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Hydrology and Biogeochemistry of a Bog-Fen-Tributary Complex in the Hudson Bay Lowlands, Ontario, Canada

Thomas A. Ulanowski
The University of Western Ontario

Supervisor
Dr. Brian Branfireun
The University of Western Ontario

Graduate Program in Geology
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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Thomas Ulanowski

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The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

Abstract

The Hudson Bay Lowlands (HBL) contains 26 Gt of carbon sequestered in a 2 meter thick layer of peat which blankets a quarter of Ontario, Canada. The hydrological and chemical influence of the HBL peatlands to surface waters is recognized, but information on peatland runoff processes and the evolution of groundwater through this vast, carbon-rich landscape remains scant. This study focused on elucidating the groundwater flow patterns of a bog-fen-tributary complex in the central region of the HBL, and estimating exports of groundwater, dissolved organic carbon (DOC), total (THg), and methyl (MeHg) mercury during the 2011 ice-free season. Hydrometric data, combined with ions and stable water isotopes, reveal lateral flows in the uppermost meter of peat dominate the bulk transfer of groundwater and solutes in the bog (73-137 mm) and fen (55-131 mm). The direction and magnitude of the measured vertical gradients in the bog (-0.2 to 0.1) and fen (-0.1 to 0.2) are spatiotemporally variable, and are dictated by position within the landscape, water table elevation relative to the peat surface, and micro-to-mesoscale topography. The seasonal exports of DOC from the bog and fen are small, and comprise 5.4% (2.0±0.3 g C m^{-2} yr^{-1}) and 1.4% (0.5±0.1 g C m^{-2} yr^{-1}) of the net ecosystem carbon balance, respectively. Exports of THg and MeHg from the bog (132.9±45.4 and 3.4±2.8 ng m^{-2} yr^{-1}) and fen (50.0±8.4 and 1.9±1.2 ng m^{-2} yr^{-1}) are lower than reported in other boreal wetlands. The swamp and thicket riparian zone between the ribbed fen and tributary appears to influence the quality of water and augment solute concentrations of the water in small surface flows that flow directly into the nearby second-order stream.

Keywords

Ecohydrology, Groundwater, Biogeochemistry, Wetlands, Peatlands, Bog, Fen, Hudson Bay Lowlands, Dissolved Organic Carbon, Carbon Balance, Mercury, Stable Isotopes, Tracers

Co-Authorship Statement

I hereby declare that I am the sole author of this thesis, except where noted (below). I understand that my thesis may be made electronically available to the public.

Exceptions to sole authorship:

For all chapters, Dr. Brian Branfireun acted as an advisor, editor, and offered suggestions to the treatment and presentation of data in this thesis, and will be listed as a co-author on any subsequent publications stemming from this work.

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Dedication

This thesis is dedicated to my parents, Adam and Bozena Ulanowski, for their limitless support throughout not only this thesis, but also every other moment in my life. Thank you, for everything.

Table of Contents

List of Tables

List of Figures

Chapter 1

1 Introduction

1.1 Wetlands: Global Distribution and Significance

Wetlands are areas of land that are saturated with water for all or the majority of the year, and that that are able to support unique, flood-tolerant vegetation and microbial communities because of their reducing biogeochemical soil conditions (Mitsch and Gosselink, 2007). Wetland ecosystems currently cover an estimated 5-8% of the Earth's total land surface (*Ibid.*), and store nearly a quarter (350-535 Gt) of global belowground terrestrial soil carbon (Gorham, 1991a). Over 14% of the Canada's land mass is blanketed by wetlands, which represent nearly a quarter of all wetlands in the world (Kennedy and Mayer, 2002). Wetlands provide many benefits to society, including improvements to water quality, climate moderation, drainage regulation and flood attenuation, serving as sources of energy and raw building materials, and offering areas for recreation and tourism (Mitra *et al.*, 2005; Mitsch and Gosselink, 2007). Despite such clear ecological, social, and environmental importance, global wetland area has declined by 50% since the 1880s primarily as a result of drainage for development and agricultural land-use conversion (Mitsch and Gosselink, 2007).

Wetland ecosystems vary greatly in location, landscape position, areal extent, hydrology, chemistry, abundance of organic matter, and vegetation communities. The classification of wetlands into discrete classes provides a common framework for the scientific community to refer to specific ecosystem functions. Many classification systems exist, utilizing a combination of abiotic and biotic properties to define a specific type of wetland. For example, the Canadian Wetland Classification System (NWWG, 1997) classifies all Canadian wetlands into two major forms (mineral and organic soil-dominated wetlands) and five classes (bog, fen, marsh, swamp, and shallow water) based on hydrology, water chemistry, and soil and vegetation types. Organic wetlands that have accumulated thick deposits of organic material greater than 0.40 m thick (dead and decaying plant material) are classified as *peatlands*.

1.2 Peatland Ecosystems and Landforms

Peatlands are the most dominant wetland type on Earth, representing half of the world's wetlands and covering 3% (4,000,000 km^2) of the world's surface (Gorham, 1991a). These can exist as smaller, isolated units in the landscape (*e.g.,* depression peatlands or spring fens), or as expansive patterned peatland complexes spanning many thousands of square kilometres. The largest areas of peatlands are located in the northern latitudes of North America (*e.g.,* Canada and Alaska), Northern Europe, Western Siberia, and parts of the Amazon Basin (Gorham, 1991a; Belyea and Lancaster, 2002; Mitra *et al.*, 2005). These ecosystems are characterized by a thick layer of *peat*, a highly organic soil (NWWG, 1997). This sequestration of atmospheric carbon into belowground organic matter is due to the annual net primary productivity (NPP) of peatland vegetation exceeding the annual decomposition of dead organic matter (OM). In boreal and subarctic peatlands, this slow decomposition is a consequence of persistent anoxic, water-saturated conditions (where precipitation > evapotranspiration), a cold climate, and low nutrient availability (Mitsch and Gosselink, 2007). As a result, these northern hemisphere, high-latitude peatlands contain a mass of carbon (C) equal to half of that currently held in the atmosphere (Limpens *et al.*, 2008).

Bogs and fens dominate the majority of larger patterned peatland landforms (Figure 1.1A) (NWWG, 1997). A bog is a raised, frequently dome-shaped landform, and is often sparsely forested with stunted black spruce (*Picea Mariana*) (Clymo, 1984). Understory vegetation in these domes landforms typically consists of mosses (*Sphagnum spp*.), lichens (*Cladonia spp*.), and low-lying ericaceous shrubs (e.g. *Chamaedaphne calyculata, Rhododendron spp.*), which contribute to the development of the peat profile, as well as microtopography in the form of hummocks, hollows, and lawns (NWWG, 1997). As peat accumulates over thousands of years, the uppermost portion of the peat profile becomes increasingly disconnected from any mineral-rich groundwater inputs (Ingram, 1982, 1983). Bogs by definition are ombrotrophic ("cloud-fed"), as meteoric precipitation is the sole source of hydrologic and nutrient inputs. As a result, shallow pore-waters in bogs are generally acidic (pH < 4.2) and concentrations of dissolved minerals are very low (e.*g.,* $[Ca^{2+}] < 2$ mg L^{-1}) (Shotyk, 1988).

Fen peatlands differ from bogs in that they have multiple hydrologic inputs in addition to precipitation, such as surface streams and/or deeper, solute-laden groundwater (Siegel, 1992). Fens are typically wetter at the surface than bogs because peat depth is generally shallower, and a higher water table is maintained by numerous hydrologic inputs. The minerotrophic nature of fens ensures that pore-waters within the uppermost peat surface have higher concentrations of dissolved mineral solutes than bogs (*e.g.*, $[Ca^{2+}] > 2$ mg L^{-1}), and a higher buffering capacity results in a circumneutral pH between 5 and 8, depending on the fen's degree of groundwater connection (also termed fen richness) (Reddy and DeLaune, 2008). Fens are able to support a different and much more varied mix of vegetation than bogs, and are largely dominated by sedges (*Cyperaceae spp.)*, brown mosses (*Amblystegiaceae spp.*), horsetails *(Equisetum spp*.), and stunted tamarack (*Larix laricina*). These differences in vegetation often contribute to the different physical properties of peat, with fen peat having relatively higher bulk densities, and lower porosities and hydraulic conductivities than bogs (Vitt *et al.*, 2009). Larger fen systems are often characterized by patterns of ridges (strings) and linear pools (flarks or troughs) that are perpendicular to the flow of groundwater and oriented parallel to the slope of the landform. This distinct wave-like pattern of alternating strings and flarks is easily identified from aerial photographs and remote imagery (Figure 1.1B).

Figure 1.1. (A) Large peatland complexes comprise a mosaic of bogs, fens, shallow open water (ponds), marshes, and swamps, and are cross-cut by creeks and rivers, and **(B)** Parallel strings and flarks characteristic of ribbed fen systems. Photos by the author.

1.3 Hydrological Processes in Patterned Peatlands

Peatland development, groundwater chemistry, and ecology are all closely linked to surface and groundwater hydrology. The maintenance and function (*e.g.*, retention or conveyance of water, transformation of nutrients, and a habitat for wetland plants and animals) of a particular peatland type is closely linked to its hydrologic signature, which is governed by geomorphology, geology, and the balance of inflows and outflows of water (Mitsch and Gosselink, 2007). A common approach to understanding hydrological processes is to estimate the water balance (Equation 1.1) for a given area (*e.g.*, watershed) and period of time (*e.g.*, a study period, season, or year), which defines all hydrologic inputs and outputs to a landscape unit:

$$\boldsymbol{\Delta S = (P + G_i + S_i) - (ET + G_o + S_o) + \xi} \qquad \textbf{Equation 1.1}$$

where ΔS is the change in storage, P is precipitation, G_i is groundwater inflow, S_i is surface water inflow, ET is evapotranspiration, G_o is groundwater outputs, S_o is surface water outflow, and ξ is the residual term.

For larger patterned peatlands lacking channelized inputs and outputs of water, assuming steady state conditions, and combining surface and groundwater losses as a single runoff term (R), a more specific water balance equation (Equation 1.2) can be defined:

$$\boldsymbol{\Delta S = P - ET - R \pm \xi} \qquad \textbf{Equation 1.2}$$

Precipitation is typically the easiest component of the water budget to quantify, especially in peatland environments with minimal aboveground vegetation to intercept incoming rain or snow. Evapotranspiration, the loss of water to the atmosphere from peatland surface and vegetation, is often the dominant water loss process in peatlands. Rates of evapotranspiration can be estimated by a variety of methods, using simple evaporation pans or lysimeters, complex models based on an energy balance (*e.g.*, Penman-Monteith or Priestley–Taylor), or real-time flux measurements (Drexler *et al.*, 2004).

Surface and groundwater runoff processes are responsible for the delivery of water and associated solutes between peatland landforms and to nearby surface waters, and are often the most difficult to measure directly. The rate of groundwater flow through a saturated porous medium is based on Darcy's Law (Equation 1.3), which states that the rate of one-dimensional groundwater flow (Q) is proportional to hydraulic conductivity (K), a unitless hydraulic gradient (I), and cross-sectional area (A) (Freeze and Cherry, 1979; Siegel and Glaser, 2006).

$$\boldsymbol{Q = -KIA} \qquad \textbf{Equation 1.3}$$

In large peatland complexes with gently sloping surface topography, groundwater flow tends to follow the slope of the ground surface, as does the water table, and vertical hydraulic gradients are often very small and invariant over long distances. Therefore, the rate of groundwater discharge through the peat profile is primarily governed by the hydraulic conductivity of the peat and to a lesser extent topography of the landscape.

Based on observations of the physical properties of well-developed peat profiles, influential peatland (hydro)ecologists have suggested a division of the peatland soil profile into two main layers, with the boundary typically defined by the minimum depth of the water table during a drought year (or lowest annual water table position, depending on the source of the definition) (Ingram, 1982, 1983; Clymo, 1984; Belyea and Baird, 2006). In this widely accepted diplotelmic (two-layer) model, the uppermost portion of the peat profile (typically 0-50 cm below the peat surface) is called the active-layer, or acrotelm, and is relatively undecomposed with a high hydraulic conductivity (10^{-3} to 10^{-5} m s^{-1}) and porosity (>85%), permitting water to flow fairly unimpeded (Chason and Siegel, 1986). The acrotelm is also subject to a fluctuating water table, which has a strong influence on biogeochemical processes because of the short (daily to monthly) oscillation between oxygenated (aerobic) and water-logged (anaerobic) states. Preliminary efforts at elucidating peatland runoff mechanisms proposed that water losses occurred primarily at or near the surface, only through (and above) the acrotelm, dominating peatland runoff. This mechanism constrained runoff to periods of high water table, such as snowmelt or high magnitude precipitation events. However, this was later supplemented by a more comprehensive runoff hypothesis that included slow groundwater flow through the deeper peat layer, the catotelm. (von Post and Granlund, 1926; Ivanov, 1981; Ingram, 1982). The catotelm is frequently considered a hydrologically inactive layer (*i.e.,* groundwater flow is relatively slow), where the degree of peat decomposition and bulk density is much greater than in the acrotelm, and hydraulic conductivities (10^{-5} to 10^{-8} m s^{-1}) and porosities (<85%) of the peat are lower, generally decreasing with depth (Chason and Siegel, 1986).

The acrotelm-catotelm peatland model serves as a simple and effective tool for conceptualizing peatland hydrological and biogeochemical processes, but has been recently criticized for not being physically-based, or demonstrated compellingly in the field, and unable to accurately explain complex peatland phenomena, such as spatial heterogeneity of peat properties, formation of localized flow systems, and microtopographical self-organization (Belyea and Baird, 2006; Morris *et al.*, 2011). The model also does not account for the presence of macropores and soil pipes within deeper layers of the peat, which can significantly increase hydraulic conductivity (Baird, 1997). Such features are often randomly distributed and difficult to quantify by conventional hydraulic conductivity field and lab tests (Holden *et al.*, 2002).

1.4 Hydrological Connectivity in Patterned Peatlands

Hydrological connectivity describes the passage of water from one part of the landscape to another, often in terms of discrete areas in space and times of enhanced runoff (Bracken and Croke, 2007). Quantifying the connectivity of bogs to larger patterned fen systems, and fens to adjacent surface waters, is essential in identifying key areas and times of water and solute fluxes that remain poorly understood (*e.g.,* Quinton *et al.* (2003)). The degree of connectivity within expansive peatlands is largely a function of surface morphology and antecedent moisture conditions.

The movement of water through bogs and into adjacent fens can occur via three major pathways: (1) surface flow through the acrotelm during periods of high water table; (2) shallow groundwater flow through the higher-conductivity layers in the upper parts of the peat profile; and (3) deeper groundwater flow through the entire peat profile (Bleuten *et al.*, 2006), as illustrated in Figure 1.2. For the majority of the year, runoff is limited to shallow, lateral groundwater flow in bogs, since the water table is typically below the peatland surface (NWWG, 1997; Quinton and Marsh, 1999). Deeper groundwater flow systems may develop in bogs, but often contribute relatively little water to the surrounding fens because of low vertical gradients and low hydraulic conductivities at depth. In some cases, larger domed bogs can shed water horizontally through internal water track drainage features, where the convergence of hydrological flow paths into a narrow area can produce a characteristic series of ponds that run parallel to the contours of surface elevation (Glaser and Janssens, 1986; Belyea and Lancaster, 2002). Total water storage in bogs is increased when such irregularly spaced pools are present, which also act to moderate runoff during inputs of water from storms. However, the relatively high hydraulic gradients and high conductivity peat in these water tracks (as compared to the rest of the bog) likely serves to deliver water and associated dissolved chemistry downslope to fens (Glaser, 1992). The vertical exchange of groundwater between a bog and the underlying low-conductivity substrate is considered to be minimal and primarily controlled by mineral soil permeability (Reeve *et al.*, 2000).

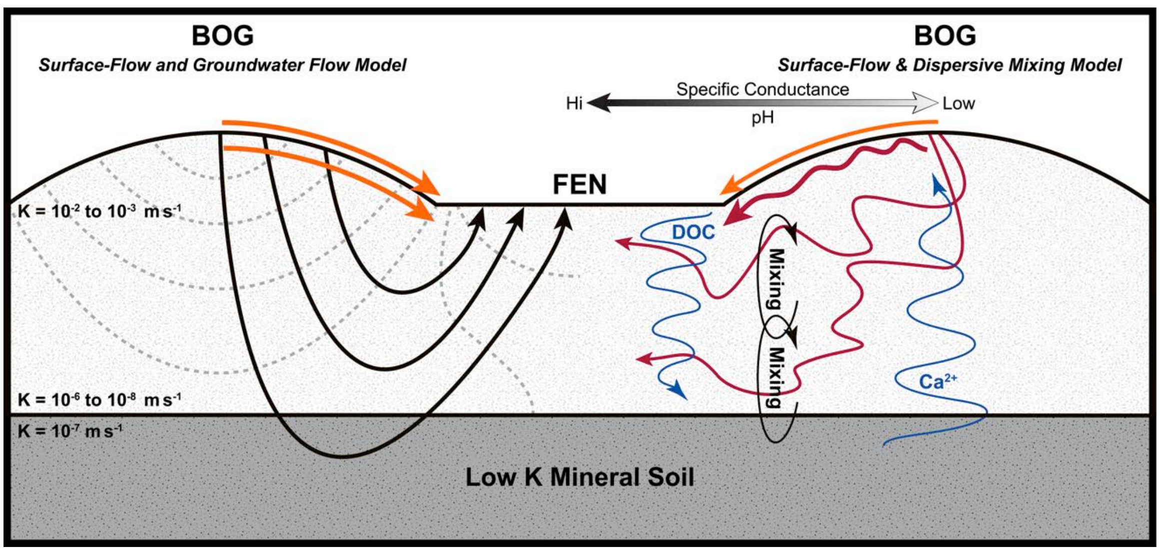

Figure 1.2. Schematic illustrating the proposed models for runoff and hydrological connectivity between bogs and fens and the underlying mineral substrate, showing how deeper vertical and horizontal groundwater flow can increase solute concentrations in the surface peat of fen systems, including: surface runoff (orange arrows) and groundwater flow through the bog profile (black arrows), shallow flow and dispersive mixing (red arrows), and diffusion (blue arrows). Adapted from Reeve *et al.* (2000, 2001).

In larger peatland complexes, fen peatlands can develop into patterned fen systems (*i.e.*, ribbed fens), which act as conduits of groundwater flow, delivering water, energy, and solutes from the landscape to adjacent surface waters (Glaser *et al.*, 1990; Glaser, 1992; Price and Maloney, 1994). In addition to precipitation, patterned fens primarily receive hydrological inputs from surrounding bog areas, either as surface flows or diffuse lateral groundwater flow, depending on the height of the water table relative to the surface. Patterned fens tend to shed water quickly after snow melt in colder climates, due to the presence of a low-permeability, near-surface frost table that permits largely unrestricted overland flow (Woo, 1986). In the absence of ground-ice, surface flows may also contribute to the majority of runoff from bogs and fens, and fens to streams during periods of extreme inundation (*e.g.,* summer storms or fall freshet) (Price and Maloney, 1994). One of the major differences between patterned and non-patterned fen systems is the abundance of alternating pool-peat ridges which can experience enhanced connectivity at periods of high water table. Surface flow between such pools can occur around the ridges through narrow surface channels that connect pools, or even above ridges themselves (Woo and Heron, 1987).

