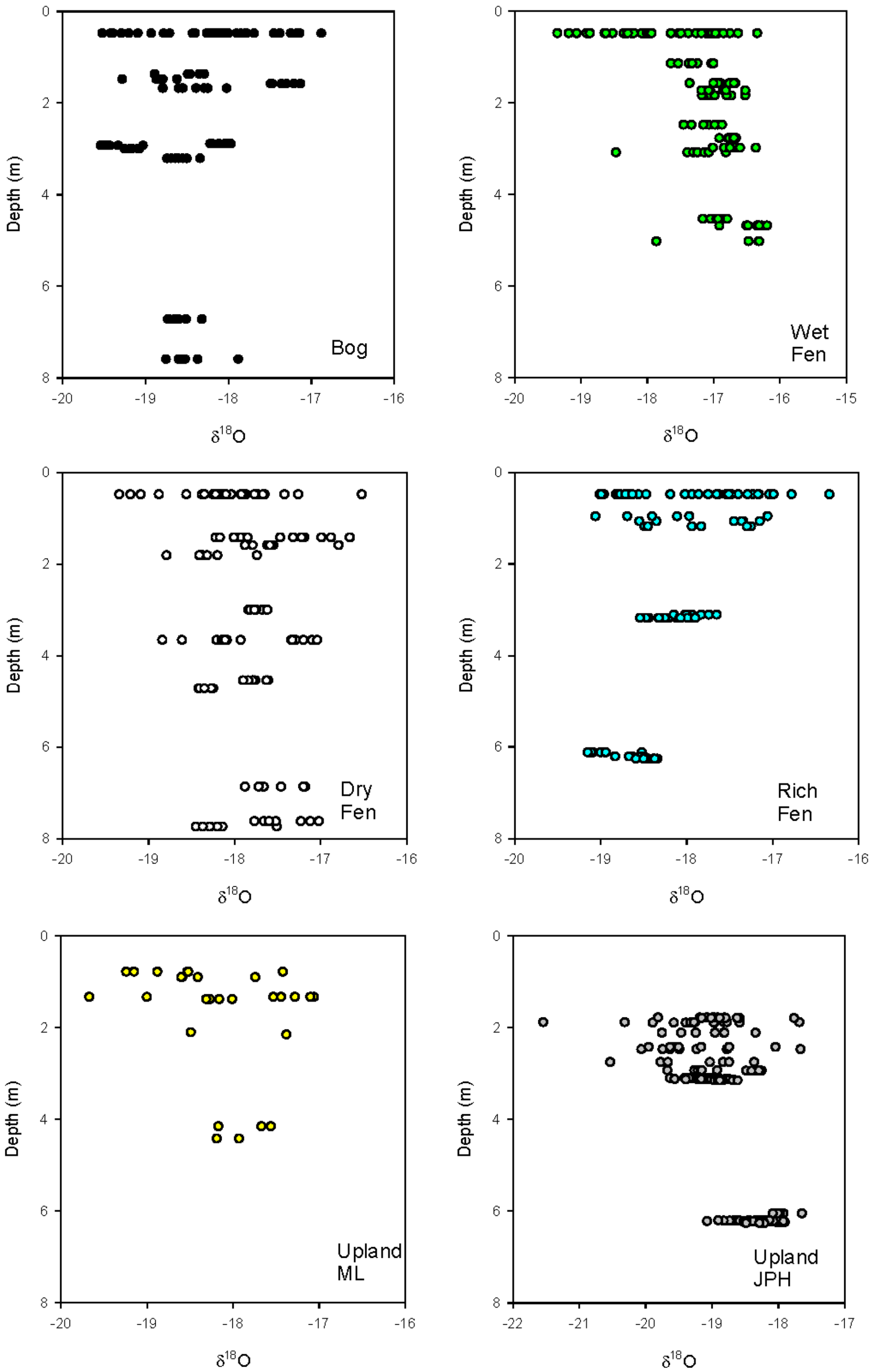
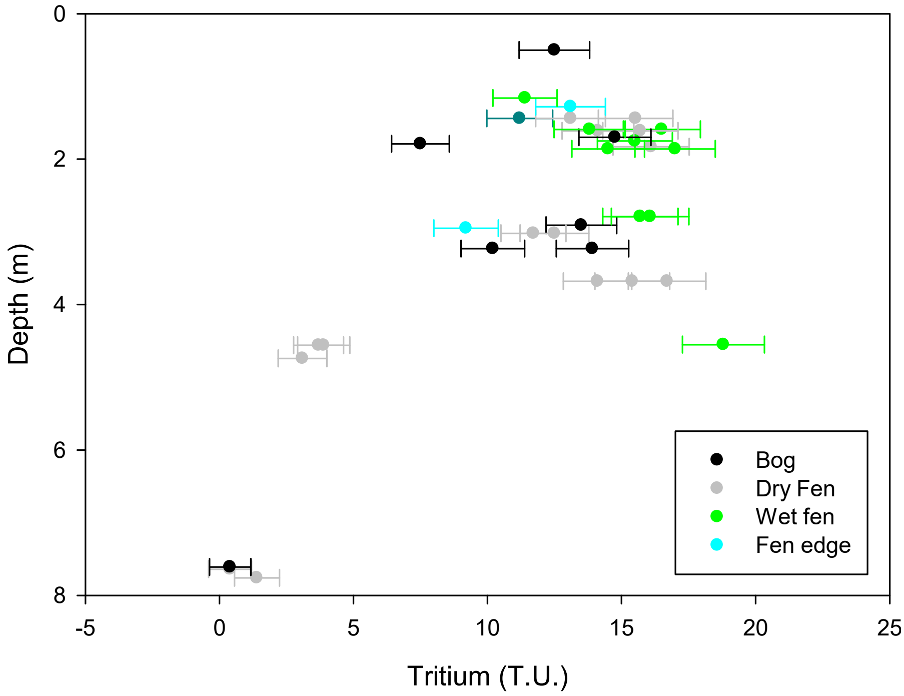
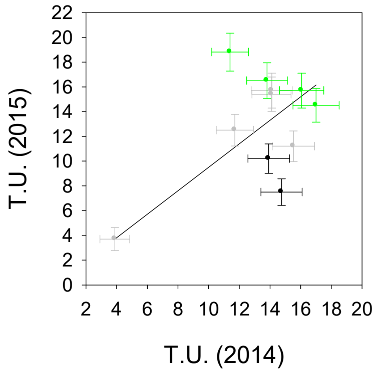


Figure 6. Depth-wise variations in $\delta^{18}O$ in various terrain units: bog, wet fen, and dry fen (ML), rich fen (JPH), upland (ML), and upland (JPH). Seasonal variability is shown to be greater for near-surface soil water. Note that 10 highly-enriched water table well samples that were evidently sourced by brief summer precipitation events were not included.

3.3. Tritium

Tritium concentrations were measured on water samples collected from piezometers and a water table well situated at the ML wetland to gain insight into the penetration depth of modern (post-1950s) precipitation containing tritium. Tritium was introduced into the atmosphere and precipitation by atmospheric thermonuclear weapons testing and has been used previously to assess hydrologic time-scales in wetlands [23]. Fifteen samples were collected from the ML wetlands in October 2014 and 19 samples were collected in July 2015. This wetland was targeted rather than the JPH wetland to test the hypothesis that a stagnant pool of porewater exists in areas of deep peat development. Results were also compared to a survey of 24 lakes and 133 groundwaters from the oil sands region [24]. Tritium was found to range from zero to 18.8 T.U. (Figure 7), with high values (>8 T.U.) occurring in the upper zone (<4.5 m) and lowest values (<4 T.U.) occurring in the lower zone (4.5 to 8 m). Systematic differences were also found for different terrain units: Tritium in the wet fens was generally elevated and showed a continuously increasing trend with a depth to 4.5 m, whereas dry fens and bogs tended to have slightly lower levels of tritium in the upper zone and rapidly transitioned to very low to negligible levels of tritium at an approximately 4-m depth. Peak tritium levels were found at approximately 2 m in bog, 3.7 m in dry fens, and 4.5 m in wet fens. Note that fens and bogs, including wet fens, had low porewater content and it was therefore difficult to obtain enough sample for a tritium analysis (0.5 L) in most cases below a 4.5 m-depth.





Terrain unit	No. Obs.	mean ^{3}H (T.U.)	Error (T.U.)
Dry fen	7	10.40	1.19
Bog	16	10.54	1.19
Fen edge	2	11.15	1.25
Wet fen	9	15.48	1.40

Figure 7. Tritium variations with depth at ML for various terrain units. Inset shows comparison of tritium measured in 2015 versus 2014. Averages for each terrain unit are tabulated and presented in order of increasing rates of turnover or hydrologic intensity.

Repeat samples were also collected for some piezometers that were more productive (see Figure 7 inset). A relationship close to 1:1 is noted; however, more variability was noted for samples with higher tritium. This is not considered to be primarily an analytical artifact but rather due to more variable tritium concentration in shallower wells, notably in the wet fen, due to more rapid exchange and mixing near surface. The results suggest that in general modern (post-1950s) precipitation has not penetrated below a 4 m depth in dry fens and bogs. For wet fens, the continuous increase in tritium between surface and a 4.5 m depth may indicate deeper penetration. Corresponding vertical rates of infiltration in the various terrain units, based on peak tritium depth, are estimated at 33, 62 and >75 mm/year, respectively, for bog, dry fen and wet fen. This corresponds to hydraulic conductivities of 1.05×10^{-9} m·s^{-1}, 1.97×10^{-9} m·s^{-1} and 2.38×10^{-9} m·s^{-1}, respectively. These are consistent with the lower ranges of hydraulic conductivities determined from bail and slug tests on piezometers at the site. Based on these rates of vertical movement in bog and dry fen, we expect that the zero tritium samples from an 8-m depth may be on the order of 1290 to 2400 years B.P. As for the application experiments, we expect that the infiltration of experimental N applied to the surface of the peatland over a 5-year period is therefore expected to have potentially penetrated only a fraction of a metre at most. Tritium results confirm that there is a relatively immobile porewater reservoir at depth in bog and dry fen, whereas wet fens may have greater rates of infiltration, an assertion that is also supported by the stable isotope gradients (i.e., enrichment) with depth. Similar to Gorham and Hofstetter [23], we interpret the tritium distribution as an indicator that precipitation falling on the peatland moves close to the surface (within the top 1.5 m) through lateral flow, while the deeper part of the peat has a relatively stagnant mass of water.

3.4. Hydrogeochemistry

The average pH of groundwater increased with depth and along the bog—poor fen—rich fen gradient (Table S2). At the near surface (WT depth), the average pH of samples was 4.28 for bog, 4.43 for poor fen (dry), 4.45 for poor fen (wet), and 5.81 for rich fen. In the deepest piezometers, bog, dry fen, wet fen, and rich fen water samples were near neutral (7.05, 7.94, 6.65 and 6.92 respectively), and slightly basic near the fen edge (8.75). In upland landscape units the average pH of groundwater also increased with depth, from 7.06 to 10.75 at ML and from 5.96 to 6.19 at JPH.