A drop in the water table can significantly increase storage availability in patterned fens, due to the abundance of string and trough microtopography (Quinton and Roulet, 1998). When this occurs, the system is better able to accommodate for large rain events and there is a decrease in runoff response (*Ibid.*). When the water table drops below the peat surface, lateral groundwater flows in the direction of the hydraulic gradient tend to dominate water flux, with the majority of flow occurring through the higher conductivity acrotelm. In general, ribbed fens exhibit lower rates of flow than the surrounding bogs because of lower hydraulic gradients than those present in domed bog systems and the lower hydraulic conductivities than in either bogs or non-patterned fens (Siegel & Glaser, 1987). Outflow rates are especially lower during the dry season when water tables are lower, forcing water to have to travel through the low conductivity catotelm (Price & Maloney, 1994). Vertical flows in patterned fens are generally small, and the increased concentrations of dissolved solutes found near the surface of the peat in larger peatland complexes are likely due to the diffusion and dispersion of solutes that originate from the rich, mineral substratum (Reeve *et al.*, 2001).

1.5 Biogeochemical Processes in Patterned Peatland

Peatland biogeochemical processes involve the transformations of elements and exchange of materials between biotic and abiotic components of the environment, and are driven by a complex relationship between physical, chemical, and biological processes (Gorham, 1991b; Reddy and DeLaune, 2008). The waterlogged and carbon-rich soils characteristic of peatlands provide a unique environment for the cycling of nutrients, which can serve as sinks, sources, and transformers of carbon, nitrogen, and sulphur, as well as pollutants and other chemical constituents (Mitsch and Gosselink, 2007). The rates of these biogeochemical transformations can exhibit multi-scale spatiotemporal variability due to changes in the position of the water table relative to the peat surface, air and soil temperature, pH, vegetation communities, and availability of terminal electron acceptors (TEAs). The convergence of hydrological flow paths of nutrient-rich waters causing enhanced biogeochemical reactions (*i.e.,* hot spots and hot moments) (McClain *et al.*, 2003; Mitchell *et al.*, 2008) and microtopographic variations within a landform (Branfireun, 2004; Ulanowski and Branfireun, 2013) can complicate the already complex cycling of nutrients in these environments.

Bogs and other *Sphagnum* dominated peatlands tend to be acidic (pH ≈ 4) due to high concentrations of carbonic and organic acids (*e.g.,* phenolic acid) released from growing vegetation and decaying organic matter (Clymo, 1964). Sphagnum also has a very high Cation-Exchange Capacity (CEC), which allows for the sorption of base cations (*e.g.,* Ca^{2+}, Mg^{2+}) onto the surface of the peat and subsequent release of acidic protons (H^{+}) (Ho and McKay, 2000). Fen peatlands are typically circumneutral (pH ≈ 5 to 8) since *Sphagnum* species are less abundant and their higher concentrations of base cations allows for greater neutralization of organic acids.

Reduction-oxidation (redox) potential (Eh) is the tendency of a chemical species to be reduced by the gain of electrons, and is important as it influences the types of microbial communities that live in the profile and the rates of dissolution and degradation of inorganic and organic substances (Reddy and DeLaune, 2008). When free oxygen is present, Eh ranges from +300 to +700 mV, and aerobic microbial metabolic processes dominate (Mitsch and Gosselink, 2007). Peatland pore-waters tend to be low in oxygen, because the consumption of oxygen by microbes and plants is greater than the diffusion of oxygen through the water-saturated soil column (*Ibid.*) As dissolved oxygen (DO) becomes increasingly scarce (Eh = +300 to 0 mV), facultative anaerobes begin to govern biogeochemical processes. The energy yields of anaerobic respiration processes are lower when compared with aerobic respiration, which greatly decreases the rates of turnover of organic matter (*Ibid.*). Obligate anaerobes begin to function below 0 mV, adapting to these anoxic environments by utilizing other TEAs (as opposed to O_2) for cellular respiration, namely NO_3^-, Mn^{2+}, Fe^{3+}, and SO_4^{2-} in decreasing order of preference. Anaerobic microbes are responsible for the cycling and transformation of important elements, such as nitrogen mineralization, the oxidation and reduction of nitrogen containing compounds (*e.g.*, NH_4^+, NH_3, NO_3^-, N_2), production of methane (CH_4), and reduction of sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S) by sulfate reducing bacteria (SRB) (*Ibid.*). SRB are also known to play a role in the anaerobic oxidation of methane (Smemo and Yavitt, 2011), and the methylation of mercury (Hg) (Ullrich et al., 2001).

1.5.1 Carbon Cycling and Dissolved Organic Carbon Export from Peatlands

Peatland ecosystems play an important role in the global carbon cycle, exchanging carbon dioxide (CO_2) and methane with the atmosphere, and delivering dissolved organic carbon (DOC) into nearby aquatic ecosystems (Blodau, 2002). Carbon dioxide and methane are greenhouse gases, molecules that absorb and emit infrared radiation, and that have been well established as drivers of global climate change (IPCC, 2013). Northern peatlands have acted as a sink of CO_2 for thousands of years, but even small changes to hydrology could shift these sensitive ecosystems to sources of CO_2 (Gorham, 1991a). Because of the complexity of the carbon cycle, there is still much uncertainty on the magnitude and direction of long-term changes to carbon dynamics in these systems (Limpens *et al.*, 2008), especially since the transformation of organic carbon into CO_2, CH_4 and DOC end products is largely mediated by aerobic and anaerobic microbial processes, which are sensitive to aforementioned local environmental conditions.

The uptake and release of CO_2 (also referred to as net ecosystem exchange, NEE) and CH_4 to and from a peatland are typically quantified in the lab or field *via* chamber (Pumpanen *et al.*, 2004) or micrometeorological (*i.e.*, eddy flux covariance) (Baldocchi *et al.*, 2000) methods. These direct and often high-resolution and time-resolved measurements can be used to estimate the atmospheric flux component of a peatland carbon budget. However, this approach does not provide information on any non-gaseous loses of carbon from the peatland, namely the transport of organic carbon via surface runoff and groundwater processes. Neglecting to quantify hydraulic fluxes of organic carbon can contribute to very large errors when determining the carbon budget of a peatland system (Waddington and Roulet, 1997; Limpens *et al.*, 2008).

Organic carbon can be exported from a peatland in both particulate (POC) and dissolved (<0.45 μm) forms, but groundwater flow through porous media only permits the transport of smaller, dissolved fractions. Dissolved organic carbon is a mixture of organic compounds that range from simple molecules to larger, more complex aromatic substances derived from the breakdown of organic matter through microbial processes. The degradation of larger organic substrates derived from animal and plant matter into DOC is governed by redox conditions, temperature, the presence of organisms, nutrient and TEA availability, and carbon source (Reddy and DeLaune, 2008). Pore-water DOC concentrations in peatlands range between 10 and 80 mg L^{-1} (Blodau, 2002) depending on peatland type, depth below the peatland surface, and time of the year. Bogs tend to have higher overall levels of DOC than fens (Reeve *et al.*, 1996; Ulanowski and Branfireun, 2013). The loading of DOC into aquatic systems has been known to affect pH, decrease the penetration of light through the water column, and has been associated with the complexation and transport of metals, which can have an impact on primary production and ecosystem health (Thurman, 1985; Blodau, 2002; Porcal *et al.*, 2009). Peatlands are established as sources of DOC to nearby surface waters (Mulholland and Kuenzler, 1979; Waddington and Roulet, 1997; Carey, 2003). Annual exports of DOC from peatland catchments can be between 1 and 50 g DOC m^{-2} yr^{-1} (Dillon and Molot, 1997), which account for 10-50% of the annual net ecosystem carbon balance (NECB) (Fraser *et al.*, 2001; Worrall *et al.*, 2003; Yu, 2012).

1.5.2 Cycling and Export of Mercury from Peatlands

Anthropogenic activities have at least doubled the amount of mercury (Hg) in the global atmosphere since the beginning of the industrialized period (Hylander and Meili, 2003). Mercury is considered a global pollutant because it is readily distributed in the environment by atmospheric processes when it is reduced to it's gaseous form (Hg^0)

(Schroeder and Munthe, 1998). Mercury undergoes a series of complex transformations in the environment, some of which produce chemical species that are more toxic than the elemental and inorganic forms. The organic species, methylmercury (MeHg), bioaccumulates and biomagnifies in the aquatic food chain, and is known to be very toxic to both humans and wildlife (Morel *et al.*, 1998). Humans and animals exposed to fish high in MeHg may suffer from reduced brain, kidney, heart, and lung function, a weaker immune system, and may lead to deterioration of the nervous system, slower growth, and reduction in reproduction (Clarkson *et al.*, 2003; Tchounwou *et al.*, 2003).

The methylation of Hg to MeHg is biologically mediated primarily by SRB that thrive in anaerobic environments, such as wetlands (Ullrich *et al.*, 2001). Peatlands have been recognized as having a high methylation potential relative to other wetland and upland ecosystems (Branfireun *et al.*, 1999; Mitchell *et al.*, 2008), and identified as significant contributors of MeHg to aquatic ecosystems (St. Louis *et al.*, 1994; Rudd, 1995). Organic matter is known to interact strongly with inorganic and organic forms of Hg and enhance solubility, mobility and transport (Ravichandran, 2004). This suggests that landscapes dominated by peatland runoff may contribute large mass fluxes of MeHg in tributaries, even in environments where deposition of inorganic Hg is low.

1.6 Thesis Objectives

Approximately 90% of all wetlands in Canada are classified as peatlands, with the vast majority of them located in the cold arctic and sub-arctic regions of the country (Tarnocai, 1998). The Hudson Bay Lowlands (HBL) in northern Ontario and Manitoba is the world's second largest contiguous peatland complex, blanketing more than 320,000 km^2 of Ontario's land mass with a 1.5-3 m thick layer of peat (known as "muskeg" by the First Nation's people of the region) (Riley, 2011). Peat began to accumulate in the HBL approximately 6,000 years ago when land began to emerge from the sea due to high rates of isostatic rebound after the melting of the Laurentide ice sheet (Mcdonald, 1969). The flat regional gradients (~1% towards Hudson Bay) and low-conductivity glaciomarine deposits of calcite and dolomite beneath the peat strata have maintained permanent inundation of the land (*Ibid.)*. This has led to the sequestration of organic carbon as peat, estimated at 26 Gt C (FNSAP, 2010). The HBL ecozone is considered to be an ecologically important ecosystem, serving as habitat for large mammals such as woodland caribou, fox, bear, moose, and a breeding ground for over 200 species of migrating birds (Riley, 2011). The region also contributes large quantities of fresh water and solutes to James Bay, and subsequently the Arctic Ocean, *via* drainage by a dozen major rivers and thousands of minor streams and tributaries that crosscut the interior (Rouse *et al.*, 1992). Orlova and Branfireun (2014) found that runoff contributions from peatlands were consistently responsible for more than half of total streamflow discharge in large tributaries of the Nayshkootayaow River. Similarly, Richardson *et al.* (2012) noted a strong relationship between discharge in surface waters and gross drainage area under low flow conditions, suggesting the groundwater contributions from peatlands in the HBL play an important role in supporting baseflow conditions.

Scientific research in the HBL has recently intensified amidst concerns regarding changes to environmental processes resulting from climate change and resource extraction. Severe shifts to global temperature and precipitation patterns (IPCC, 2013) are expected to affect the hydrology and biogeochemical cycling of such large peatland systems (Holden, 2005). In particular, increases in the export of DOC from peatlands to aquatic ecosystems are expected (Pastor *et al.*, 2003; Freeman *et al.*, 2004; Frey and Smith, 2005). Patterned fens have been shown to dominate runoff generation and lateral transfers of waters and solutes to nearby surface waters in other northern peatland catchments (Quinton *et al.*, 2003). Potential increases in DOC concentrations within fens will likely contribute to increased loading of DOC to aquatic ecosystems, assuming seasonal runoff from peatlands remains consistent. Moreover, the extraction of large mineral deposits (*e.g.*, diamonds and metals such as chromium and nickel) discovered in the HBL in the last two decades may impact hydrological processes, carbon dynamics, and mobilization of solutes such as Hg on a more localized but intensified scale (Whittington and Price, 2012). The First Nation's inhabitants of the HBL have expressed concerns that such large-scale mining operations could increase Hg loading into surface waters, given the well-known interactions between DOC and Hg (Ravichandran, 2004). Although the surface waters of some of the larger tributaries in the HBL have low levels of THg (<5 ng L^{-1}) and MeHg (<1 ng L^{-1}) (Kirk and Louis, 2009), levels of Hg in fish are relatively high

(0.1 to 1 mg kg^{-1}) (B. Branfireun, personal communication) and consumption advisories have been issued for fish for in these rivers for the past few decades (MOE, 2013).

Despite the significance of the HBL peatlands to global biogeochemical cycles, the majority of information we have on peatland hydrology and the export of DOC and Hg comes from smaller, isolated peatlands. With ever increasing concerns over changes to peatland hydrology from land use and climate change, it is becoming increasingly obvious that it is necessary to improve our current understanding of the quantity and quality of water flowing through large peatland complexes in the HBL, given their close connection to surface waters.

In Chapter 2, I investigate the groundwater flow and hydrologic connectivity during the ice-free season between peatland landforms and underlying geologic strata using hydrometric data from groundwater wells and piezometers, as well as geochemical tracers, including major ions and stable water isotopes. I compare the observed groundwater flow patterns in the bog and fen to conceptual and computer-based models that have been developed for peatland complexes in the HBL, specifically the models presented by Reeve *et al.* (2000, 2001).

In Chapter 3, I use the information on the behavior of groundwater flow to provide quantitative estimates of groundwater, DOC, THg, and MeHg fluxes through a bog and fen for the study period using a simple four-layered flux model, based on empirical hydrogeological site data and seasonal pore-water solute concentrations. The ultimate goal is to provide a baseline of groundwater hydrology and carbon and mercury dynamics to compliment research efforts at the study site, primarily the long-term monitoring of CO_2, CH_4, and H_2O fluxes between the peatland and atmosphere, run by the Ontario Ministry of Environment.

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Chapter 2

2 Groundwater Flow and Hydrological Connectivity of a Bog-Fen-Tributary Complex in the Hudson Bay Lowlands

2.1 Introduction

The second largest peatland complex in the world, the Hudson Bay Lowlands (HBL), blankets almost a quarter of Ontario’s landmass with a highly-organic, two-meter thick layer of water-logged peat (Riley, 2011). This organic-rich ecosystem has sequestered nearly 30 Gt of carbon over the last 6,000 years and continues to exert a large influence on the global carbon cycle (Gorham, 1991; Glaser *et al.*, 2004; FNSAP, 2010). The tributaries of the HBL also contribute large quantities of freshwater and dissolved solutes such as dissolved organic carbon (DOC) to the saline James Bay and the Arctic Ocean (Rouse *et al.*, 1992; Kirk and Louis, 2009). The HBL ecozone is predicted to experience significant changes to climate (*i.e.*, temperature and precipitation patterns) during the next century (Colombo *et al.*, 2007; IPCC, 2013; Keller *et al.*, 2014), which are likely to modify the current hydrological regimes of these peatlands (Holden, 2005; Whittington and Price, 2006; McLaughlin and Webster, 2014). In addition, current and future mining operations in the HBL threaten to disturb natural peatland hydrological processes on a more localized but intense scale (Whittington and Price, 2012). Peatland hydrology and the accompanying transport of solutes is the most important factor influencing peatland initiation, development, and maintenance, and governs key aspects of peatland function including the accumulation of carbon, redox conditions, and nutrient availability (Mitsch and Gosselink, 2007). However, information on the movement of water through large contiguous northern peatland complexes, such as those found in the HBL, is scant, as most studies examining the groundwater hydrology of bogs and fens have been undertaken at scales, or in hydrogeological contexts, that are likely not transferrable to the peatlands of the HBL.

The majority of peatlands in the HBL are classified as either a bog or a fen, comprising 36% and 24% of the total area, respectively (Sjörs, 1959, 1963; Riley, 2011). Bogs are domed and often teardrop-shaped peatland landforms, typically >1 km^2 in size and with a crest rising at least 1 m above the neighboring landscape. The pore-water in bogs is acidic (pH < 4.2) due to their ombrotrophic nature (meaning that their only hydrological and nutrient inputs come from rain and snow) and vegetation cover is dominated by *Sphagnum* mosses and a sparse cover of stunted *Picea mariana* (black spruce) (*Ibid*.). They are considered to be largely disconnected from groundwater sources rich in base cations (*e.g.*, K^+, Ca^{2+}, Mg^{2+}), and thus are unable to neutralize the organic acids produced by *Sphagnum* species (van Breemen, 1995).

Fens are minerotrophic because of their lower geomorphic position in the landscape, receiving additional inputs of water and solutes from adjacent bogs and sometimes underlying unconsolidated and consolidated aquifers (NWWG, 1997). Because of these additional hydrological inputs, the water table in fen peatlands is less variable than in bogs, usually remaining at or near the ground surface throughout the growing season. Higher nutrient concentrations in the upper portion of the fen peat profile promote a greater diversity of vegetation, including *Carex spp.* (sedges), *Equisitem spp.* (horsetails), and stunted *Larix laricina* (tamarack) (*Ibid.*). Larger fens may develop into ribbed fens (also called patterned fens or water tracks) (Sjörs, 1948; Glaser, 1992). Ribbed fen systems exhibit characteristic parallel, alternating strings (ridges) and pools (troughs or flarks) situated perpendicular to the prevailing hydraulic gradient flow (Glaser, 1992), and tend to terminate at surface waters, delivering water, solutes, and energy to streams and tributaries which drain the peatlands. The arrangement of patterned ribbed fens draining into adjacent surface waters, interspersed with tear-drop shaped bog islands, is characteristic in the central regions of the HBL (Glaser, 1989).

The movement of groundwater in large, contiguous peatland complexes is generally governed by topography, the position of the water table relative to the surface, and the physical properties of the peat soils themselves, such as hydraulic conductivity (K) (Siegel and Glaser, 2006). In the Ivanov (1981) peatland runoff model (Figure 1.2), the flow of water is assumed to occur laterally only through the upper portion of the peat (often referred to as the acrotelm), a highly porous and hydrologically conductive layer that is relatively undecomposed, and which contains low concentrations of dissolved solutes (Bleuten *et al.*, 2006). During periods of high water table, or in the presence of an impermeable frost layer during snowmelt, water losses in peatlands can also occur as lateral surface flows, around ridges and through narrow surface channels (Holden *et al.*, 2008). According to Ingram (1982, 1983) and (Siegel and Glaser, 1987) (Figure 1.2), water may also flow laterally through the deeper, lower K peat or as vertically recharging/radially discharging groundwater through the entire peat profile including the permanently saturated catotelm.

Recently, peatland-derived runoff has been shown to consistently contribute about half of the total stream discharge of higher-order major tributaries of the Attawapiskat River, one of the largest rivers in the HBL (Orlova and Branfireun, 2014). Similarly, large-scale geomorphic analyses of high-resolution imagery of the Attawapiskat River watershed by Richardson *et al.* (2012) showed that relationships between stream discharge and gross drainage area were strong at low flows, but weakened during periods of high flows. Combined, the findings from these studies indicate that peatlands provide a consistent and crucial baseflow component to surface waters of the HBL, however the nature of hydrologic connectivity between peatland landforms and the delivery of water from the peatlands and into adjacent surface waters in this vast ecosystem is not well understood, particularly during wet (extremely saturated) conditions.