Eh was typically positive near surface in the fens, indicating oxidizing conditions, and approached more negative values with depth, indicating more reducing conditions. Bogs tended to be less reducing overall than fens, and uplands displayed more variable conditions: reducing at depth at JPH and oxidizing at depth at ML.

The average conductivity of wetland water samples at ML (Table S2) increased with depth, from 29 to 576 μS·cm^{-1} for bog, from 26 to 2025 μS·cm^{-1} for dry fen, and 23 to 421 μS·cm^{-1} for wet fen. Note that the deepest wetland piezometers may be in contact with mineral substrates. Conductivity representative of the bottom of the peat is more likely in the range of 93 to 199 μS·cm^{-1}, as noted for medium depth piezometers. The average conductivity of near surface wetland samples was higher for the rich fen at JPH fen (74 μS·cm^{-1}) than poor fen or bog and increased with depth (to 203 μS·cm^{-1}). Conductivity for uplands at JPH ranged from 41 μS·cm^{-1} at surface to 93 μS·cm^{-1} at depth. Although gradients were not measured at ML uplands, conductivity for the near-surface piezometers averaged 176 μS·cm^{-1}.

Both the alkalinity and dissolved inorganic carbon (DIC) showed systematic increases from surface to depth across the bog to rich fen continuum, and as anticipated, were highly correlated. DIC was found to range from 114 to 872 mg·L^{-1} for bog, 146 to 1059 mg·L^{-1} for dry fen, 149 to 492 mg·L^{-1} for wet fen, and 70 to 234 mg·L^{-1} for rich fen. Uplands at ML and JPH had DIC in the range of 57 to 101 mg·L^{-1} and 36 to 168 mg·L^{-1}, respectively.

Dissolved organic carbon (DOC) concentrations were generally higher at ML (29–73 mg·L^{-1}) than at JPH (7.2–22 mg·L^{-1}). In the near surface zone (WT depth), DOC average concentrations of samples decreased along the bog—rich fen gradient: 73 mg·L^{-1}, 63 mg·L^{-1}, 54 mg·L^{-1} and 22 mg·L^{-1} for bog, dry fen, wet fen, and rich fen, respectively. Compared to near surface samples, DOC concentrations of ML bogs decreased slightly in shallow and mid-depth piezometers and then increased to 111 mg·L^{-1} in the deepest piezometers. For ML fens, DOC was higher in shallow and mid-depth piezometers (62–77 mg·L^{-1}) than in WT (43–50 mg·L^{-1}) or deepest piezometers (45–57 mg·L^{-1}). At JPH, a systematic decrease in DOC was noted between shallow (32 mg·L^{-1}) and deep (9 mg·L^{-1}) piezometers located in the rich fens. DOC at upland sites also increased with depth; for JPH (1.8 to 18 mg·L^{-1}) and ML (7 to 20 mg·L^{-1}). DOC was strongly correlated with dissolved organic nitrogen (DON), which is attributed to similar controlling mechanisms (i.e., peat decomposition and pH).

Trends for major ion concentrations were consistent with those noted for conductivity (Table S2). Whereas wetland, near-surface ion concentrations of waters were lower at ML than JPH, increases with depth were greater at ML than JPH. For example, calcium average concentrations increased with depth from 1.3 to 118 mg·L^{-1} for bog, 1.5 to 142 mg·L^{-1} for dry fen, 1.2 to 24 mg·L^{-1} for wet fen, and 7.4 to 26 mg·L^{-1} for rich fen. Throughout the porewater profile at JPH, cation concentrations followed the pattern: $Ca^{2+} > Na^{+} \approx Mg^{2+} > K^{+} > NH_4^{+}$. At ML, different patterns were noted at surface versus at depth and for different terrain units. Near surface cations in bog and fen units followed the pattern: $Ca^{2+} > Na^{+} \geq K^{+} > Mg^{2+} > NH_4^{+}$ whereas for uplands Mg^{2+} and K^{+} were reversed. At depth, the pattern for bog and fen units was $Ca^{2+} > Mg^{2+} > NH_4^{+} > Na^{+} > K^{+}$. For uplands, Na+ was more abundant than NH4+. The average concentrations of sulfate were lower for ML than JPH. Sulfate concentrations typically decreased with depth in uplands, from 3.1 to 1.5 mg·L^{-1} for ML and 8.3 to 2.5 mg·L^{-1} for JPH. Sulfate tended to peak at shallow to intermediate depths in the wetlands, ranging from 0.07 to 0.53 mg·L^{-1} for poor fen (both dry and wet), 0.18 to 0.31 mg·L^{-1} for bog, and 0.95 to 7.3 mg·L^{-1} for rich fen. While uplands and rich fen sites tend to be dominated by SO_4^{2-}, particularly at surface, poor fens and bogs have $NO_3^{-} > SO_4^{2-}$ at surface and along the fen edges and $SO_4^{2-} > NO_3^{-}$ at depth. Hydrogen sulfide was also measured, and average concentrations were generally <0.04 mg·L^{-1}, except at a 6.5 m depth at the JPH upland (0.14 ± 0.11 mg·L^{-1}) and at the JPH fen (0.38 ± 0.25 mg·L^{-1} at a 1.5 m depth, and 0.20 ± 0.09 mg·L^{-1} at a 3 m depth).