Despite their ecological significance, importance to global biogeochemical cycles (Riley, 2011), and concerns regarding the impact of climatic and landscape change to natural peatland processes and exports of DOC (Pastor *et al.*, 2003; Porcal *et al.*, 2009), the hydrology of bogs and fens in the HBL remains relatively understudied, with the exception of earlier studies by Sjörs (1959, 1963); Glaser (1989); Reeve *et al.* (1996, 2000, 2001) and more contemporary work by Richardson *et al.* (2012); Whittington *et al.* (2012); and White *et al.* (2014). Much work has been done on smaller peatlands, generally only a few square kilometres in size [*e.g.*, the Mer Bleue bog in southeastern Ontario (Fraser *et al.*, 2001b; 2001a)], and often underlain by impermeable bedrock or higher conductivity glacial till in close proximity to uplands (Branfireun *et al.*, 1996; Waddington and Roulet, 1997). Hydrological processes in larger peatlands, such as the Glacial Agassiz peatlands of Minnesota (USA), have been studied in some detail as well (see Wright *et al.*, 1992), but the underlying geology, topography, and scale of these systems are different from the peatlands of the HBL. Indeed, the very flat regional gradients (0.57 m km^{-1} towards Hudson Bay), nearly continuous wetland cover, absence of any significant upland contributing areas, and a low-conductivity ($K < 10^{-7}$ m s^{-1}) mineral substratum present a unique hydrogeological setting.

The most recent, and to our knowledge the most comprehensive, efforts at elucidating the meso-scale flow of water and transport of solutes between peatland landscape features in the HBL are the two-dimensional numerical simulations of groundwater flow in bogs and fens by Reeve *et al.* (2000, 2001) (Figure 1.2). These conceptual computer models have shown that lateral flows in the uppermost peat layer dominate the transport of water and dissolved solutes between bogs and fens in large peatland complexes with a gently sloping topography, and which are underlain by a thick layer of low permeability sediments. The vertical redistribution of solutes in the peatland is a result of dispersive mixing (and to a lesser extent diffusion) processes rather than advection, since vertical movement of water between bogs and the low permeability mineral substratum was found to be negligible, given the small vertical gradients and large hydraulic conductivity contrast between layers. These computer simulations were found to conform to field observations obtained from the Albany River drainage basin in HBL, but the limited spatiotemporal dataset, as well as oversimplification of the physical structure of the peatland landscape units in the model itself, demands further detailed, empirical investigations of groundwater flow in this environment. More specifically, the presence of heterogeneities in the physical properties of the peat (*i.e.,* anisotropy and soil pipes) (Beckwith *et al.*, 2003b, 2003a; Morris *et al.*, 2011), subtle fluctuations (*i.e.,* microtopography) (Van der Ploeg *et al.*, 2012) and breaks in topography (Freeze and Witherspoon, 1967), and the occurrence of other landforms such as ponds and open bodies of water (White *et al.*, 2014) not incorporated in these elementary two-dimensional models have the potential to significantly influence the flow of water, hydrologic connectivity, and the translocation and export of dissolved solutes in shallow groundwater systems of the HBL.

The objectives of this study are to improve our understanding of peatland groundwater hydrology in the HBL, with a particular focus on the distinctive bog-fen-tributary systems. Here we test the lateral surface flow versus vertical groundwater bog flow conceptual models discussed above using hydrometric measurements and geochemical tracers, and compare the resulting flow patterns of groundwater flow between an ombrotrophic bog and patterned fen to the theoretical numerical simulations presented by Reeve *et al.* (2000, 2001). Further, the groundwater hydrology of an adjoining patterned fen was explored in order to determine the degree of hydrological connectivity between peatland landscape units and the fen peatland to an adjacent, low-order tributary of the Attawapiskat River.

2.2 Study Site

A layer of 1.8-2.5 m deep peat covers the majority of the HBL, underlain by varying depths (0-65 m) of clay and silt-sized calcite and dolomite rock flour, layers of coarser sand deposits, and interspersed with pebble-sized clasts of igneous and metamorphic rock (Mcdonald, 1969; Glaser *et al.*, 2004). Large-scale topography is virtually non-existent, and discrete zones of discontinuous permafrost (palsas) and outcrops of karst limestone bedrock (bioherms) are the only upland features (< 6 m high above adjacent peatland surface) in the landscape (Kuhry, 2008; Whittington and Price, 2012). The cool and moist low-subarctic climate of the region is strongly influenced by Hudson Bay and the Arctic Ocean (Riley, 2011). Historical meteorological data (1971-2000) from the nearest long-term meteorological station in Lansdowne House, Ontario (52.23 °N, -87.88 °W) shows an average annual precipitation of 699 mm for the region with ~30% falling as snow (Environment Canada, 2011). The region experiences on average 153 days with a minimum temperature above 0 °C and average daily temperatures for January and July are -22 and 17 °C, respectively (*Ibid.*).

The study site location is a 4.9 km^2 subwatershed of the Trib 5 drainage basin [204 km^2, Richardson *et al.* (2012)], approximately 100 km west of Attawapiskat, Ontario, and 15 km south of the De Beers Victor Mine (Figure 2.1, 52.70 °N, -83.60 °W). The study location is the site of the Government of Ontario's Ministry of Environment (MOE) long-term carbon monitoring program, with two carbon dioxide, methane, and water vapour monitoring towers situated in the bog and fen (Figure 2.2B). The site comprises a *ca.* 6 km long patterned ribbed fen with an average topographic slope of 0.0013 that drains northwards towards a large, second-order tributary (Trib 5) of the Nayshkootayaow River (Figure 2.2A). Two raised, domed bogs bound the fen on the east and west margins (0.51 and 0.12 km^2, respectively) which taper off approximately 500 m away from the tributary.

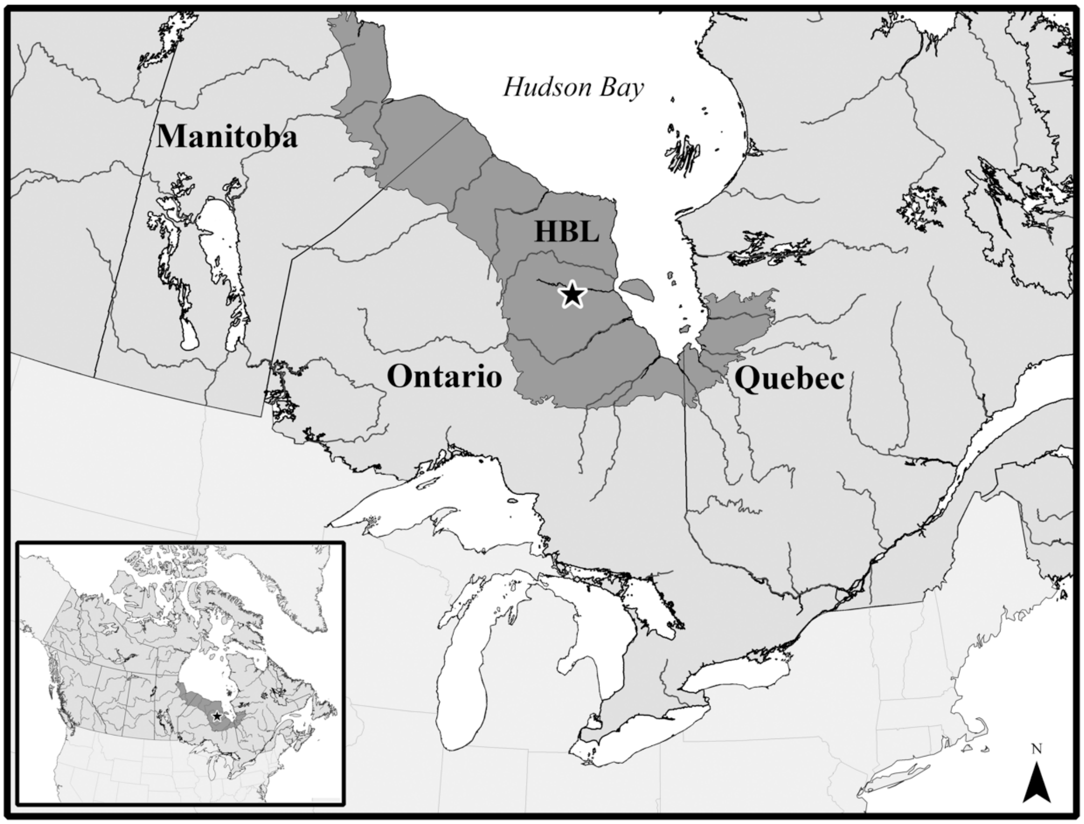

Figure 2.1. The study site (indicated by the black star) is located in the Hudson Bay Lowlands (HBL, dark grey), 100 km west of Attawapiskat, in northern Ontario, Canada.

This study focuses on the hydrological connectivity between the larger eastern bog and the ribbed fen. The eastern bog is classified as a domed bog (NWWG, 1997) because of its large, convex shape raised ~1 m above the surrounding fens. Multiple drainage features (internal water tracks) are present within the bog, consisting of large, circular ponds (up to 750 m^2) separated by ridges (5-10 m wide) at the bog crest, with ponds decreasing in size to <75 m^2 as they cascade downwards on either side of the bog divide toward the ribbed fen. Peat depth in the bog ranges between 2.0 and 2.3 m, and slightly less in the ponded areas. Average topographical slope along the bog water track feature is

-0.0018; nearly double that of the neighboring fen. Vegetation in the bog is dominated by an understory of mosses (*Sphagnum fuscum, rubellum, magellanicum, and capillifolium*) and lichen (*Cladonia rangiferina, mitis, and stellaris*). A sparse cover of stunted (<4 m) black spruce (*Picea mariana)* and tamarack (*Larix laricina*), as well as ericacheous shrubs including labrador tea (*Ledum groenlandicum)* and leatherleaf (*Chamaedaphne calyculata*), make up the majority of aboveground flora in the bog ridges and hummocks.

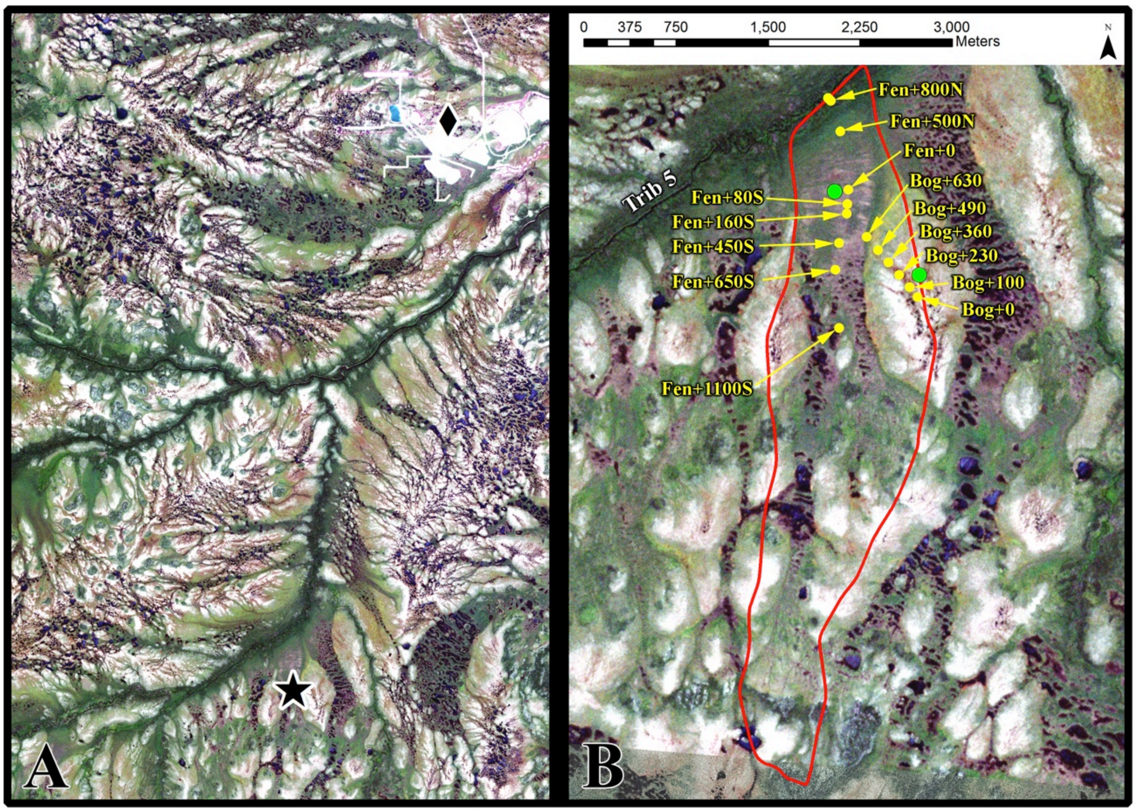

Figure 2.2. Satellite imagery showing **(A)** the location of the study site (black star) relative to the De Beers Victor Mine (black diamond) in the Hudson Bay Lowlands, and **(B)** the study site including the subwatershed (red line), locations and names of groundwater monitoring nests (yellow circle and labels), and position of the meteorological and eddy flux towers (green circles). IKONOS and RapidEye satellite imagery kindly provided by De Beers Canada and the Ontario Ministry of Natural Resources, respectively.

Bog edges are rather sharply demarcated by the large ribbed fen (Kuhry, 2008), where long, alternating ridges (strings) and hollows (troughs) extend throughout the width of the system perpendicular to the flow of groundwater. Troughs are 3-10 m wide and are dominated by sedges (*Carex lasiocarpa*) and horsetails (*Equisetum fluviatile*), while ridges are typically 1-2 m wide and comprise mosses (*Sphagnum rubellum* and *Dicranum* *fuscescens)* and stunted tamarack. This fen system is fed by groundwater from a loosely defined, large peat plateau contributing area to the south of the study site, in addition to the two domed bogs. Large circular ponds and open bodies of water (13-24,000 m^2) occur most frequently at the narrowest point in the fen (400 m width), diminishing in size and frequency to smaller, elongated shallow pools (<1,000 m^2) as the ribbed fen approaches the tributary, gradually doubling in width to more than 800 m at the tributary. The vegetation communities begin to transition slowly with increasing proximity to Trib 5, from sedge and tamarack dominated, to a dense thicket and swamp riparian zone of ericaceous shrubs such as bog birch (*Betula pumila*) and leatherleaf, and larger varieties of trees (>6 m in height) including tamarack, white spruce (*Picea glauca*), balsam poplar (*Populus balsamifera*), and paper birch (*Betula papyrifera*). Peat cover slowly decreases from 2.0-2.3 m in the fen to less than 1 m in the dense thicket, and effectively disappears approximately 100 m away from the tributary, where only a thin (<0.5 m) layer of tree roots and organic matter is in direct contact with the mineral substratum. This riparian environment has little resemblance to the fen, and contains small streams and surface waters incised into the marine sediment that deliver water directly into Trib 5.

2.3 Methods

The site is situated in a remote area of the HBL, so site access was limited to daylong visits by helicopter from the De Beers Victor Mine at *ca.* weekly intervals during the 2010 and 2011 snow- and ice-free seasons. A 1250 m raised wooden boardwalk connecting two eddy covariance flux towers was constructed in June 2010 to maintain long-term site integrity and minimize potential disturbance to the peatland. Two transects were established: a 630 m Bog-to-Fen (BF) transect running alongside the boardwalk within the large drainage feature in the bog, and an 1800 m Fen-to-Tributary (FT) transect traversing the ribbed fen and ending near the adjacent tributary (Figure 2.2B).

2.3.1 Hydrological Measurements

Snow surveys and frost table measurements were taken between April 13 and May 14 2013. Snow depth was surveyed at 10-20 m intervals along the boardwalk using a metal ruler. Depth to frost table was measured along the BF and FT transects by driving a 1 cm diameter steel rod into the ground until contact with ice was made. Frost table thickness was determined by driving the steel rod into the ice until breakthrough at depth.

Groundwater monitoring wells and piezometer nests were installed along the two transects beginning in November 2010, and continuing from May to June 2011 when the majority of seasonal ice had thawed (Figure 2.2B). Wells and piezometers were constructed from 0.125 m I.D. Schedule 40 PVC pipe; wells were slotted throughout the length of the pipe, while a 0.1 m slotted intake was placed at the bottom of each piezometer. All wells and piezometers were screened in 250 μm Nitex® nylon mesh to prevent coarse particulate matter from clogging the pipe or slot intake. Piezometers were installed into the peat by boring a hole with an auger slightly smaller in diameter than the PVC pipe to minimize smearing of the slotted intake during installation. All piezometers were sealed with vented caps to prevent any contamination from debris entering the top of the pipe throughout the season, while allowing for pressure equalization with the atmosphere. All piezometers and wells were developed (purged) after installation by repeated pumping with a peristaltic pump, removing any loose material present due to installation.

Six piezometer nests were installed in the BF transect, placed at approximately 100 m intervals within the series of ponds and ridges in the internal water track feature. Eight piezometer nests were installed in the ribbed fen along the longitudinal axis (presumed direction of groundwater flow). Each of the fourteen monitoring nests comprise one fully-penetrating well installed to a depth of 1 m below the peat surface, and piezometers at 0.5, 1.0, 1.5, and 2.0 m below the peat surface. When peat depth was less than 2 m, piezometers were installed just above the contact of the marine sediment. Piezometers were also installed into the first metre of marine sediment within 200 m of Trib 5, where peat cover was typically less than 0.5 m. A monitoring well was also installed at the tributary to measure water level over the season. Monitoring nests in the bog and fen were named according to approximate distance in metres (and relative direction) from the bog crest (*e.g.*, Bog+100) and fen flux tower (*e.g.*, Fen+500 N), respectively.

Continuous water table measurements were obtained at hourly intervals from eight of the fourteen monitoring nests for the majority of the snow and ice-free season (May 15 to October 19, 2011) using pressure transducers (Schlumberger Micro-Divers®, accuracy = ± 0.01 m) placed inside the wells, and later corrected for barometric pressure using a continuously logging Schlumberger Baro-Diver ®. Manual measurements of hydraulic head at each well and piezometer were taken at *ca.* weekly intervals (exact measurement interval was dependent on accessibility to piezometer nests) by measuring distance from the pipe top to water level using a blow stick, a 1.5 m long, 0.013 m O.D. PVC conduit with a tape measure encasing 2.5 m of Tygon® tubing (measurement error = ± 0.004 m). Each of the piezometers and wells were adjusted to the original installation depth throughout the season, if needed. Bail tests (Hvorslev, 1951) were conducted on all piezometers to determine the *in situ* saturated hydraulic conductivity of the peat at various depths and locations (Freeze and Cherry, 1979). Results from multiple bail tests at each piezometer taken throughout the year were averaged to provide a mean value of K at the specific location and depth of peat.

Continuous stage data for Trib 5 was collected by placing a pressure transducer into the well installed within the tributary, and missing data was filled by regressing stage data for Trib 5 from a regularly gauged station 3 km downstream, kindly provided by De Beers Canada, who monitor the major streams and tributaries in this area as part of their environmental monitoring program.

All monitoring wells, piezometers, and land elevations were surveyed at least once with a Topcon (Tokyo, Japan) HiPER GL RTK differential global positioning system (DGPS) (horizontal and vertical accuracy is +/- 0.01 and 0.003 m, respectively), relative to the UTM Zone 17N NAD83 datum (henceforth referred to as meters above sea level or m.a.s.l.). Peat depth was surveyed along each transect by driving an auger through the peat until contact with the underlying sediment was made.

Precipitation and evapotranspiration data were collected by the Ontario Ministry of the Environment (MOE) and kindly provided for this study. Total precipitation was measured from the two flux towers at the site, compared and gap-filled with data from a nearby station 15 km away. Evapotranspiration (ET) in the bog and fen was measured at two 4 m tall eddy flux towers (fetch = 400 m radius). Actual ET was modeled using the following approach, presented here for transparency as per Humphreys (2013): Latent heat fluxes were measured via eddy covariance methods which utilized an LI7200 IRGA and Gill HS-50 sonic anemometer to measure water vapour mixing ratio and vertical velocity, respectively. Data was collected at 10 Hz and calculated as 30 min flux intervals after 3-axis coordinate rotation. Missing data was gap-filled using an interpolation method for periods with gaps of 1 or 2 samples. Otherwise, a linear relationship was developed using a 200 sample moving window (in steps of 40 samples) with net radiation. When no net radiation data was available, the potential global radiation was used to estimate net radiation.