Mean stable isotope signatures of $\delta^{13}C_{DIC}$ at wetland landscape units increased with depth (Table S2). The average $\delta^{13}C$ values in DIC increased with depth from −14.60‰ to +6.84‰ for bog, and similarly though within smaller ranges for poor fen at ML; from −11.37‰ to +9.92‰ for dry fen and −6.50 to 4.29‰ for wet fen. In contrast, the average $\delta^{13}C$ values of DIC were relatively depleted for rich fen at JPH, also increasing with depth, from −18.49‰ to −13.98‰. Uplands at JPH showed similar depth-wise trends in $\delta^{13}C$, ranging from −19.41 to −13.00‰, although profiles for upland at ML were relatively constant (−17.57 to −20.86‰). In general, $\delta^{13}C$ in DIC closely follows the changes noted in the alkalinity and DIC concentrations.

The average signatures of stable isotopes of water from peatland near surface waters (WT depth) were similar: average $\delta^{18}O$ values ranged from −17.42‰ to −17.92‰. At depth $\delta^{18}O$ was ranged from −18.08‰ to −18.66‰ for rich fen, −17.69‰ to −17.91‰ for dry fen, and −17.80‰ to −18.77‰ for bog. Wet fens are enriched at depth compared to other wetland types, ranging from −16.66‰ to −17.0‰. Ranges in $\delta^{13}C_{PM}$, reflecting particulate sources of carbon in the porewater of the wetlands and soils, are also shown (Table S2) and confirm that most particulates are organic in origin. Ranges in $\delta^{15}N_{PM}$ likewise, reflect variations in the sources of nitrogen to the wetland.

Ammonium (NH_4^{+}) in porewaters increased with depth in bog, dry fen and upland units, but peaked at shallow or mid-depth in wet fens. The steepest gradients are noted for bog and dry fen, with average ammonium concentrations increasing from 0.07 to 23 mg·L^{-1} and 0.04 to 24 mg·L^{-1}, respectively. Weaker gradients were noted for uplands: 0.02 to 0.14 mg·L^{-1} for JPH and 0.22 to 0.42 mg·L^{-1} for ML. The rich fen had a near-constant depth profile. Overall, similar trends were noted for DON, with highest concentrations reaching 21.2 mg·L^{-1} at depth in dry fen areas.

Nitrates (NO_3^-) ranged from 0.82 to 2.62 mg·L^{-1} at JPH, peaking in mid-depth piezometers in the rich fen and deep piezometers in the upland. At ML, NO_3^- peaked at surface in bog and dry fen units, ranging from 1.03 to 1.35 mg·L^{-1} near surface to 0 to 0.18 mg·L^{-1} at depth. Wet fens and upland were generally in the same range but showed NO_3^- peaks at mid-depth (Table S2).

Nitrites (NO_2^-) are not included in Table S2 as they were either absent or present in very low concentrations. At JPH, upland sites were found to have NO_2^- in porewaters which decreased with depth from 0.24 to 0.07 mg·L^{-1} [25,26]. NO_2^- was absent in the rich fen. At ML trace quantities of NO_2^- were observed in fen and bog with highest concentrations at surface and in the wet fen [25,26]. Extremely low concentrations of nitrite are found throughout the rest of the peatland and uplands.

Overall, one of the main processes that controls geochemistry of the wetlands is methanogenesis, which is associated with reducing conditions and leads to the consumption of DOC and production of DIC. The characteristic pattern observed is for an increase in pH, conductivity, and alkalinity and a decrease in redox potential with depth. The other major geochemical process is mineral soil weathering which leads to higher conductivity and major ion concentrations in uplands, as well as in the bottom-most piezometers in wetlands that were driven to refusal at the mineral soil interface.

Temperature gradients in the bogs were also found to be steeper than in fens with coldest average temperatures (8.3 °C) noted for deep bog piezometers. Bogs in the area are well insulated, often raised above groundwater influence and therefore relatively cool, and have been known to contain permafrost in some cases. Enhanced groundwater exchange in fens and uplands is likely responsible for higher temperatures in these terrain units.

3.5. Nitrogen Inventory and Cycling

Based on the geochemical analysis of 889 water samples at the two sites we have developed an understanding of nitrogen species distributions within the upland and wetland systems at JPH and ML. Quantitative summaries of NO_3^-, NH_4^+, and DON concentrations are provided in Table S2. Limited results available for NO_2^- were described previously [25,26]. A summary of the speciation results is provided in Figure 8 (JPH) and Figure 9 (ML).

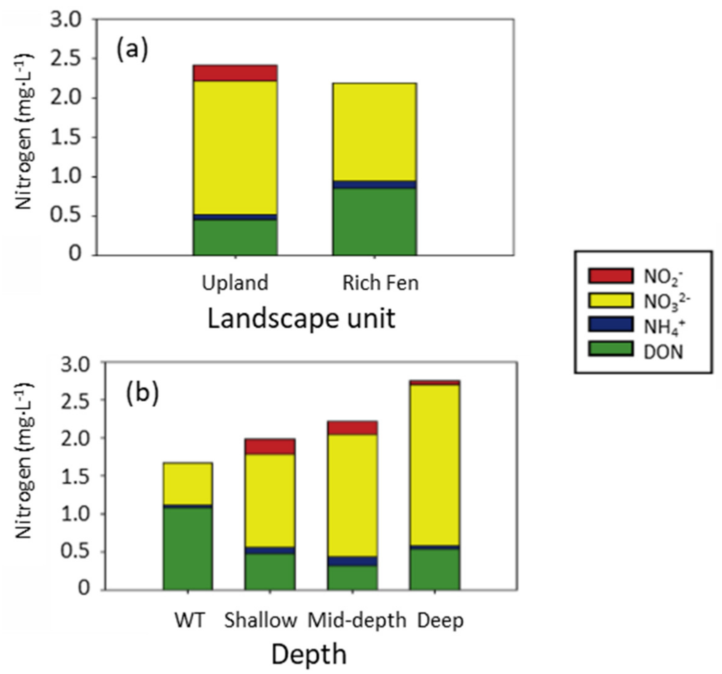


Figure 8. Summary of average nitrogen concentrations observed at JPH by (**a**) landscape unit and (**b**) depth (modified after [25]).