Watershed delineation was courtesy of Jean Bouffard and Murray Richardson at Carleton University, done using Digital Elevation Model (DEM) data from a partial Light Detection and Ranging (LiDAR, 5 m resolution) dataset acquired for a previously funded research project, and combined with Shuttle Radar Topography Mission data (SRTM, 30 m resolution), IKONOS satellite imagery, and aerial interpretation of aerial photographs.

2.3.2 Water Sampling and Analysis

Sample collection of major ions and stable water isotopes was campaign-based, where the majority of surficial pore-waters (integrated 0-5 cm relative to the water table) and piezometers were sampled on May 17, June 25, August 20, and October 19, 2011. Water sample collection was accomplished using a low-flow peristaltic pump and pre-cleaned PTFE sample tubing, and collected into clean 125-250 mL PETG bottles. Piezometers were regularly (*ca.* biweekly) purged to dryness, and 1-3 days before samples were taken. Samples were also taken by hand from the snow, ponds, rivulets, and the tributary throughout the season. Rain samples for stable water isotope analysis were collected at the De Beers Victor Mine using a funnel that drained into a sealed container that was emptied and replaced after the majority of precipitation events. Deep groundwater samples from the limestone bedrock aquifer were obtained from monitoring wells installed by De Beers located <20 km away from the study site. Although these bedrock wells are not in close proximity to the site, they were utilized since they are the only way to estimate the isotopic composition of the karst limestone aquifer. A local meteoric water line (LMWL) of stable water isotopes was generated using samples of rain and snow collected within 15 km of the site between 2008-2011.

Multiple sample duplicates and field and sample line blanks were taken during each sampling campaign as part of a Quality Assurance and Quality Control sampling program (QA/QC). Samples were stored in the dark at 4 °C and filtered under vacuum using 0.45 μm nitrocellulose membrane filters within 48 hours of sample collection. Measurements of sample pH were done on the unfiltered sample fraction during sample filtration using a bench top pH meter, calibrated daily and checked before use. Sample filtrate was then split into appropriately sized HDPE bottles and preserved, depending on analytical requirements: samples for ion analysis were poured into 30 mL HDPE bottles and frozen for the duration of the study period, whereas samples for stable water isotope analysis were stored at 4 °C without headspace in sealed 20 mL HDPE scintillation vials and PTFE-lined displacement caps.

Samples were analyzed at the end of the field season at University of Western Ontario analytical laboratories (Ecohydrology Lab and the Biotron Institute for Experimental Climate Change) in London, Ontario under strict QA/QC guidelines. Water samples were analyzed for stable oxygen ($\delta^{18}O$) and hydrogen (δD) water isotopes using Cavity Ring Down Spectroscopy (Picarro L2120-i), with values reported relative to Vienna-Standard Mean Ocean Water (VSMOW, precision: $\delta^{18}O \pm 0.1$ ‰, $\delta D \pm 0.5$ ‰). Cations (Na^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, SO_4^{2-}) were analyzed in the Biotron (CALA ISO 17025 certified) using Dionex ICS-3000 and Dionex ICS-1600 ion chromatography systems, respectively. Limits of detection for major ions were typically between 0.1-0.5 mg L^{-1}. All sample, filter, field, and travel blanks contained unquantifiable concentrations of solutes (where applicable) and the relative percent difference of sample duplicates was consistently less than 20%, thus the resulting analytical data was deemed acceptable.

ArcGIS 10.0 (Esri) was used in the creation of study site maps and water table contouring. Surfer (Golden Software) was used for contouring of cross sections and pore-water chemistry. Statistical analyses and data presentation was done using Prism® (Graphpad Software).

2.4 Results

2.4.1 Hydrology

The site received 657 mm of total precipitation in 2011, slightly below the mean annual precipitation for this region, with 443 mm falling during the study period (May 15 to October 19; 157 days) (Figure 2.3A). Five major storm events, particularly in the latter half of the year, contributed to more than half of the total precipitation for the study period. Total annual (and duration of study period) evapotranspiration in the bog and fen was 333 (280) and 354 (293) mm, respectively (data not shown).

A snow and frost-depth survey conducted on April 13, 2011 (before any observed significant snowmelt) revealed considerable heterogeneity in snow depth along the two transects. Forested areas (*i.e.*, patches of black spruce in the bog, and the thicket/swamp riparian zone at the distal end of the fen) had slightly greater snow cover, consistent with recent work by Whittington *et al.* (2012). Mean (±standard deviation) snow depth in the bog was 33.3±18.3 cm, with some treed areas containing 80 cm of snow cover while other smaller patches some open areas were completely barren. Snow cover in the fen was less variable and averaged 34.0±7.7 cm, with the majority of the land surface covered in >18.0 cm of snow before any significant melt had occurred. The frost table in the bog was generally closer to the surface, thicker, and persisted longer than in the fen. Average surface-to-frost table depths in bog hummocks and hollows were 8.8±1.8 cm and 8.1±3.4 cm on April 30, 2011, respectively. The ground-ice layer in the bog was 11.4±5.9 cm thick, on average. Depth to the frost table in fen ridges was 14.0±3.4 cm, and was much more variable in the troughs (14.0±29.5 cm). The frost layer in the fen was much thinner, as compared with the bog, only 2.8±6.4 cm thick.

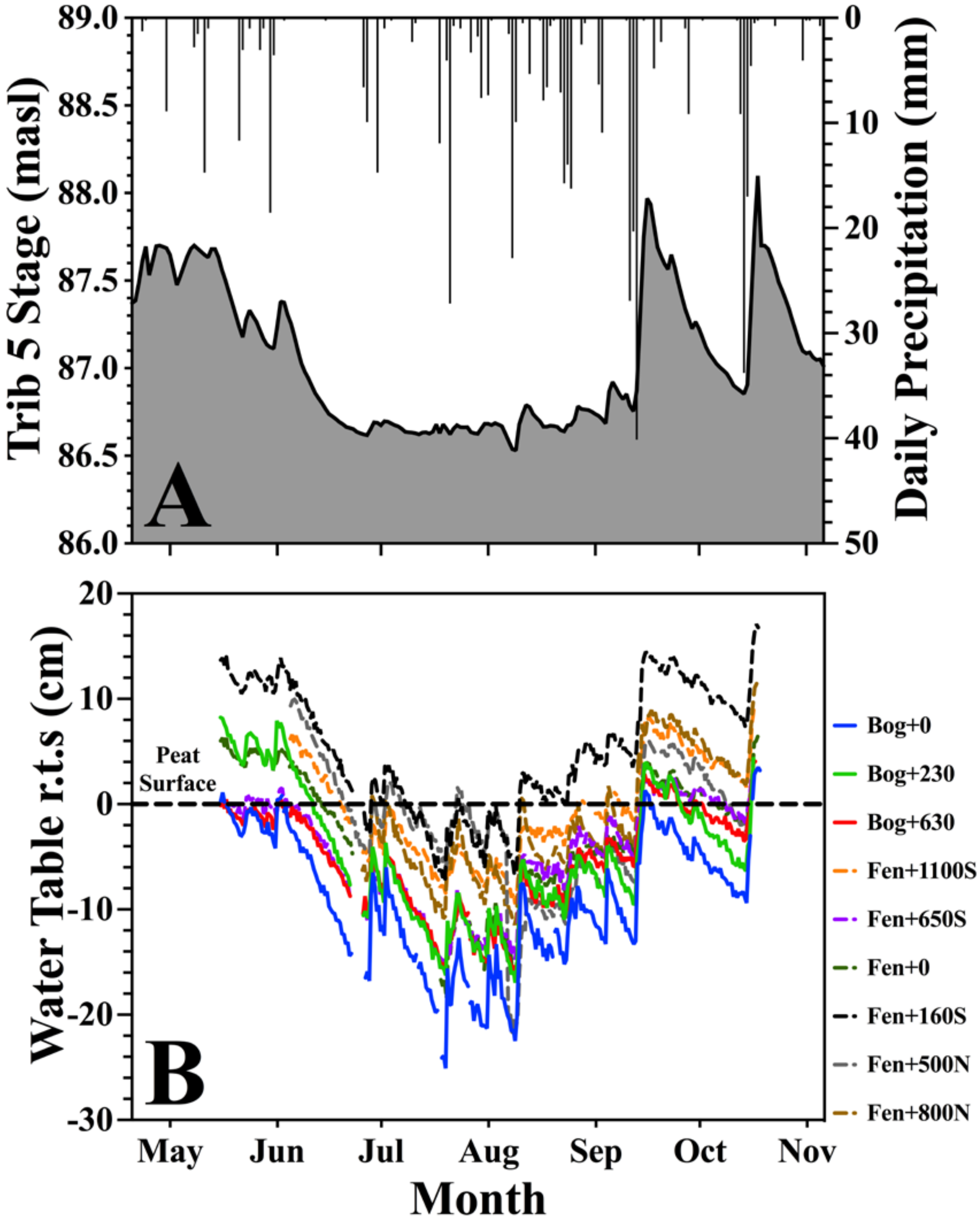

Figure 2.3. (A) Continuous stage measurements in Trib 5 (dark grey, m.a.s.l.) and total precipitation (black bars, mm), and **(B)** continuous water table position in groundwater monitoring wells relative to the average peat surface (r.t.s.) at each monitoring nest for the duration of the study period. Solid and dashed lines represent wells in the BF and FT transect, respectively.

Although mean daily air temperatures remained below 0 °C until May 25, 2011, above-freezing daytime temperatures in early May caused virtually all snow and frost at the site to melt by May 14, 2011; however, sporadic patches of snow in the riparian zone near Trib 5 persisted until early June. The rapid melting of snow, and small inputs in the spring resulted in high water tables across the peatland landscape, as well as high stream level in Trib 5. The rate of the stage recession in Trib 5 was faster than the water table recession in all of the monitored peatland wells. Stream levels fell more then ~0.4 m during the month of May, yet high water tables (at or above the average peat surface) did not start to recede until early June.

The pattern and magnitude of water table fluctuation in response to precipitation events was distributed similarly across all locations along both transects throughout the study period (Figure 2.3B). The major differences between sites are related to microtopography as well as the position of the water table relative to the peat surface (r.t.s.), where fen wells tended to have water tables at or above the peat surface (0 to 10 cm r.t.s) during the wetter periods in spring and fall. Rapid snowmelt in early May sustained a high mean water table in both the bog water track (~2.5 cm) and ribbed fen (8.2 cm), peaking in early June. Immediately after the snowmelt period, the water tables in the bog tended to remain below the peat surface in ridges and lawns, and 5-10 cm above the peat surface around lower-lying ponds and in hollows. The fen water table generally peaked at 5-10 cm above the peat surface in troughs (and in areas adjacent to ponds), but it did not appear to consistently rise above any of the numerous ridges within the fen. Significant and prolonged overland flow was not observed at the site after the melting of the frost table, because of the prevalence of hummock and hollow microtopography, pools, and ridges, which act as barriers to extended flow and limit the amount of surface runoff that can occur over long distances.

Little precipitation over the month of June resulted in a steady decline in water table position. Wells placed at the bog crest (Bog + 0) and in the middle of the bog water track (Bog + 230) exhibited slightly higher rates of water table recession (-0.67 to -0.61 cm d^{-1}) than at the bog margins (Bog +630) and wells placed throughout the ribbed fen (-0.59 to -0.35 cm d^{-1}). Larger (>20 mm) precipitation events in the later part of summer resulted in rapid rises to the water table (8 to 12 cm), followed by comparable rates of decline in all wells. Water tables remained below the average peat surface for the majority of the summer at nearly all monitored wells at the site, and climbed steadily in the beginning of September due to large, frequent precipitation events, returning to snowmelt levels in October.

2.4.2 Hydraulic Conductivity

Saturated hydraulic conductivity was highly heterogeneous in the upper portion of the peat profile (Table 2.1). In general, the bog (0.079-10.337 m d^{-1}) had on average higher K than the fen (0.003-9.861 m d^{-1}), and both landforms showed significant decreases in K with depth. The K in the bog and fen at a depth of 2 m (0.003-0.0193 m d^{-1}) was typically 2-3 orders of magnitude lower than in the shallowest measured layers (3.887-10.337 m d^{-1}), and was similar to the K of marine sediment (0.004±0.001 m d^{-1}). Areas near bog ponds exhibited the highest K measured, particularly at the shallowest (0.5 m) piezometers (10.337 m d^{-1}), whereas measured K values of lawns and ridges were slightly slower and comparable to each other. A similar trend was observed between piezometers installed near ponds in the patterned fen, where near-pond K measurements were approximately twice as high in the upper 1 m of peat (1.029-9.861 m d^{-1}) when compared to other portions of the fen at the same depths (0.592-5.868 m d^{-1}). Interestingly, piezometers installed at 1.5 m in bog ponds and ridges exhibited higher K values (6.892±3.516 and 1.635±2.506, respectively) than shallower or deeper piezometers at the same nests.

Table 2.1. Saturated hydraulic conductivities (m d^{-1}) for each landform and depth below peat surface, as determined by *in situ* bail tests. Multiple tests per standpipe piezometer throughout the study period are reported as the arithmetic mean±standard deviation, with the number of bail tests for each landform and depth given in brackets.

Depth Below Surface (m)	Bog – Lawns	Bog – Pools	Bog - Ridges	Fen - Troughs	Fen – Pools
0.5	3.887±0.699 (3)	10.337±4.661 (3)	7.224±3.986 (5)	5.868±5.981 (12)	9.861±5.393 (5)
1.0	0.615±0.319 (2)	0.979 (1)	0.051±0.048 (4)	0.592±0.375 (8)	1.029±1.094 (2)
1.5	0.280±0.028 (2)	6.892±3.516 (3)	1.635±2.506 (7)	0.176±0.041 (8)	0.900 (1)
2.0	0.100 (1)	0.079 (1)	0.193±0.143 (4)	0.005±0.007 (4)	0.003 (1)

2.4.3 Hydraulic Gradients

A plan view of the water table topography for dry (July 19, 2011) and wet (October 17, 2011) conditions is shown in Figures 2.4A and 2.4B, respectively. Lateral hydraulic gradients follow the general topographic relief of the landscape. Under both wet and dry conditions, the higher water table elevations in the bog direct groundwater down through the water track in the bog, and into the fen. The overall water table gradient of the subwatershed is northwards towards the Trib 5, and coincides with the string and trough vegetation patterns in the ribbed fen (Figure 2). Equipotential lines show a slight outwards movement of water along the FT transect, matching the increasing width of the ribbed fen with decreasing distance to Trib 5. Differences in lateral hydraulic gradients throughout the peatland are very small between low and high water tables. Bog water table gradients are slightly higher (-0.0018 to -0.0016) than in the majority of the fen (-0.0016 to -0.0012) because of the greater topographic relief. The highest lateral gradients (-0.007 to -0.005) occur in the ribbed fen in close proximity (100-200 m) to Trib 5 where peat depth significantly decreases and marine sediments begin to outcrop. Groundwater flow is shown to concentrate around the nest at Fen+900 N that is adjacent to a rivulet, which is likely a major source of fen drainage during periods of high water table.

Two-dimensional cross sections displaying groundwater flow through the peat profile, generated from hydraulic head measurements in piezometers for the BF and FT transects at low (June 25) and high (October 17) water table positions, are shown in Figures 2.5 and 2.6, respectively. In all instances, equipotentials are principally vertical, signifying that groundwater flow in both peatland types is dominantly lateral, as indicated by the generalized flow lines (black arrows). The hydraulic gradient in the bog is quite uniform throughout the length of the BF transect (~ -0.002), with a slight steepening approaching the break in slope in the underlying substrate between 400-600 m along the transect. Equipotentials are very evenly spaced along the majority of the FT transect (-0.0014), but the hydraulic gradient steepens considerably (0.004) at 1600 m (Fen+500 N), associated with increased proximity to the surface water tributary and the thinning of the surface peat layer (Figure 2.6).

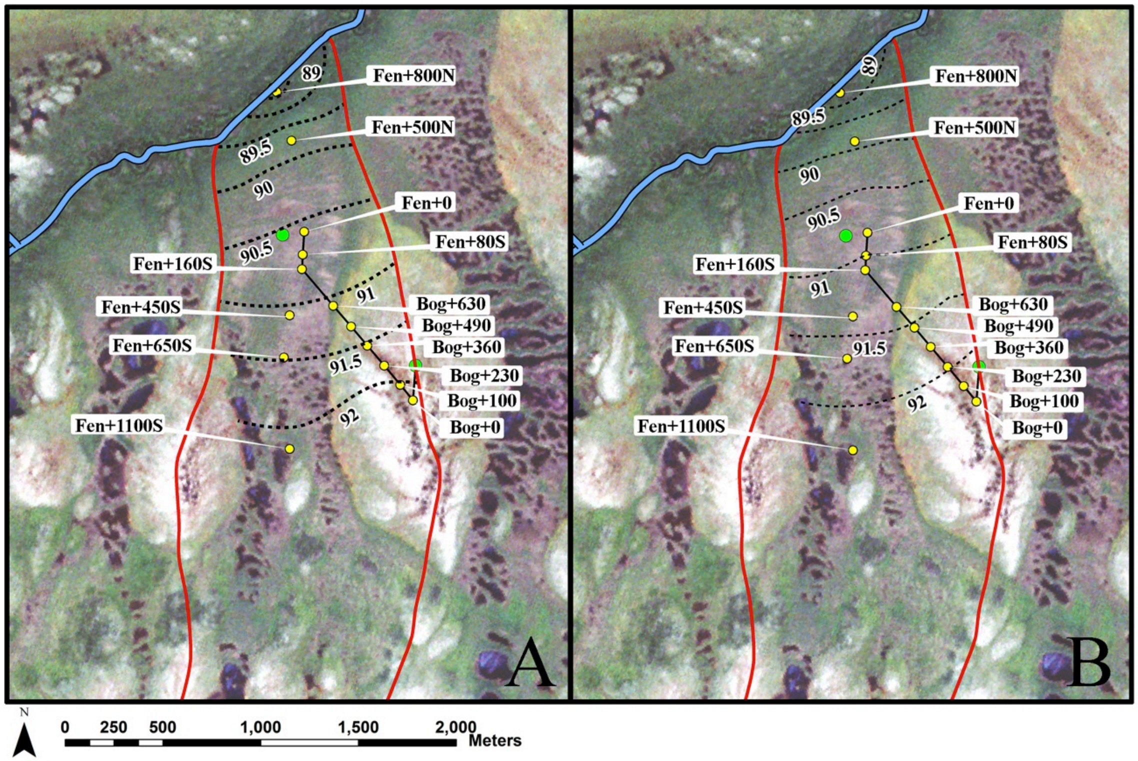

Figure 2.4. Map view of lateral hydraulic gradients at the study site during at two periods of water table extreme: **(A)** dry (low water table) on July 19, and **(B)** wet (high water table) on October 17, 2011. Dashed lines indicate equipotentials generated using the hydraulic head data from groundwater wells, relative to surveyed datum. A solid red line, and yellow and green circles denote the study site subwatershed, groundwater monitoring nests, and eddy flux towers, respectively.