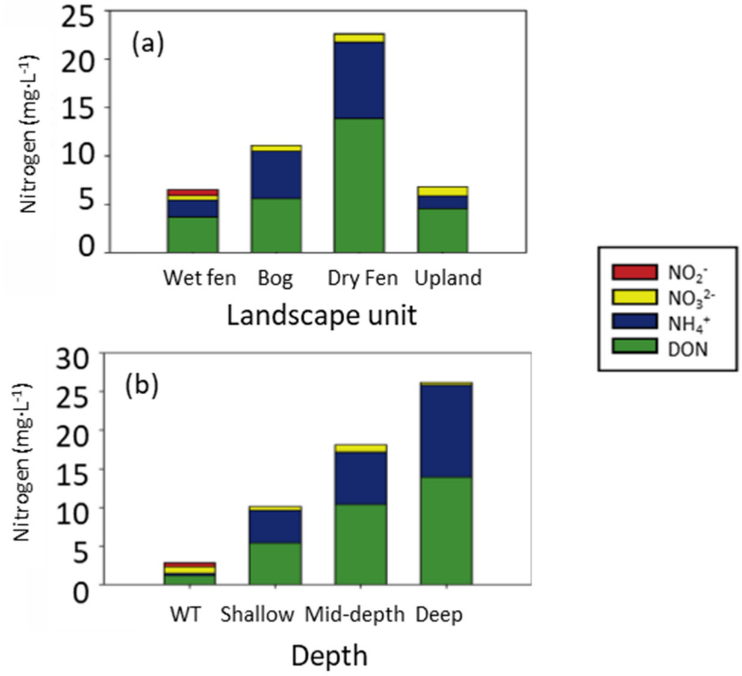


Figure 9. Summary of average nitrogen concentrations observed at ML by (**a**) landscape unit and (**b**) depth (modified after [25]).

Overall, it is evident that NO_3^- is the dominant form of nitrogen at the JPH site, while DON and NH_4^+ dominate at the ML site, with overall nitrogen concentrations approximately 10-fold higher at the ML site. Nitrogen is more abundant in upland soils than wetland soils at JPH, whereas at ML the nitrogen is distributed according to: dry fen > bog> wet fen ≈ upland. At JPH, NO_2^- and NH_4^+ show weak variations with depth, whereas DON tends to decrease slightly and NO_3^- tends to increase slightly in upland soils. The nitrogen distribution reflects the production of DON (and DOC) in shallow forest soils, and the accumulation of NO_3^- due to downward hydraulic gradients. At ML, nitrogen speciation appears to be strongly controlled by redox conditions, with NO_3^- (and lesser NO_2^-) being dominant at the water table and less important at depth. Reduced forms of nitrogen (NH_4^+), as well as organic nitrogen in the form of DON, increase significantly with depth, especially in the ML wetland (Figure 10). Due to the extremely low vertical hydraulic conductivity, these deeper stores are thought to be relatively immobile.

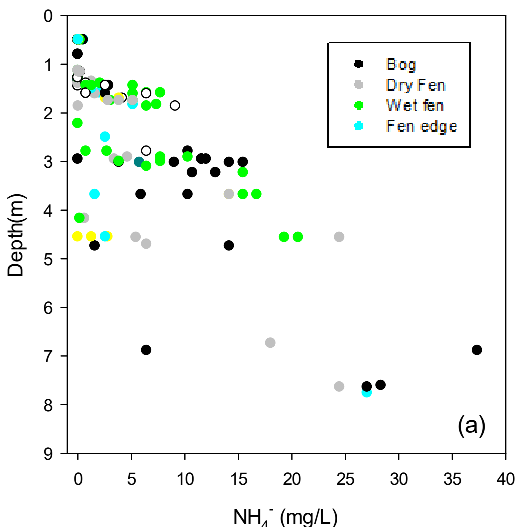
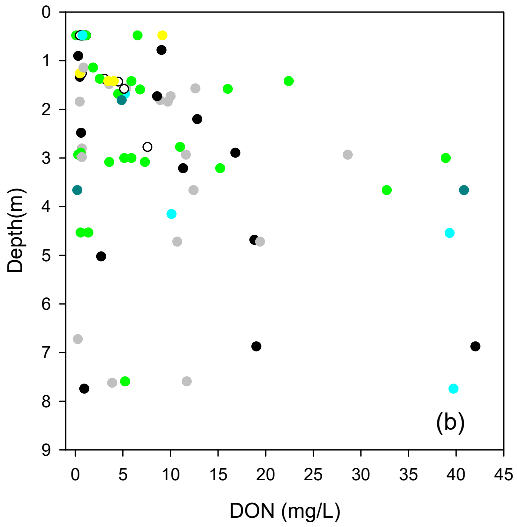