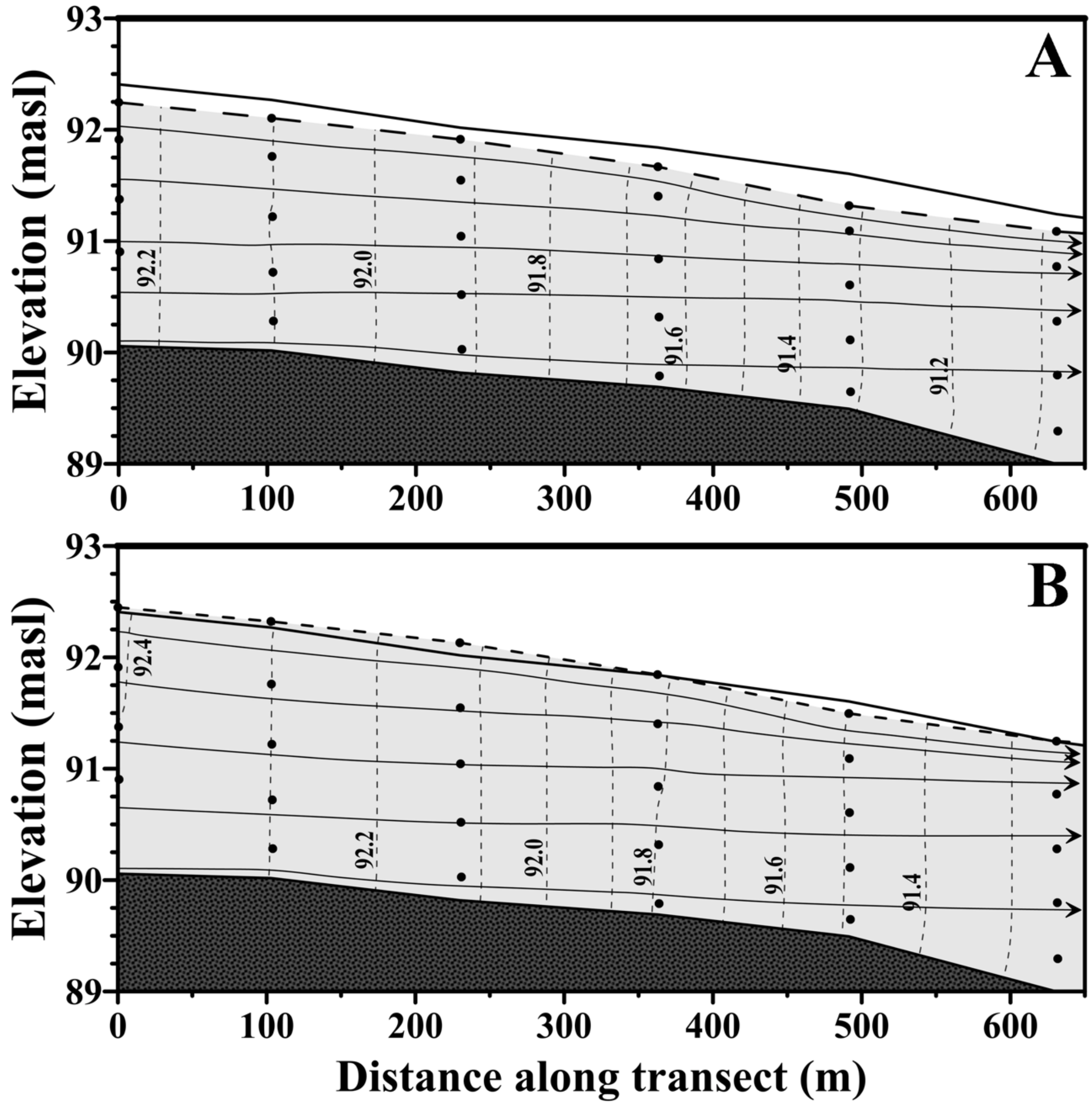

Figure 2.5. Vertically exaggerated (75x) peat cross section of the BF transect overlying marine sediment (speckled dark grey) during **(A)** low water table on June 25, and **(B)** high water table on October 17, 2011. The uppermost dashed and solid lines show water table and peat surface, respectively. Generalized flow lines are shown as black arrows. Black dots represent piezometer measurement points and vertical dashed lines represent equipotential at 0.1 m intervals, relative to the surveyed datum.

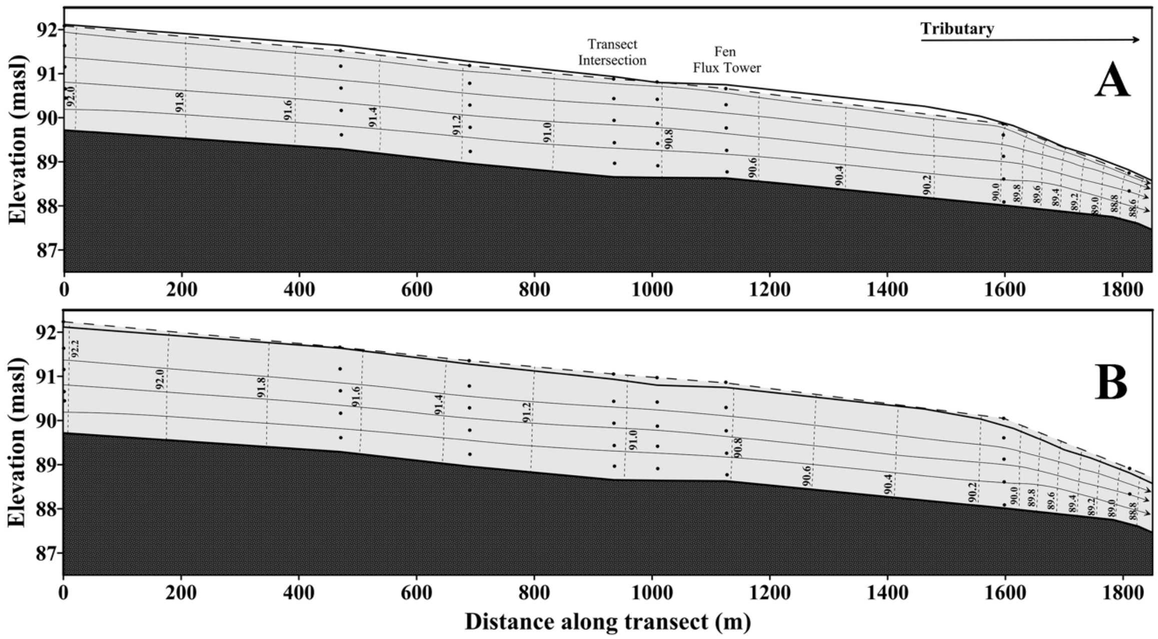

Figure 2.6. Vertically exaggerated (80x) peat cross section of the FT transect overlying marine sediment (speckled dark grey) during **(A)** high water table on June 25, and **(B)** low water table on October 17, 2011. The uppermost dashed and solid lines show water table and peat surface, respectively. Generalized flow lines are shown as black arrows. Black dots represent piezometer measurement points and vertical dashed lines represent equipotential at 0.2 m intervals, relative to the surveyed datum.

Water levels in the piezometers in the BF and FT transects varied depending on season, height of water table, proximity to open bodies of water, and distance from tributary (Figures 2.7 and 2.8). The majority of piezometers in the bog had water levels below the water table, signifying downward vertical flow through the peat column (indicated by the negative sign). Vertical gradients were small (<-0.01) and often negligible between the surface and 0.50 m piezometers at all nests. Larger downward vertical gradients (-0.01 to -0.1) typically occurred in the middle portion of the peat profile. The largest vertical gradients were measured between the 0.5 and 1.0 m piezometers, at Bog+0 on May 26 (-0.13) and October 18 (-0.11), as well as at Bog+100 on May 15 (-0.09) and May 26 (-0.12). The magnitude and variability in vertical gradients in the BF transect decreased downslope approaching the ribbed fen. Vertical gradients were largely absent at the bog margin (Bog+630) throughout the study period. Groundwater flow reversals (a change from negative to positive vertical gradients) were identified at many of the bog nests during extended periods of low water table and low incident precipitation (June 22-July

17. The most significant reversal in vertical hydraulic gradients occurred at Bog+100 on July 17 (0.07, between 0.5 and 1.0 m) and Bog+230 on May 26 (0.06, between 1.0 and 1.5 m).

Vertical gradients in the FT transect were typically much more subtle and temporally consistent than in the BF transect. Small upward gradients (<0.06) were measured in most of the shallower piezometers (0.5 and 1.0 m) in nests between Fen+650S and Fen+0. Below a depth of 1.5 m, water levels in the piezometers were at or below the water table in all deep majority of the season, indicating consistent downward gradients at depth. The largest of these deep downward gradients (-0.24 to -0.02) occurred at Fen+160S. One significant groundwater reversal was also detected at this nest on May 15 at the shallowest piezometer (0.04). The nest at Fen+500N did exhibit the largest overall variation in vertical gradients (-0.01 to 0.28), with the highest gradients observed during higher water table conditions. The monitoring nest at Fen+1100S showed consistent downward gradients for the duration of the study period (-0.04 to -0.07) between the surface and 0.5 m piezometers, and positive gradients (0.10 to 0.13) between 0.5 and 1.0 m for the duration of the study. A very large positive gradient was also detected at this nest on July 26 (0.26); however, this is likely a measurement error as there is no physical basis for such a high calculated gradient nor was it observed at any other time.

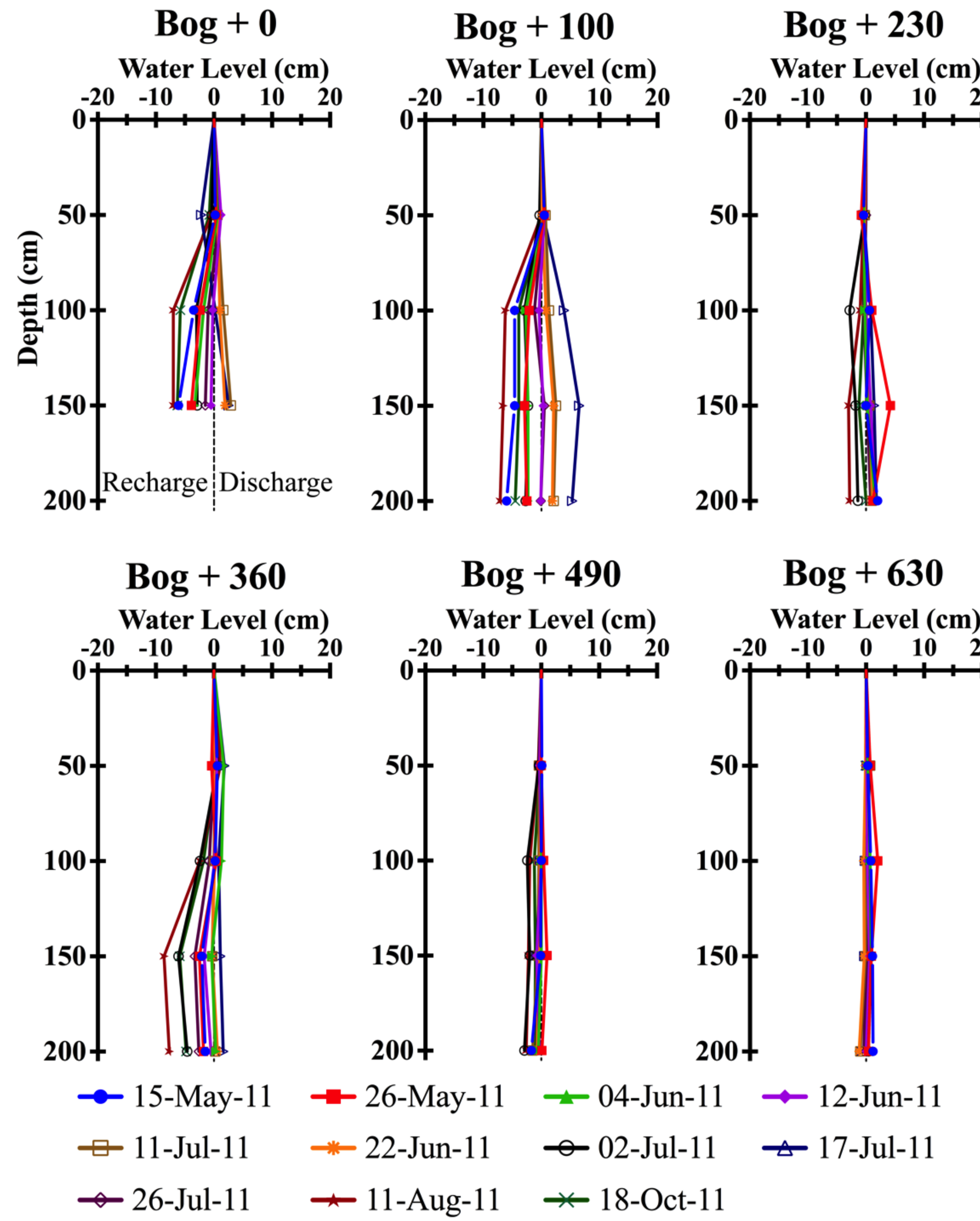

Figure 2.7. Water level measurements relative to the water table (cm) at each groundwater monitoring nest in the BF transect, Hudson Bay Lowlands, Canada. Positive and negative values of water level indicate areas of discharge and recharge, respectively, at a given point, and slope of the line between two points signifies the magnitude of the vertical hydraulic gradients.

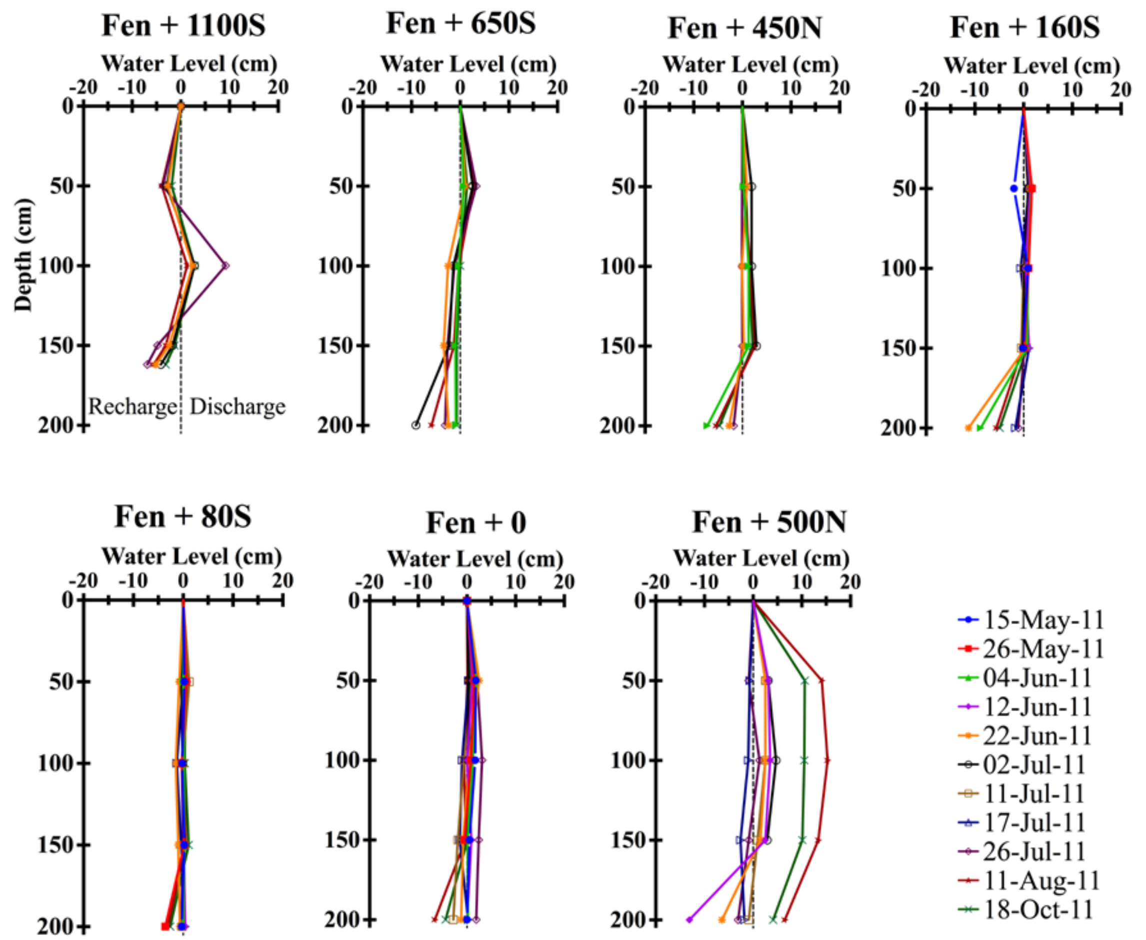

Figure 2.8. Water level measurements relative to the water table (cm) at each groundwater monitoring nest in the FT transect, Hudson Bay Lowlands, Canada. Positive and negative values of water level indicate areas of discharge and recharge, respectively, at a given point, and slope of the line between two points signifies the magnitude of the vertical hydraulic gradients.

2.4.4 Pore-Water Chemistry

2.4.4.1 Major Ions

Surface and pore-waters along the BF and FT transects were generally dilute in dissolved major ions, and only chloride (Cl^-), sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) were consistently quantifiable in all samples (Cl^-, Na^+, and Mg^{2+} data not shown). Concentrations of Cl^- were very low in the BF transect throughout the study period, <1 mg L^{-1} near the peat surface and increasing very slightly to <2 mg L^{-1} in the deepest piezometers. FT transect pore-water Cl^- concentrations were similar to those in the BF transect, but slightly more variable in space throughout the season. Concentrations of Na^+ were also very low in the bog (<2 mg L^{-1}), with no significant change with depth. Fen Na^+ concentrations were slightly higher (2-15 mg L^{-1}), exhibiting a gradual linear change increasing with depth. Changes in Na^+ concentrations due to seasonality were small, and imperceptible due to large spatial variability within each transect.

Interpolated and contoured cross sections of calcium (Ca^{2+}) groundwater concentrations in the bog and fen are presented in Figures 2.9-2.10. Concentrations of calcium was fairly stratified along the length of the BF transect, particularly in late spring, showing a gradual, linear increase in concentrations from <5 mg L^{-1} at the surface to nearly 100 mg L^{-1} near the peat contact with the mineral soil. However, some undulating patterns of Ca^{2+} are visible in the interpolated bog cross sections, where areas adjacent to ponds show slightly lower concentrations at depths of 1 m. Increases to Ca^{2+} in the near surface peat pore-waters seem to occur in late August (data not shown), suggesting greater influence from deeper calcium-laden groundwater or evaporative enrichment. These higher concentrations seem to occur in close proximity to ridges in the bog's internal water track feature as well as the transition zone between the bog and fen. Increases in bog pore-water alkalinity also correspond to changes to pH (data not shown), increasing from very acidic (pH 4.0-5.0) at the surface to circumneutral (pH 6.5 to 7.2) near the marine sediment. Changes to pore-water pH over the course of the study period were observed at most of the sites, but were often small (<0.5 pH units) and inconsistent.

Fen pore-water Ca^{2+} concentrations also increased with depth and proximity to the marine sediment, but spatial heterogeneity was more significant along the length of the FT transect than the BF transect. Near-surface Ca^{2+} concentrations were typically 10-40 mg L^{-1}, more than 2-5x higher as compared with the bog. Increases in Ca^{2+} concentrations over the season were significant throughout the fen (data not shown), especially at Fen+500N. Discrete zones of higher Ca^{2+} concentrations (80-100 mg L^{-1}) at 1 m below the peat at 700 m and 1300 m along the FT transect suggest an enhanced localized influence from the underlying mineral substratum. Higher pH values in the fen reflect increased alkalinity, where even shallow pore-waters range from pH 6.5 to 7.0. Like the bog, peat profiles in the fen showed increasing pH with depth to a maximum of 7.1-7.5. However, seasonal changes to pH were small and less pronounced than in the bog.

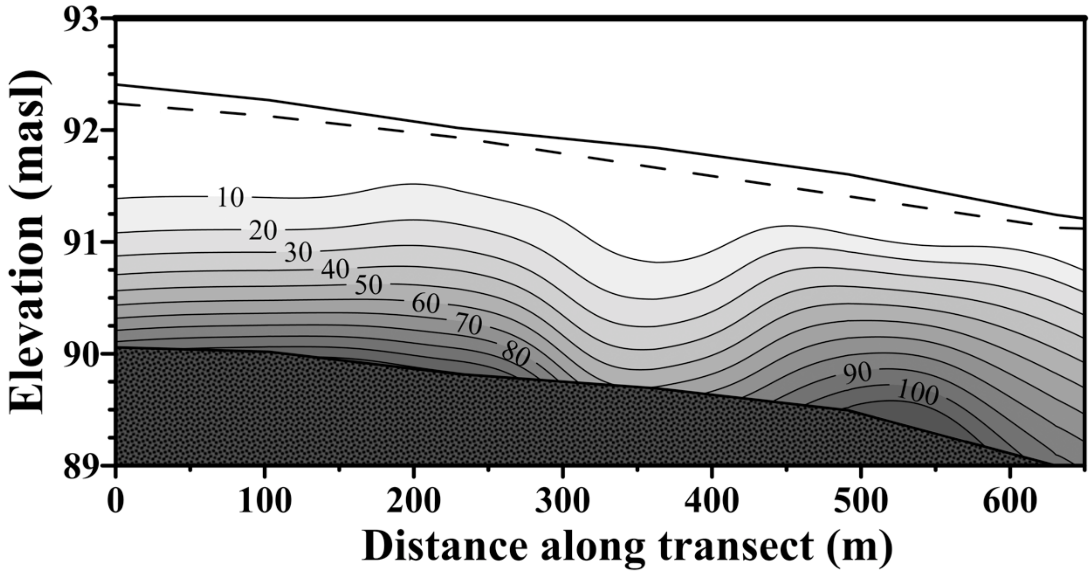

Figure 2.9. Vertically exaggerated cross sections of the BF transect showing interpolated Ca^{2+} concentrations (mg L^{-1}) overlying marine sediment (speckled dark grey) on June 25, 2011. Contours are shown every 10 mg L^{-1}. The uppermost dashed and solid lines show the water table and peat surface, respectively.

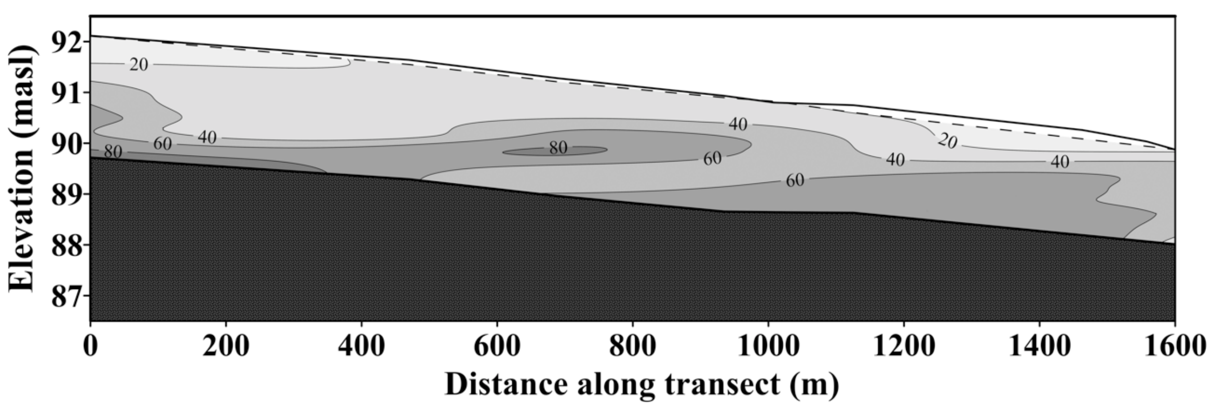

Figure 2.10. Vertically exaggerated cross sections of the FT transect showing interpolated Ca^{2+} concentrations (mg L^{-1}) overlying marine sediment (speckled dark grey) on June 25, 2011. Contours are shown every 20 mg L^{-1}. The uppermost dashed and solid lines show the water table and peat surface, respectively.

2.4.4.2 Stable Water Isotopes

Stable oxygen and hydrogen isotope compositions of waters obtained from various sources, including precipitation (rain and snow), peat pore-waters, marine sediment and bedrock-derived groundwater, and Trib 5 are reported in Figure 2.11. The Local Meteoric Water Line (LMWL, $\delta D = 7.72\delta^{18}O + 6.63$ ‰) for the region is comparable to the Global

Meteoric Water Line (GMWL, $\delta D = 8\delta^{18}O + 10$ ‰). Rain and snow samples exhibit a large seasonal range in isotopic compositions ($\delta^{18}O$ -24 to -8 ‰; δD -170 to -50 ‰). Precipitation tends to become more depleted in the heavier isotopes throughout the year, and is especially lighter in the winter months ($\delta^{18}O$ = -24 to -16 ‰, δD = -117 to 115 ‰). Although the spread of water isotope values is large within the different source of water in the study site, the isotopic composition of peatland pore-water samples is heavily influenced by fall and winter precipitation. With the exception of the bedrock groundwaters, all water samples plot on or below the LMWL, suggesting evaporative enrichment in the heavier oxygen and deuterium isotopes. Many bog waters at the peat surface and in the shallower (<1 m) piezometers plotted directly on the LMWL, whereas nearly all of the fen pore waters displayed isotopic compositions characteristic of evaporation. The heaviest evaporative signatures were found in larger ponds located in the fen. Pore-waters from marine sediments generally exhibited spatiotemporal coherence at each site, and revealed nominal evaporative enrichment. The isotopic composition of Trib 5 surface waters resembled fen pore-waters at 2.5 and 50 cm ($\delta^{18}O$ = -12.6 to -13 ‰, δD = -92 to -98 ‰), as well as marine sediments at lower flow conditions ($\delta^{18}O$ = -14.6 ‰, δD = -108 ‰). Most of the samples obtained from limestone bedrock plot above the LMWL, which indicate exchange between water and oxygen containing minerals such as carbonates, and have a lighter isotopic composition that is similar to winter precipitation.

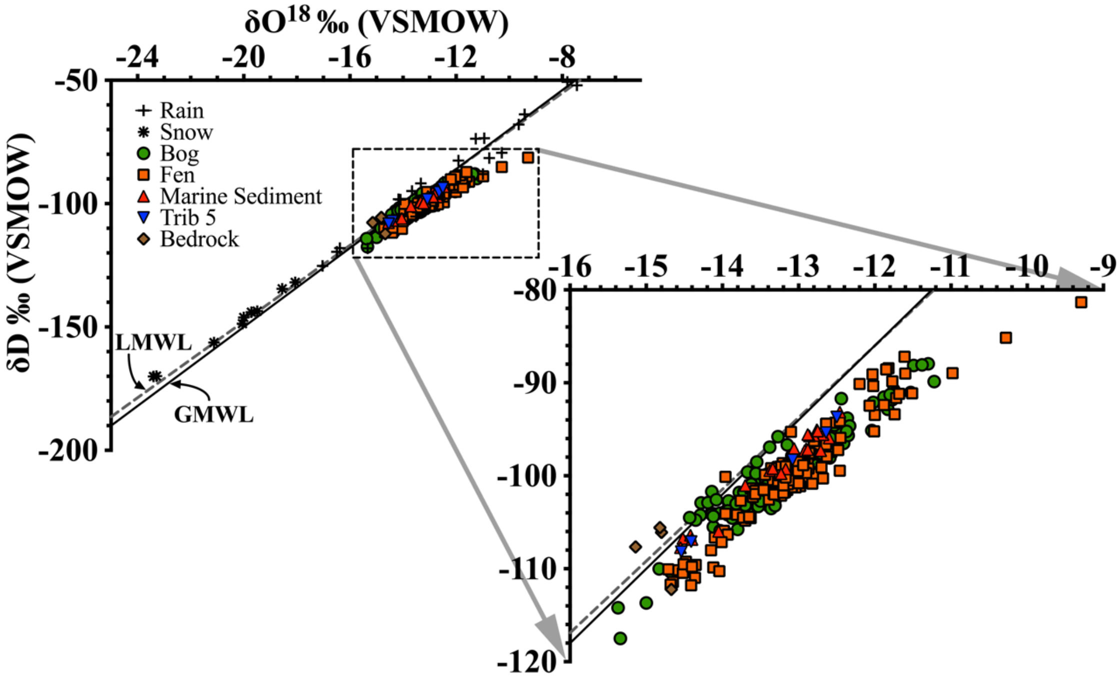

Figure 2.11. Plot of stable water isotopes ($\delta^{18}O$ versus δD, ‰ VSMOW) of rain (crosses), snow (stars), Trib 5 Surface waters (blue triangle), bog pore-waters (green circles), fen pore-waters (orange squares), marine sediment (red triangles) and bedrock (brown diamonds) for the entire study period. Solid and dashed lines define the Global (GMWL) and Local (LWML) meteoric water lines, respectively.

Contoured δD values in the BF and FT transect cross sections (Figures 2.12 and 2.13) show the distribution of δD over the summer months within the peat. Contours of $\delta^{18}O$ values exhibit identical patterns of layering (data not shown). The BF transect exhibits undulating stratification of δD values, similar to contoured Ca^{2+} concentrations, but reveals a more complex “hot spot” patterning of lighter isotopes (δD = -100 to 104 ‰) at 250 and 550 m along the transect. These patterns do not appear to change significantly over the season. The uppermost portion of the peat shows a slight enrichment in heavier δD and $\delta^{18}O$ isotopes over the summer, due to excessive evaporation and inputs of relatively heavier precipitation.

The FT transect exhibits more complex distributions of δD that are comparable to patterns of contoured Ca^{2+} concentrations. A strong band of isotopically-depleted water (δD = -110 to -100 ‰) is evident between 0-500 nm from the start of the FT transect earlier in the season, which gradually slopes upwards at 700 m. Beyond this portion of the transect, much of the water shows a smaller range in isotope values centered around -100 ‰ δD, particularly at >1 m depth. Slightly more depleted water *(ca.* -104 ‰ δD) is present in deeper peat near the end of the transect. The distribution of isotope values in the FT transect in August is largely comparable to that of June, however slight propagation of water down slope towards the tributary is evident throughout. Most noticeable is the heavily depleted slug of water that has progressed slightly down gradient (<50 m), and slightly closer to the surface. Likewise, the depleted portion of water at the northernmost portion of the transect has moved downgradient, being mixed and/or replaced by slightly isotopically heavier water.

Depth profiles of $\delta^{18}O$ values at each piezometer nest along the BF and FT transect are shown in Figures 2.14 and 2.15, respectively (depth profiles of δD are comparable, but not shown). Overall, $\delta^{18}O$ values show significant fluctuations in the uppermost 1 m of the peat profile throughout the study period, and more conservative changes at greater depths. In the BF transect (Figure 2.14), $\delta^{18}O$ values typically range between -15 to -11 ‰ at the water table and 0.5 m piezometers and exhibit changes between May and October. At depths greater than 1 m, the spread in $\delta^{18}O$ values narrows (-14 to -12.5 ‰), and values remain unchanged throughout the season. Near the surface of the bog, $\delta^{18}O$ values tend to reflect the isotopic composition of seasonal precipitation, with relatively negative values during snowmelt, gradually increasing throughout the season until cooler rains and snow in October. Values of $\delta^{18}O$ in deeper piezometers at nests Bog+0, Bog+490 and Bog+630 were focused around -14 to -13.5 ‰, while deep piezometers located in the middle of the transect showed slightly more isotopically enriched values between -13.5 and -12.5 ‰. Whereas most of the nests in the BF transect showed a gradually more depleted isotopic composition with depth, Bog+630 (within the bog-fen transition zone) generally exhibited very little differentiation with depth, centered around -13.5 ‰ (with the exception of the 0.5 m piezometer in May at -15.4 ‰).

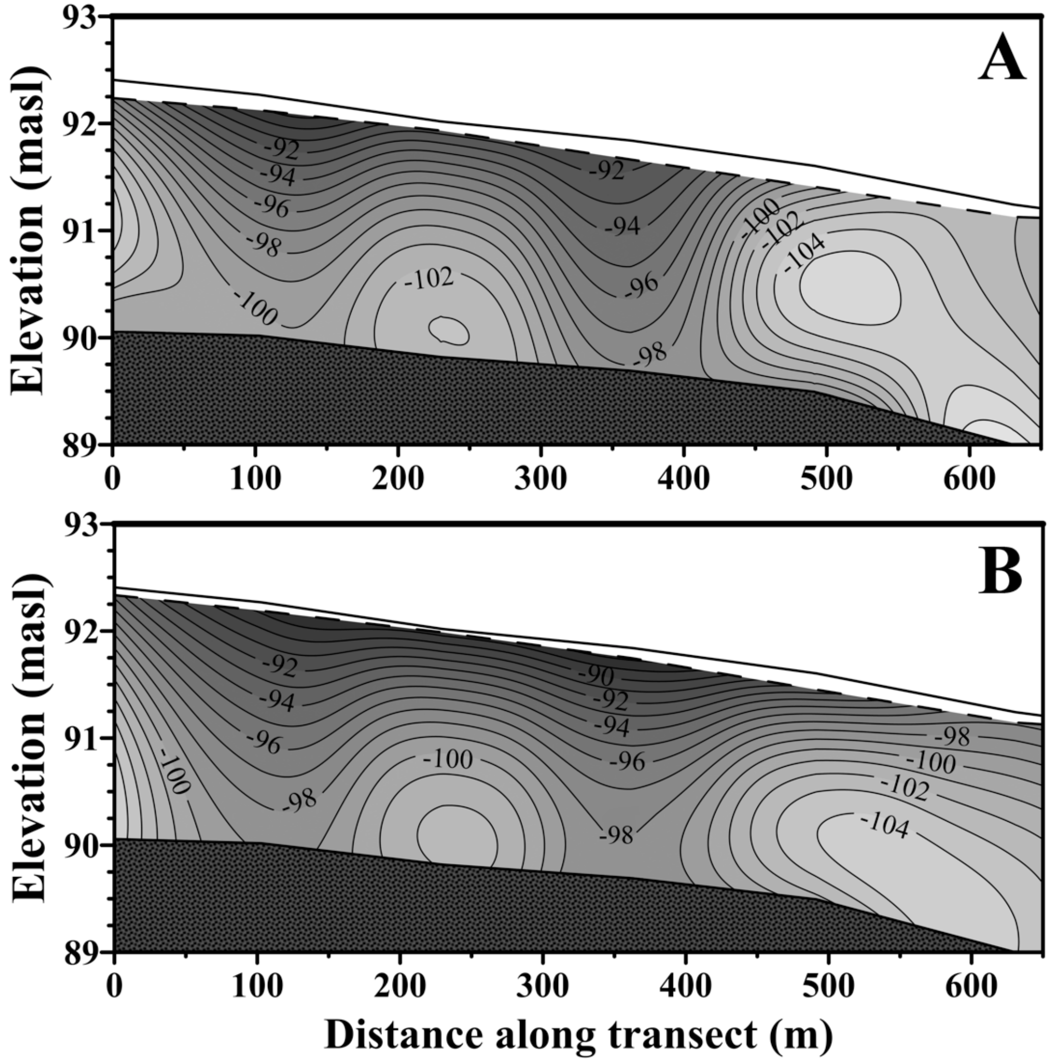

Figure 2.12. Vertically exaggerated cross sections of the BF transect showing interpolated δD (‰ VSMOW) values on **(A)** June 25 and **(B)** August 20, 2011. Contours are shown every 2 ‰. The uppermost dashed and solid lines show the water table and peat surface, respectively.

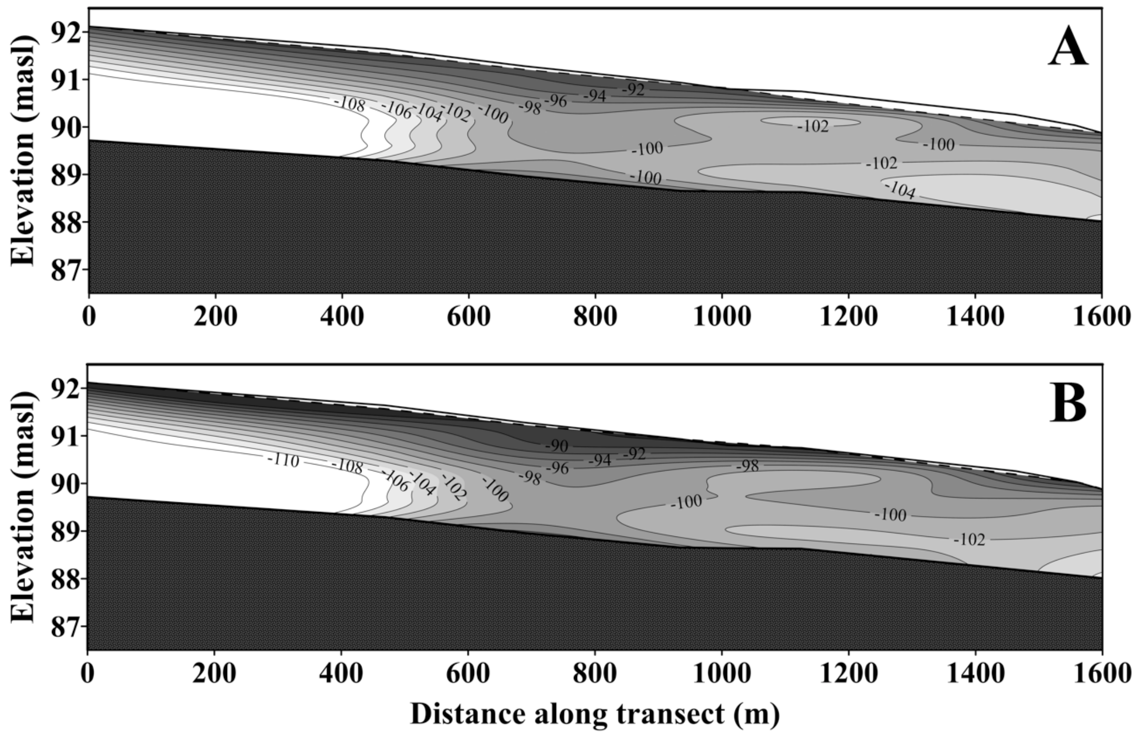

Figure 2.13. Vertically exaggerated cross sections of the FT transect showing interpolated δD (‰ VSMOW) values on **(A)** June 25 and **(B)** August 20, 2011. Contours are shown every 2 ‰. The uppermost dashed and solid lines show the water table and peat surface, respectively.

Profiles of $\delta^{18}O$ (Figure 2.15) and δD (data not shown) in the FT transect generally exhibit a smaller spread with depth, and only tend to exhibit seasonal variability at 0 and 50 cm depths. Alike the bog, in the near surface section of the peat, $\delta^{18}O$ values mirror the highly depleted values of winter precipitation and snow melt mixed with existing peat groundwater. At the southern end of the transect (Fen+1100S and Fen+650S), there is strong enrichment in $\delta^{18}O$ over the season (June to August), and with increasing proximity to the peat surface. Beyond Fen+650S, $\delta^{18}O$ values tend to stabilize throughout the transect at *ca.* -13.2 to -12.5 ‰ 50 cm below the peat surface, and show minimal changes over the study period. Piezometers at Fen+800N (where peat depth starts to noticeably decrease) gradually increase from -13.7 ‰ in the marine sediment (0.75 m below the peat/sediment interface) to -12.5 ‰ $\delta^{18}O$; however, values in the peat itself are quite consistent.