Figure 10. *Cont.*



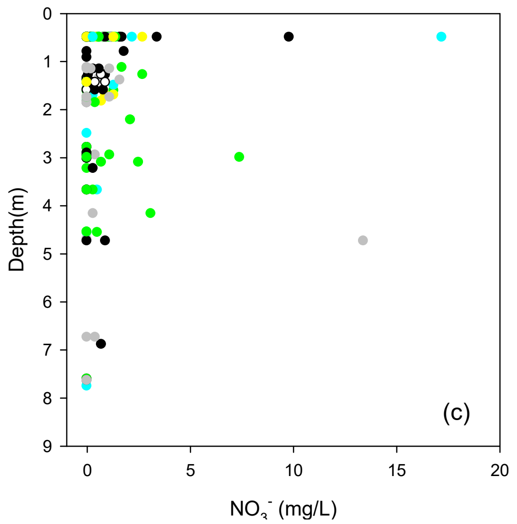


Figure 10. Distribution of major nitrogen species concentrations with depth at ML for individual samples, (**a**) NH4$^+$, (**b**) DON and (**c**) NO_3^-. Wetland terrain units are colour-coded. Upland is shown in yellow.

3.5.1. Nitrogen Storage Estimates at ML

The total inventories of NH_4^+ and DON throughout the ML peatland were calculated using a simple linear regression approach based on observed correlation of average nitrogen concentrations measured at depth (Table S3). While both species were found to generally increase in concentration with depth, the DON correlation was somewhat weaker. Note that our estimates did not consider peat stratigraphy or species-specific development and productivity [27]. A porosity of 0.9 was used in accordance with Turcheneck [28]. Nitrate and nitrite storage calculations were excluded due to their low concentrations throughout the peat. Units are expressed as kg·N·ha^{-1}. In general, ammonium concentration increases with depth and varies across landscape units. The bog has the highest ammonium storage of 512 kg·N·ha^{-1} over the 7 m depth, while the wet fen shows the lowest storage of 313 kg·N·ha^{-1}. The dry fen lies between the two at 448 kg·N·ha^{-1}. From 0–3 m the bog and the dry fen show a similar storage of ammonium with 239 and 237 kg·N·ha^{-1}, respectively. The dry fen also shows the highest ammonium storage from 0–3 m (913 kg·N·ha^{-1}). The wet fen has the lowest storage throughout all depths. Overall the correlation between the DON concentrations and depth are weaker than with ammonium. The bog and wet fen show similar DON storage throughout all depths and increasing with depth ranging from 82 kg·N·ha^{-1} from 0–3 m to 472 kg·N·ha^{-1} from 0–7 m. The dry fen has DON storage values twice that of the bog and wet fen for all depths ranging from 219 kg·N·ha^{-1} at 0–3 m to 1070 kg·N·ha^{-1} from 0–7 m. Total N storage for the wetland is estimated at 963 kg·N·ha^{-1}, with total N storage following the general pattern: dry fen > bog > wet fen.

3.5.2. Mobility of Nitrogen Species in Groundwater and Surface Water

Correlations between the various nitrogen species and indicators of movement, such as depth, hydraulic conductivity, and tritium concentration, were used to gain insight into the zones of mobility for the various species. Depths for the various wells and piezometers were measured at the time of installation. Hydraulic conductivity was estimated based on a series of bail and slug tests carried out in 2011 and 2012, as noted previously. Tritium was measured on water sampled in 2014 and 2015, whereas the various nitrogen species were measured on water samples collected during 2011 to 2015.

Depth-wise trends are shown in Figure 10. For peatlands, depth is a surrogate for degree of compaction or peat permeability, and so increased concentrations of NH_4^+ and DON at depth suggest that these species are concentrated mainly in the less mobile zone. In contrast, NO_3^- is found to occur at higher concentrations in porewaters in the upper 4 m where higher mobility is expected.

Plots of hydraulic conductivity versus NO_3^- and hydraulic conductivity versus NH_4^+ (Figure 11a,b) confirm, based on more direct hydraulic measurements, that zones of the highest potential for water movement are dominated by NO_3^-,whereas zones of NH_4^+ concentration have the lowest potential for water movement. A depth versus hydraulic conductivity plot (Figure 11c) establishes a more limited range of hydraulic conductivity below a 2 m depth. While quantifiable readings below 4 m were not obtained due to lack of response of the wells to bailing and injection, we anticipate that this zone has extremely low values in the range of 10^{-9} m·s^{-1} and below.

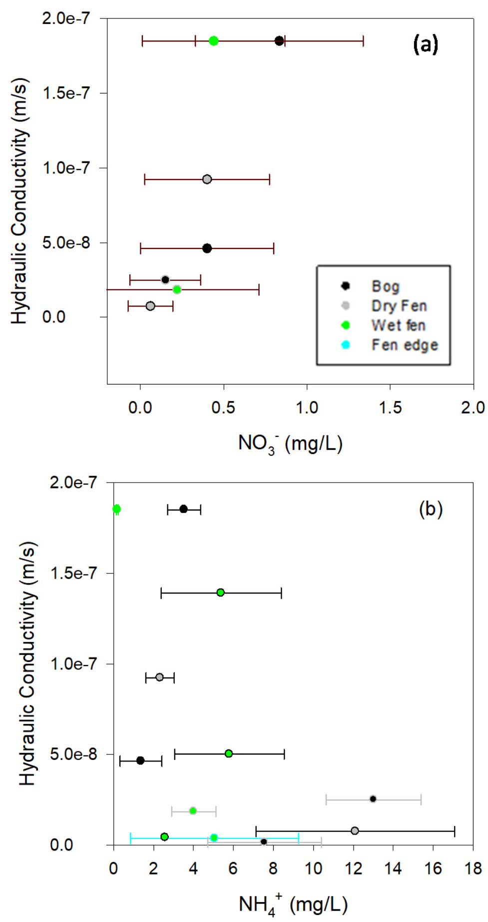


Figure 11. *Cont.*

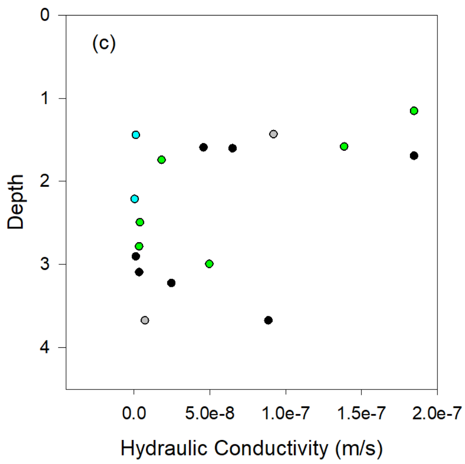


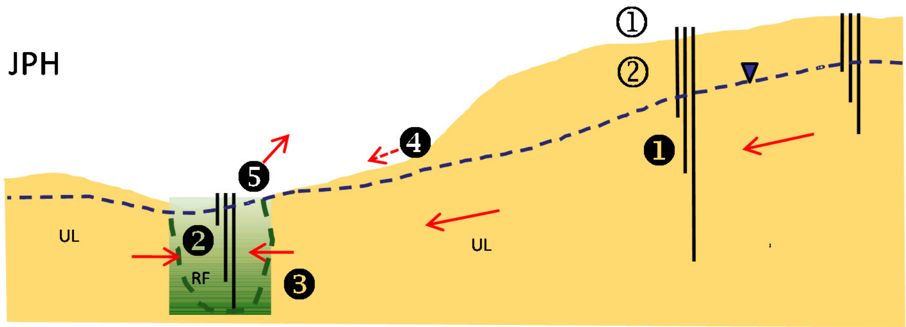
Figure 11. Plots of (**a**) nitrate and (**b**) ammonium species versus hydraulic conductivity ($m \cdot s^{-1}$) and (**c**) depth versus hydraulic conductivity for ML wetlands. Terrain units are colour-coded. Error bars represent 1 standard deviation of measurements. Note that hydraulic conductivity and depth were one-time determinations.

3.5.3. Conceptual Model

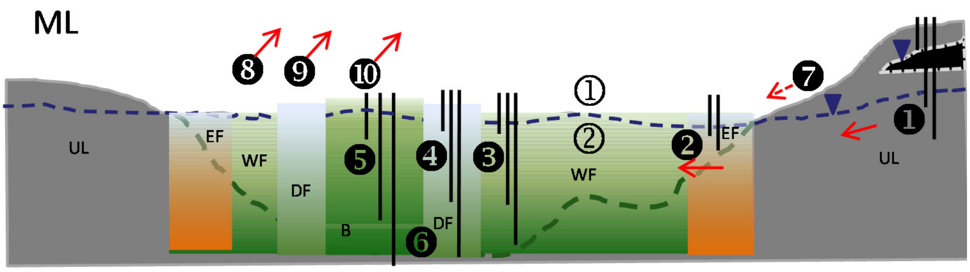
Based on the hydrologic and geochemical evidence collected during this study, a conceptual model of water and nitrogen flows was constructed (Figure 12). Various lines of evidence are shown.

At JPH, nitrogen flows, mainly in the form of NO_3^- and DON, are directed downward to the water table in uplands, followed by a lateral transfer by saturated groundwater flow to adjacent lowlands or the rich fen. Only brief, intermittent pulses of nitrogen may be carried by rill flow on upland hillslopes during high runoff events. Saturated flows containing NO_3^- and DON within rich fens are directed upwards and feed persistent outflows which occur from the rich fen. Storage of reducing species such as NH_4^+ is significantly less important than at ML due to regular flushing and oxidation of the rich fen.

At ML, nitrogen flows in the uplands, mainly in the form of NO_3^-, are similarly directed downward to the water table and then laterally by saturated groundwater flow to the fen margins, where the nitrogen is then carried upward into the wetland. Adjacent areas of wet fen may interact with the fen margins and typically support very slow downward flows of water and nitrogen. Dry fen and bog represent increasingly isolated terrain units with neutral and/or evaporative (upward) gradients, respectively. Surface flows of water and nitrogen from fen and bog units, mainly in the form of NO_3^-,are prevalent at ML. The slow decomposition of organic matter leads to the production of large storages of NH_4^+ and DON at depth that are relatively immobile.



From ammendment experiments:
① Plots: 1/3 N intercepted, N mainly stored in plants
② Plots: little experimental N leaving rooting zone
From hydrology and geochemistry component
❶ No experimental N detected; downward hydraulic and isotopic gradients
❷ No experimental N detected; upward hydraulic and isotopic gradients
❸ water isotope signatures match
❹ Large event runoff only
❺ Runoff and NO_3^- export characterized



From ammendment experiments:
①Plots: Sphagnum reduced, vascular plants increased
② Plots: Negligible experimental N in upper 1 m of peat
❶ No experimental N detected; downward hydraulic and isotopic gradients
❷ No experimental N detected; upward hydraulic and isotopic gradients; water isotope signatures match
❸ No experimental nitrogen detected; downward hydraulic and isotopic gradients
❹ No experimental nitrogen detected; neutral gradients
❺ No experimental nitrogen detected; neutral to upward gradients
❻ Stagnant porewater pool with abundant NH_4^+, DON
❼ Large event runoff only
❽❾❿ Runoff and NO_3^- export characterized

Figure 12. Conceptual model showing evidence of water and nitrogen flows at JPH and ML. UL—uplands, RF—rich fen, EF—edge fen, WF—wet fen, DF—dry fen, B—bog. Red arrows indicate water and nitrogen flows. See notes below each panel.