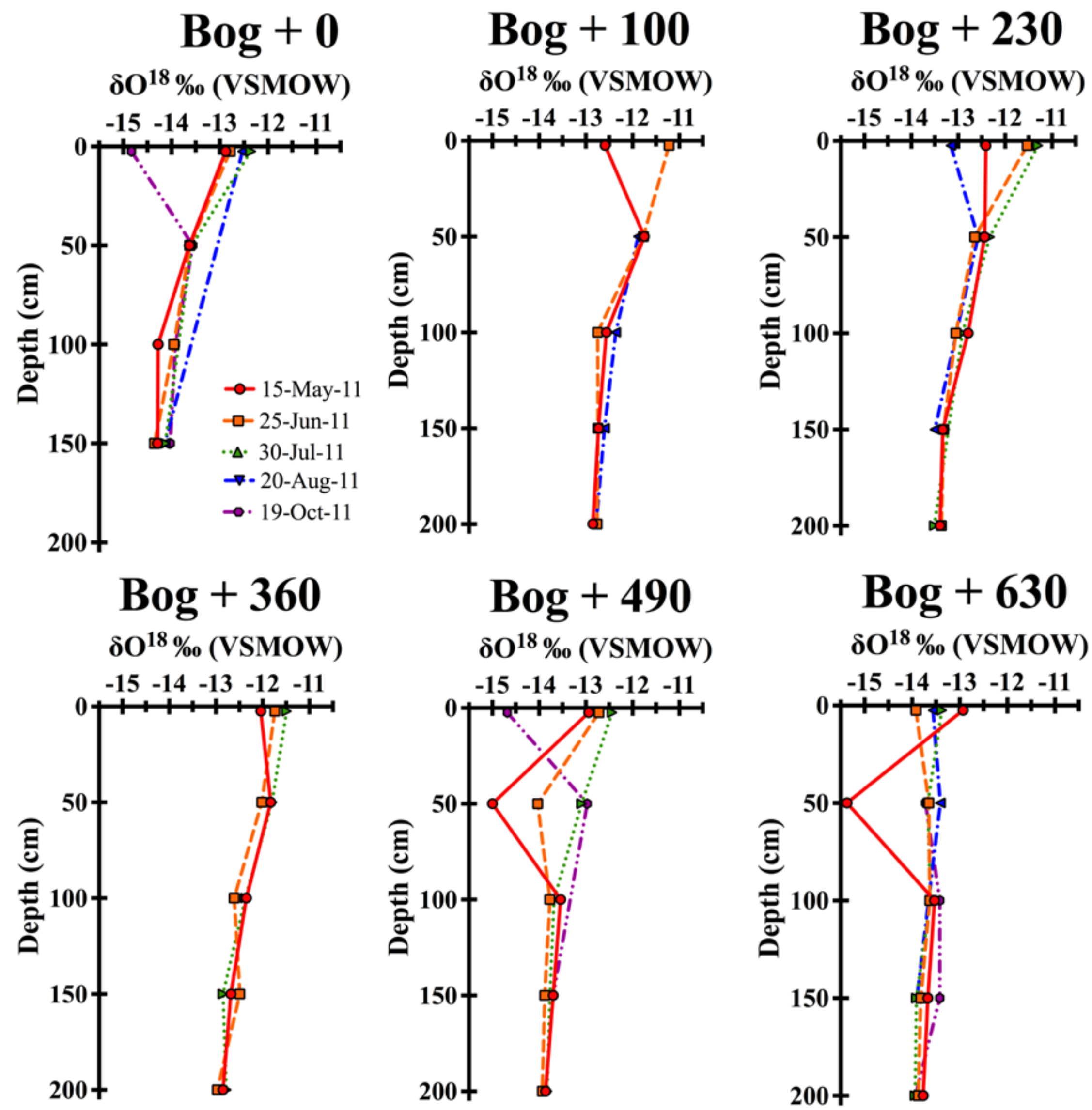

Figure 2.14. Values of $\delta^{18}O$ (‰ VSMOW) with depth at each nest in the BF transect, Hudson Bay Lowlands, Canada.

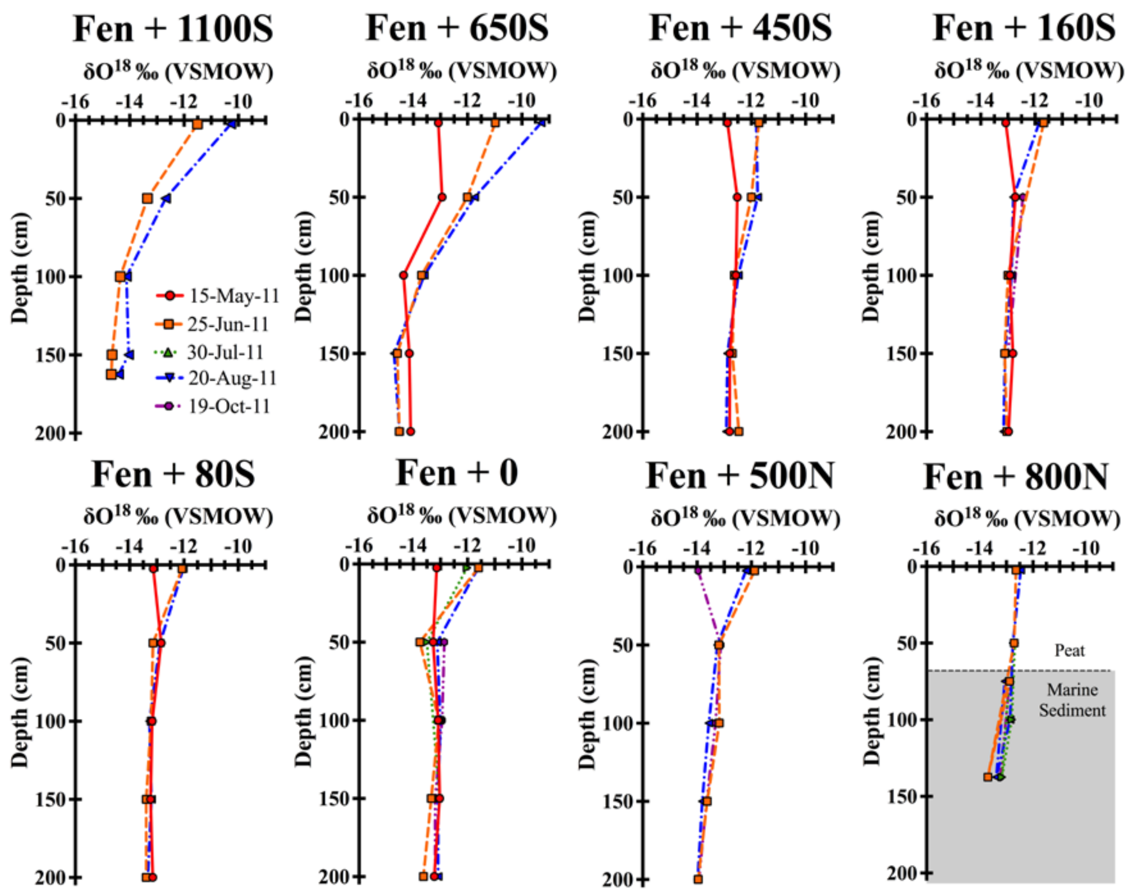

Figure 2.15. Values of $\delta^{18}O$ (‰ VSMOW) with depth at each nest in the FT transect, Hudson Bay Lowlands, Canada.

2.5 Discussion

2.5.1 Hydrologic Connectivity in the Landscape

It appears that there is a need to satisfy a threshold moisture deficit (or water table position), regardless of the amount of incoming precipitation the peatland receives during a storm event (Quinton and Roulet, 1998). Unless this threshold is satisfied, hydrological connectivity between landscape units occurs only *via* diffuse groundwater flow, and remains relatively low throughout the majority of the snow and ice-free season or during extended periods of drought. The bog, fen, and tributary all exhibit the highest degree of hydrological connectivity during spring freshet and the occurrence of high frequency rain events in the fall, when water tables exceeded the average peat surface in the bog and fen, respectively. This rapid connection to the surface waters can only occur when the ribbed fen (the portion of the peatland that is directly coupled to the fen) drains as a single source area and is able to deliver water as overland surface flows or through the shallow, very high K acrotelm. It is unlikely that a similar physical linkage of channels causes transmission of water from the bog to the fen, as channelized flow due to the large surface storage created by the pool-ridge sequence in the bog water track feature (Price and Maloney 1994).

The presence of an impermeable frost table appears to amplify runoff from the peatland in the spring (Woo, 1986), where even small hydrologic inputs to the landscape are related to rapid and substantial increases in Trib 5 stage (Figure 2.3B). As soon as the frost table begins to melt, the water table is lowered enough that the occurrence of ridges and troughs in the ribbed fen impedes rapid overland flow for significant (>10 m) distances, requiring that runoff occurs as groundwater flow through the peat. The absence of any significant meteorological inputs and increasing evapotranspiration rates throughout the summer, as well as groundwater losses to the adjacent surface waters, lower water tables throughout the site, and the hydrological connectivity of the entire landscape decreases in direct response to a reduction in water table elevation relative to the peat surface. The higher rates of water table decline in the bog are the result of higher hydraulic table gradients and hydraulic conductivities.

2.5.2 Patterns of Groundwater Flow

Large scale vertical flows have been reported to occur in larger patterned peatland systems (Siegel, 1983; Siegel and Glaser, 1987), but the seasonal hydraulic head measurements at the study site indicate that groundwater flow in this bog-fen-tributary sequence is principally horizontal with the majority of mass transport occurring in the shallowest peat layers (Figure 2.5). Figures 2.5 and 2.6 show the consistent generalized flow of groundwater in the bog and fen from equipotentials constructed from hydraulic head which is conceptually similar to simulations by Tóth (1962) and Freeze and Witherspoon (1967) in which lateral groundwater flow dominates in a thin homogenous aquifer under a constant gentle water table slope.

Hydraulic head measurements in piezometers along the BF and FT transects indicate that most of the study site experiences no vertical hydraulic gradients in the top 0.5 m of the peat column, and slight-to-moderate vertical gradients below this depth. At certain times and locations, the measured vertical gradients are larger than those reported in Glacial Lake Agassiz peatlands (Siegel and Glaser, 1987; Romanowicz *et al.*, 1993). Downwards (negative) vertical gradients were measured in some nests, particularly at the crest of the bog, indicating that water table mounds can drive local ground-water flow cells, particularly at very dry or wet conditions. However, the low K at depth means that the volume of water flowing downwards through the peat column is relatively small, even in the presence of strong vertical hydraulic gradients. Additionally, numerical simulations of groundwater flow in bogs in the Albany River drainage basin by Reeve *et al.* (2000) showed that vertical flows through the peat profile (and into the underlying geologic layers) are small when the peat itself is underlain by low permeability deposits (<0.008 m d^{-1}). The low K (<0.004 m d^{-1}) fine-grained calcite sediment at the study site likely results in a very small vertical exchange of water between the bog and low K mineral substratum even if strong vertical gradients were present.

In the fen, vertical hydraulic gradients were generally small, but when present, positive (upward), consistent with other studies of peatland groundwater hydrology (Siegel and Glaser, 1987; Price and Maloney, 1994). The only consistently strong upwards hydraulic gradients were at Fen +500N, and were greatest during high water tables in the spring and end of summer. This nest is located in a break in peatland topography, where peat depth starts to decrease toward the transition to the tributary. This small break in slope and underlying mineral topography is sufficient to promote groundwater discharge within this area (Freeze and Witherspoon, 1967). We measured some consistently negative hydraulic gradients at 1.5-2.0 m below the peat surface at nearly all nests along the FT transect. As there is no physical basis for such strong negative gradients (given the low hydraulic conductivity of the underlying mineral layer), we believe that these are most likely an artifact of the slow response of the water level in the piezometers to changes due to very low K peat in the fen, and not a true measure of downwards gradients at depth.

The groundwater flow reversals (oscillation between groundwater upwards and downwards vertical hydraulic gradients) observed at the study site during periods of low water table have also have been reported in large peatlands (Siegel and Glaser, 1987;

Romanowicz *et al.*, 1993), and have been shown to enhance vertical mixing of solutes in the peat column (Reeve *et al.*, 2006). In our study, the flow reversals did not persist for more than 1-2 weeks (the determination of the exact duration is limited by our measurement interval) and no significant changes to pore-water chemistry were detected throughout this time. The differential influence of local versus regional flow systems during periods of low water table (Devito *et al.*, 1997), and episodic overpressurization of the peat column by biogenic methane gas during droughts (Kellner *et al.*, 2004) have been cited as reasons for such apparent reversals in measured hydraulic heads.

It is clear that accurate values of K are required for the interpretation of groundwater flow patterns, to aid in interpretation of hydraulic gradients, and for the quantitative evaluation of fluxes of groundwater within the peat profile (Freeze and Witherspoon, 1967). We utilized *in situ* bail tests (Hvorslev, 1951) for the determination of K in the field because of their simplicity, and ability to incorporate field-scale heterogeneities in the peat (Siegel and Glaser, 2006). The values of K from our study site are similar to what Chason and Siegel (1986) reported for peats in the Lost River Peatlands of northern Minnesota, however they did not observe such large changes of K vertically along the peat profile. A consequence of this significant decrease in K with increasing peat depth is that the uppermost portion of the peat surface (<1 m depth) is effectively the main conduit for flow between peatland landscape units in the HBL.

While our estimates of K appear to coincide with the other published studies of in HBL peats (Whittington and Price, 2013), we are aware of the limitations the Hvorslev bail test method for the determination of K in highly compressible media such as peat (Chirlin, 1989; Surridge *et al.*, 2005), and the additional benefits of laboratory-based methods of K testing [*e.g.*, Nagare *et al.* (2013)]. One major disadvantage with bail tests (and the design of our piezometers) is that it is not possible to obtain independent measures of anisotropy [the ratio of the horizontal (K_h) and vertical (K_v) hydraulic conductivity of the medium]; rather the resultant K represents some "average" of K_h and K_v, usually biased towards K_h. Anisotropy can lead to complex patterns of groundwater by influencing the proportions of vertical and horizontal flow in the soil profile. Whittington and Price (2013) measured anisotropy in HBL peats within 20 km of our study site and found that $K_h>K_v$ in 90% of samples, but the magnitude of anisotropy was fairly small ($K_h = 1.8K_v$). It is likely that the spatial heterogeneities and variability in measured K within the peat profile trumps the effect of such relatively minor anisotropy (Beckwith *et al.*, 2003a).

2.5.3 Pore-Water Chemistry

Differing hydrology, geomorphology, and vegetation assemblages influence the pore-water chemistry in the bog and fen systems of the HBL (Reeve *et al.*, 1996). Peatland features and landforms (*i.e.*, ponds and ridges), and horizontal and vertical gradients can explain the distribution of calcium and stable water isotopes along the BF and FT transect. Overall, changes in peatland groundwater chemistry at the site were small over the course of the study period, and the redistribution of groundwater chemistry is most significant within the top 1 m of the peat, where the majority of groundwater flow occurs. Flow reversals did not seem to affect pore-water chemistry, but our monthly sampling interval and moderate spatial resolution may be too infrequent to capture finer-scale temporal changes to peatland geochemistry due to oscillations in flow direction.

Shallow pore-waters in the bog were predictably acidic (pH < 4.5) due to ubiquitous *Sphagnum* cover, but were circumneutral at depths below 1 m. Large-scale patterns of Ca^{2+} concentrations can be explained by diffusional and dispersive processes that transport the highly concentrated ($[Ca^{2+}]$ >100 mg L^{-1}) pore-waters from the underlying marine sediments (Reeve *et al.*, 2001), but are made more variable by very localized flow cells flushing dilute waters from the surface down through the peat (Siegel, 1983). The lower concentrations of Ca^{2+} in deeper peat at 0-100 and 300-400 m along the BF transect corresponded to areas with more persistent downward gradients. Such downward flows must exceed the upward diffusional gradient in order to have a measureable effect on Ca^{2+} concentrations.

Calcium concentrations in the shallow fen pore-waters were at least double than in the bog, and exhibited much more complex distributions throughout the peat profile. These distributions are also the result of an interplay between diffusion, dispersive mixing, and the vertical gradients along the FT transect. The effects of dispersive mixing in the fen are enhanced by greater heterogeneity in K, and longer horizontal flow paths (Reeve *et* *al.*, 2001). Negative vertical gradients at the start of the FT transect (0-200 m) and the consistent strong upward gradients at the distal end (>1000 m) result in lower and higher concentrations of Ca^{2+} in shallower peats, respectively.

Stable water isotopes are useful tools as geochemical tracers because they are chemically conservative, meaning physical processes such as evaporation and condensation, or exchange reactions with geological materials, only affect their isotopic signature. Stable water isotopes are also a complementary tracing technique to Ca^{2+} since they are consistently replenished by meteorological precipitation at the surface (rather than derived from the basal sediments) and have a large seasonal range in values, which can be useful in distinguishing between different mixing end members.

The majority of pore-water samples from the bog and fen exhibit a departure from the LMWL and have gentler slopes (4-6) on the $\delta^{18}O$ versus δD plot, signifying high rates of evaporative enrichment in heavy stable water isotopes ($\delta^{18}O$ and δD). Shallow fen pore-waters have higher slopes than in bogs due to enhanced evapotranspiration because of large areas of standing water and presence of vascular vegetation. Patterns of stable water isotopes along the BF and FT transects resemble the patterns of Ca^{2+} concentrations, indicating that similar hydrological processes are responsible for both the top-down (downward hydraulic gradients) and bottom-up (dominantly diffusional and dispersive) redistribution of water chemistry within the bog and fen. Fen pore-waters are much more isotopically lighter at the southern portion of the FT transect, where downwards vertical gradients and large extent of open pools results in recharge of more isotopically depleted water from snowmelt (White *et al.*, 2014).

Changes to stable water isotopes throughout the season are substantial only at the surface and 0.5 m piezometers, similar to what is reported in the Glacial Lake Agassiz peatlands (Levy *et al.*, 2013). This provides further evidence that connectivity of the peatland landscape on an annual scale primarily occurs within the high conductivity acrotelm. A large spread in water isotope values exists in all samples, but most are centered around the isotopically heavy precipitation, indicating that peatland groundwaters are recharged primarily during periods of high magnitude and frequency storm events during late summer and fall. Snowmelt does result in a rapid addition of water to the peatland systems, but most of it does not infiltrate the deeper peats due to the near surface impermeable frost table.

2.6 Conclusions

Seasonal-scale hydrometric data and geochemical tracers used in this study provide the first high-resolution, empirical confirmation of the numerical simulations of peatland groundwater flows in the HBL by Reeve *et al.* (2000, 2001). Consistent hydraulic gradients throughout the site ensure groundwater flow in a bog-fen arrangement is largely horizontal, and occurs primarily through the high K ($>10^{-4}$ m s^{-1}) surface peat layers. The translocation of solutes from basal sediments occurs through diffusion and dispersion transport processes, governed by the physical characteristics (*i.e.*, height, length, topography, and hydraulic conductivity) of the peatland landforms and underlying strata. The distribution of solutes within the peat profile along the longitudinal axis of flow can be influenced by fine-scale local upward and downward flow cells that can develop near peatland features such as ridges and ponds, especially during extreme high and low water table elevations. Small breaks in topography within ribbed fen systems can result in consistent upward vertical flows, amplifying the flux of solutes from deep to shallow peats.