3.5.4. Net Nitrogen Exchanges Due to Terrain Connectivity

Hydrology and geochemistry studies have indicated that the dominant water fluxes from wetlands are via surface flow pathways, which was quantified for the various wetland terrain types over multiple years during the course of the amendment experiments (Table S1). Nitrate was also confirmed as the most abundant and mobile species of nitrogen that is available for transport via surface flow pathways [25,26]. The major challenge of the hydrology and geochemistry studies was to quantify the exchange rates of nitrogen between the various terrain units, to evaluate whether critical loads of nitrogen could be assessed based on the response in individual isolated units or whether interaction between terrain units needed to be assessed and accounted for. In order to estimate the net exchanges that were comparable to the amendment loads, runoff potentials (in $mm \cdot yr^{-1}$) and nitrate concentrations ($mg \cdot L^{-1}$), both for individual water table wells, were used to calculate the annual exchange of nitrogen (in $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$), as well as inter-annual variability.

The results (Table S1) reveal that the wetland terrain units were net sinks for nitrogen during most of the 2011–2015 study period. On average, wet fen appears to receive the least nitrate on an annual basis (-0.12 ± 0.25 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$), while dry fen receives the highest amount of nitrate (-0.93 ± 1.66 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$). Intermediate amounts are predicted for rich fen (-0.22 ± 2.17 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$) and bog ($-0.66 \pm 1.42$ $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$). However, note that the rich fen site was strongly influenced by beaver activity during 2012–2015, and so variability is enhanced for this reason. Unfortunately, we were less successful at constraining net fluxes for uplands, although based on less continuous groundwater monitoring, we confirm that they are positive (i.e., net sources), on the order of <1 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$ and directed to wetlands at both sites.

Based on the magnitude of the potential exchanges between terrain units and the range of critical loads of nitrogen being tested (i.e., control, 0, 5, 10, 15, 20, and 25 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$), we anticipate that connectivity is largely a minor issue and only creates significant interference at lower loading levels (i.e., control, 0 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$ and possibly for the 5 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$ experiments). We expect the influence of nitrogen exchanges between terrain units at the sites evaluated to be less important than issues with characterizing current spatial variability in the atmospheric loadings of nitrogen.

4. Summary and Conclusions

This study has significantly improved the understanding of hydrologic and geochemical characteristics of selected terrain types in northeastern Alberta, including jack pine upland and a range of wetlands including rich fen, poor fen (both wet and dry) and bog.

New inventories of nitrogen concentrations in surface water and various levels of groundwater have been compiled. The collection of physical, geochemical, and isotopic data, in conjunction with nitrogen data, has provided insight into the nitrogen cycle and new information on the mobility of various nitrogen species in important terrain units.

Overall, based on hydrological and geochemical monitoring of a network of 25 water table wells and 30 multi-level piezometers, nitrate is identified as the major nitrogen species transported mainly via surface flow pathways among various landscape units. Flux estimates based on water yield and geochemical monitoring suggest only minor exchanges of nitrogen between wetland terrain units, likely less than ± 1 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$ for rich fens, poor fens and bogs representative of the region. Uplands are generally negligible sources of nitrogen. Given that the critical load for nitrogen was estimated to be on the order of 17 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$ for wetlands based on a 5-year experimental amendment field program [5], we can now conclude that exchanges of dissolved nitrogen species related to hydrologic connections, primarily surface water exchanges, are likely to be uninfluential in buffering acidification of these wetlands if exposed to oil sands deposition levels approaching the critical load. As connectivity is expected to alter the critical load estimate by less than 7%, we suggest that wetland terrain types may also be effectively considered as self-contained mosaics for the purpose of critical loads assessment mapping across the region. As noted by Nilsson [29], critical load is defined as the highest load that will not cause chemical changes leading to long-term, harmful effects on an ecosystem. Importantly, this threshold has not so far been approached in the oil sands region where nitrogen loads are currently predicted to fall in the range of 1 to 2.85 $kg{\cdot}N{\cdot}ha^{-1}{\cdot}yr^{-1}$ [30].

The storage of nitrogen, mainly in the form of NH_4^+ and DON, is on the order of 963 $kg{\cdot}N{\cdot}ha^{-1}$ for wetlands in the Mariana Lakes area. While much of this nitrogen is currently immobile, the future alteration of such systems by the promotion of vascular plant growth under higher rates of atmospheric deposition [5], hydroclimatic changes and/or excavation of wetlands for oil sands development, could result in water table decline (or increased variability) leading to the release of stored nitrogen. Given the enormous magnitude of nitrogen storage in bogs and fens, careful consideration should be given to the preservation of these landscape features as part of a sustainable strategy for regional oil sands development.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/w13162204/s1, Figure S1: Stable isotope plots for Mariana Lakes and Jack Pine High by terrain type, Table S1: Runoff potential, mean nitrate, net N flux by year and statistics, Table S2: Geochemical inventory of wells and piezometers by terrain unit. Depth categories include water table wells (WT), shallow (S), moderate (M), and deep (D) piezometers, Table S3: Mariana Lakes nitrogen inventory including NH_4^+ and DON.

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