The degree of hydrologic connectivity within the landscape, and with the surface waters, is primarily governed by the position of the water table relative to the average peat surface. The system appears to behave differently between it’s completely connected (wet) and partially connected (dry) states, demarcated by a threshold water table position near or exceeding the average peat surface in the fen. During periods of enhanced connectivity (snowmelt in spring and fall freshet), surface waters responded rapidly to inputs of water to the system, and redistribution of solutes occurs in shallow (< 1 m) peat. Even small reductions in the water table correspond to reduced hydraulic connectivity between landscape units. Predicted lowering of water levels in the future from increased evapotranspirative water losses due to increased air temperatures could reduce the export of water and solutes from the peatlands to the surface waters of the HBL.

2.7 Acknowledgements

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Chapter 3

3 Water, Carbon, and Mercury Fluxes in a Bog-Fen-Tributary Complex, Hudson Bay Lowlands, Canada

3.1 Introduction

Northern peatland complexes play an important role in the global carbon cycle, where cool temperatures and waterlogged soils have contributed to the sequestration of more than 400 Gt carbon (C) worldwide since the beginning of the Holocene (Gorham, 1991). Peatlands are long-term (millennial) sinks of carbon dioxide (CO_2), but are also sources of methane (CH_4, a potent greenhouse gas) to the atmosphere, and thus function as important regulators of the global climate (Smith *et al.*, 2004; Frolking *et al.*, 2006). Because of their reducing biogeochemical soil conditions, and their low-lying, ecotonic position in the landscape (which links the terrestrial and aquatic ecosystems), peatlands are often considered significant sources of dissolved organic carbon (DOC)-laden groundwater to surface waters (Dillon and Molot, 1997; Moore, 2009). DOC is a varied mixture of simple low-molecular to complex high-molecular weight organic molecules (operationally defined as <0.45 μm in size), which originate from the decomposition of organic matter and senescent vegetation (Porcal *et al.*, 2009). The production and transformation of DOC, and the associated reactions with other chemical constituents, are governed by a multitude of biogeochemical factors, including pH, temperature, redox potential, availability of terminal electron acceptors (TEAs), and the activity and structure of microbial communities (Blodau, 2002; Reddy and DeLaune, 2008).

Concentrations of DOC in peatland pore-water can vary depending on peatland landform type (*i.e.*, bog or fen) (Ulanowski and Branfireun, 2013), and depth from the surface, but typically range between 5 and 80 mg L^{-1} (Moore, 2009). Exports of DOC from northern peatlands can account for 10% to 50% (1 to 50 g C m^{-2} y^{-1}) of the annual net ecosystem carbon balance (NECB) (Roulet *et al.*, 2007; Nilsson *et al.*, 2008; Olefeldt *et al.*, 2012; Yu, 2012). The NECB is the overall sum of fluxes of carbon to and from a peatland, including CO_2 uptake and release (or net ecosystem exchange, NEE), CH_4, and DOC (Bridgham *et al.*, 2006).

Dissolved organic carbon is also an important carbon and energy source for microorganisms, and is recognized as a significant modifier of aquatic ecosystems, where high concentrations of organic acids can affect pH, and it's chromophoric properties can attenuate light transmission through the water column by imparting a yellow-brown colour to the water (*Ibid.*). Metals can form strong complexes with DOC, which can affect transport, bioavailability, speciation, and toxicity (Buffle *et al.*, 1988). For example, DOC can bind to various inorganic and organic species of mercury (Hg) (Ravichandran, 2004). Mercury is a global pollutant, since it is readily introduced into the atmosphere from natural (*i.e.*, geologic) and anthropogenic (*e.g.*, mining and combustion of fossil fuels) sources, where it is efficiently transported over long distances, and subsequently deposited globally even in the most pristine landscapes (Fitzgerald *et al.*, 1998; Morel *et al.*, 1998; Clarkson *et al.*, 2003).

Concentrations of total mercury (THg) are below levels of direct toxicological concern in peatland pore-waters (<20 ng L^{-1}) (Mitchell *et al.*, 2008a), however it is the *in situ* production, and export, of the potent neurotoxin *methylmercury* (MeHg) that can have harmful effects on ecosystems (Boening, 2000; Mozaffarian and Rimm, 2006). Peatlands are recognized as important sources of MeHg to surface waters (St. Louis *et al.*, 1994; Branfireun *et al.*, 1996; Branfireun *et al.*, 1999), since the anaerobic conditions within peatlands facilitate the microbially mediated methylation of inorganic Hg to MeHg. Although concentrations of MeHg in peatland pore-waters are also generally very low (< 5 ng L^{-1}) (Heyes *et al.*, 2000), bioaccumulation and biomagnification within the aquatic food chain can increase concentrations of MeHg in fish by more than six orders of magnitude (Morel *et al.*, 1998). Over 90% of the THg in fish occurs as MeHg (Bloom, 1992), and so the consumption of fish with a high MeHg body burden is major pathway of mercury exposure to humans and wildlife, which can lead to impaired neurological function and decreases in reproductive success, respectively (Wolfe *et al.*, 1998; Tchounwou *et al.*, 2003).

Hydrology governs biogeochemistry and the export of solutes from peatlands (Shotyk, 1988; Siegel and Glaser, 2006), but forecasted perturbations to moisture regimes due to climate and land-use change (Turetsky *et al.*, 2002; Whittington and Price, 2013) demand a better understanding of such processes in larger peatlands if the effects of these changes are to be reasonably predicted. There is still incomplete knowledge and a scarcity of comprehensive field-based studies investigating groundwater and carbon exchange in large contiguous peatland complexes, such as Canada's Hudson Bay Lowlands (HBL) where these changes may be most dramatically manifested.

The HBL is an ecologically important region with an area of more than 300,000 km^2 extending across northern Quebec, Ontario, and Manitoba (Riley, 2011), and is almost entirely covered by a ~2 m layer of peat which began to accumulate 6-7000 years ago, following the melting of the Laurentide Ice Sheet and regression of land from the Tyrell Sea (Lee, 1960; Glaser *et al.*, 2004). The peatlands of the HBL currently contain 26 Gt C (FNSAP, 2010) and contribute approximately half of the total water discharge in the rivers and tributaries that drain the HBL, supplying large amounts of freshwater and DOC to the saline James Bay and the Arctic Ocean (Kirk and Louis, 2009; Orlova and Branfireun, 2014). Changes to hydrology from climate change (Colombo *et al.*, 2007) and the exploitation of recently discovered mineral deposits (*e.g.*, Hattori and Hamilton (2008) have the potential to increase exports of peatland-derived DOC and solutes (Siegel *et al.*, 1995; Pastor *et al.*, 2003; Frey and Smith, 2005; Colombo *et al.*, 2007; Cortizas *et al.*, 2007). Despite the importance of these HBL peatlands to the global carbon cycle (Riley, 2011), and existing fish consumption advisories due to elevated levels of mercury in fish in HBL rivers and tributaries (MOE, 2013), we still lack the information to quantify and assess the effects of disturbance to these ecosystems on water quality. Most of our policy-making and long-term predictions of change are based on peatlands significantly smaller in size, within a much different climatic, geographic, and geologic setting (Strack *et al.*, 2008; Waddington *et al.*, 2009).

Given the demand for high quality field-based information on the current state of HBL peatlands and their connection with the surface waters, we have collaborated with De Beers Canada and the Ontario Ministry of the Environment (MOE) to establish a long-term study of water and carbon cycling in a bog-fen-stream complex typical of the central regions of the HBL. Here we present the first assessment of the annual fluxes of water, DOC, and Hg that flow through, and out of, such a system. The objectives of this research are to 1) assess the spatial and temporal patterns of DOC, THg and MeHg in a typical bog-fen-tributary sequence in the HBL, and 2) estimate groundwater, DOC, THg, and MeHg export from the bog to fen, and fen to an adjacent surface water channel during the snow and ice-free season.

3.2 Study Site and Methods

3.2.1 Site Description and Hydrological Measurements

The study site was established in late 2010 and early 2011 in a 4.9 km^2 subwatershed of the 204 km^2 Tributary 5 (Shreve Stream Order 5) drainage basin, located within the Attawapiskat River Basin of the Hudson Bay Lowlands, Ontario, Canada (52.70°N, -83.60°W, Figure 3.1). The site is situated at the boundary between two distinct climatic regions (Köppen-Geiger system), Humid Continental (DFb) and Subarctic (Dfc) (Peel *et al.*, 2007), and experiences long, cold winters and mild-to-hot summers. Long-term (1971-2000) mean annual air temperature, mean annual precipitation, and days above 0 °C (recorded at the nearest meteorological station in Lansdowne House, Ontario) are -1.3 °C, 700 mm (70% falling as rain), and 153 days, respectively (Canada, 2011). A detailed description of the site, including vegetation, topography, watershed area and delineation, and landforms is provided in Section 2.3.

Two study transects run partially along a 1250 m raised wooden boardwalk, which connects two 4 m tall eddy flux covariance/meteorological towers that are operated by the MOE as part of a long-term carbon flux monitoring program (Figure 3.1B). The Bog-to-Fen (BF) transect is 630 m long and runs from the crest of a 0.51 km^2 raised bog, through an internal water track drainage feature, and into an adjacent ribbed fen system. Six piezometer nests spanning the length of the BF transect were placed at 100-130 m intervals, with each nest containing a fully penetrating well to a depth of 1 m, and four piezometers (0.1 m slotted intake) placed at 0.50, 1.00, 1.50, and 2.00 m below the peat surface. The Fen-to-Tributary (FT) transect extends 1900 m along the ribbed fen system to the west of the bog, which runs in a north-south direction towards the Trib 5 tributary, intersecting the BF transect 1100 m north of the most southerly piezometer (Fen+1100S). A total of eight piezometer nests (one groundwater well and four piezometers) were installed along the FT transect at 100-500 m intervals. Additional piezometers were installed at 0.25, 0.50, and 0.90 m in the marine sediment at Fen+800N. Piezometer nests were labeled with an approximate distance in meters along the transect from the crest of the Bog in the BF transect (*e.g.*, Bog+230), and approximate distance in metres and bearing (North or South) relative to the O-MOE Flux tower in the ribbed fen system (*e.g.*, Fen+500N).

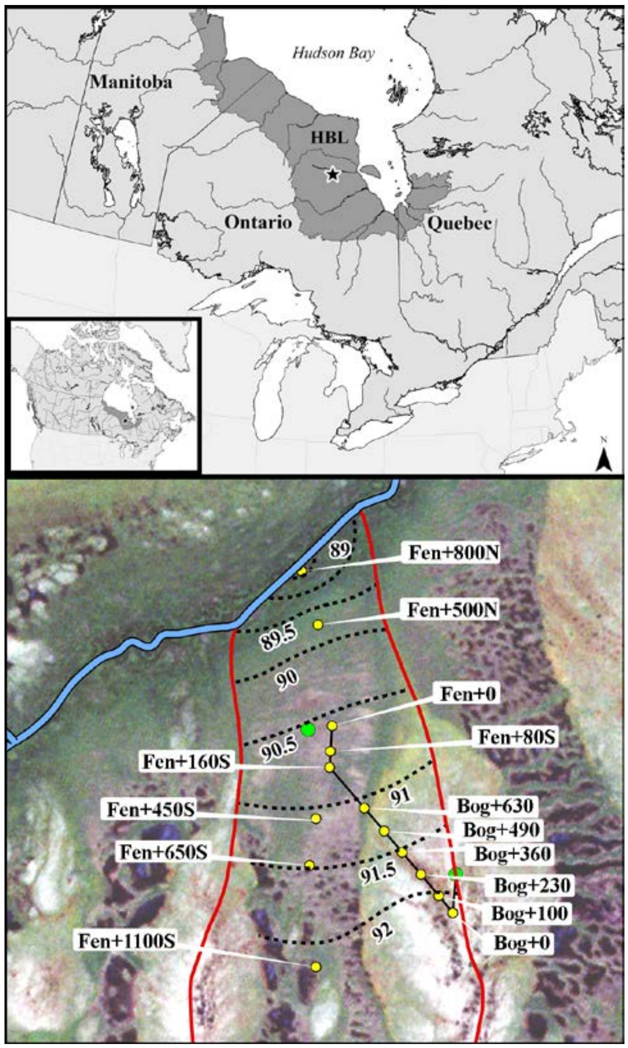

Figure 3.1. (TOP) Location of study site in the Hudson Bay Lowlands, Ontario, Canada (denoted as black star), and **(BOTTOM)** IKONOS satellite imagery showing the study watershed (red line), boardwalk (black line), locations and names of piezometer nests (yellow circles), eddy flux and meteorological towers (green circles), and Trib 5 (blue line).

Wells and piezometers were fabricated from Schedule 40 0.125 m I.D. PVC pipe, and installed according to methods described in Section 2.3.1. Wells and piezometers were fully purged (developed) at least three times before any hydraulic head measurements or samples were taken. Piezometers were continuously developed throughout the study period, and especially before sampling. Bail tests (Hvorslev, 1951) were done on all piezometers to provide estimates of saturated hydraulic conductivity (K) of the peat at various depths along the peat profile (Freeze and Cherry, 1979). Bail tests were also conducted on the 1 m fully penetrating wells during various water table positions to provide an estimate of the bulk effective hydraulic conductivity in the uppermost metre of peat with changes to the water table.

Pressure transducers (Schlumberger Micro-Divers®) logged hourly measurements of hydraulic head at eight monitoring wells (three and five loggers in the BF and FT transects, respectively) during the snow and ice-free season (May 15 to October 19, 2011). Manual measurements of hydraulic head in the wells and piezometers were taken on a *ca.* weekly basis and used to check and calibrate the continuous transducer measurements. Peat depth was surveyed at each piezometer nest and throughout the transect by augering through the peat profile until contact was made with the marine sediment. All measurements of hydraulic head, and peatland and marine sediment elevations were adjusted to the NAD83 datum by surveying with a Topcon (Tokyo, Japan) HiPER GL RTK differential global positioning system (DGPS) (horizontal and vertical accuracy +/- 0.01 and 0.003 m, respectively).

Estimates of total daily precipitation (P) and evapotranspiration (ET) were kindly provided to us by the Ontario Ministry of the Environment (see Section 2.3.1 for detailed description of meteorological data collection methods).

3.2.2 Water Sampling and Chemical Analysis

Site access is periodic and only by helicopter. Sampling of piezometers for DOC, THg and MeHg was done on four campaigns during the study period: May 17, June 25, August 20, and October 19, 2011. Water sample collection from piezometers was accomplished using a low-flow peristaltic pump and pre-cleaned and acid-washed PTFE sample tubing, and collected into clean 125-250 mL PETG bottles. Surface pore-water samples (0-5 cm relative to the water table) were obtained by inserting a 0.0125 cm I.D. PTFE pore-water sipper (0.05 m slotted opening) to the water table in an undisturbed portion of peat near each of the piezometer nests. Approximately 100 mL of water was pumped from three separate locations within a meter of each other to provide a 300 mL field-composited sample of solutes near the surface, in recognition of the potential local variability of dissolved solutes in the peatlands of the HBL (Ulanowski and Branfireun, 2013). Sample tubing was kept clean and rinsed with DI water between samples.

Additional precautionary measures were taken when samples were being collected for ultratrace level mercury analysis, and included extra rinsing of all sampling lines, components, and collection vessels with DI between samples and additional environmentalization with the sample water. In particular, the “clean hands, dirty hands” (EPA Method 1669) method was utilized to ensure sample integrity was maintained throughout the entire sampling process. The method dictates that two people are to collect the sample, wearing clean nitrile gloves and utilizing two sealable plastic bags for sample storage: the “clean hands” person is only permitted to handle the sample bottle and inner plastic bag, while the “dirty hands” person handles the outer bag and any sampling equipment. Field, travel, and sample line blanks were included for each sampling session, and duplicate samples were collected every 10-15 samples. Double-bagged samples were stored in clean, large plastic bags to reduce the potential for cross contamination in the field, held on ice in coolers for the duration of the field-sampling day, and then returned to the laboratory and transferred to a dark refrigerator (4 °C) for a maximum 24-48 hours before further processing and preservation.

Samples were vacuum filtered using an acid-washed PTFE filter apparatus using 0.45 μm nitrocellulose membrane filters. The sample filtrate was then split into appropriately sized bottles, preserved, and stored depending on analytical requirements. Samples for DOC analysis were poured into 30 mL HDPE bottles and frozen with headspace, whereas samples for total and methylmercury analysis were collected in 250 mL PETG bottles, acidified to 1% v/v with OmniTrace Ultra™ concentrated hydrochloric acid, rebagged and sealed inside two clean plastic bags, and frozen until analysis. Filter and acidification blanks were collected periodically during sample processing to monitor potential contamination of samples during sample processing.

Samples were analyzed after the 2011 field season at the University of Western Ontario (London, Ontario). Dissolved Organic Carbon was analyzed using an OI Analytical Aurora 1030W TOC analyzer using heated persulfate oxidation (limit of detection, LOD = 0.2 mg L^{-1}). Ultratrace mercury analysis was done in the metals lab at the Biotron Institute for Experimental Climate Change Research (CALA ISO 17025 Certified). Total mercury was analyzed on a Tekran 2600 mercury analyzer according to EPA Method 1631 (LOD = 0.05 ng L^{-1}). Methylmercury analysis was performed on a Tekran 2700 analyzer according to EPA Method 1630 (LOD = 0.0054 mg L^{-1}). All of our analytical data was deemed acceptable as it passed our strict field and laboratory Quality Assurance and Quality Control (QA/QC) standards, where levels of DOC, THg or MeHg where below the limit of quantitation in all blank samples, and the relative standard deviation of all sample duplicates was below 20%.

Prism® (Graphpad Software) was used for the generation of all graphs and Surfer (Golden Software) was used for contouring of DOC concentrations in the BF and FT transect cross sections.

3.2.3 Water and Solute Flux Calculations

A four-layered peat model (Figure 3.2) was employed to calculate the water and solute fluxes through the BF and FT transects for the snow and ice-free study period between May 15 and October 19, 2011. Runoff and solute flux calculations are based on the average peat depth and hydraulic gradients between the terminal monitoring nests for the BF and FT transects, Bog+230 and Bog+630 (l = 400 m) and Fen+0 and Fen+500N (l = 500 m), respectively. Hydraulic gradients were calculated directly from continuously logged water level data (1 hour resolution). Groundwater flow is assumed to be lateral, given the very low average seasonal vertical gradients in both the BF and FT transects (Chapter 2), as well as the high horizontal (versus vertical) hydraulic conductivity of the peat reported in HBL peatlands ($K_h = 1.8K_v$) by Whittington and Price (2013).

For the bog and fen models, each layer within the peat profile was assigned an average bulk hydraulic conductivity determined by taking the arithmetic mean (and standard deviation) of multiple bail tests done throughout the season to piezometers installed at equivalent depths within each transect (Table 3.1). For the uppermost layer (layer 1), it was necessary to account for changes in effective hydraulic conductivity related to fluctuations in the water table position, since hydraulic conductivity of near-surface peat changes significantly with depth from the surface (Boelter, 1965; Baird and Gaffney, 1996). The water table in the bog fluctuated 30 cm over the course of the summer, so the dependence of K on water table in layer 1 was resolved by relating water table depth to measured hydraulic conductivity of the 1 m long fully-penetrating groundwater wells at each piezometer nest (Figure 3.3). A strong exponential relationship was found to exist between depth of water table and K in the bog. No such relationship was found for the much smaller water table changes in the fen, so a bulk K was calculated from the arithmetic mean of all fully penetrating groundwater well bail tests conducted in the fen throughout the season.

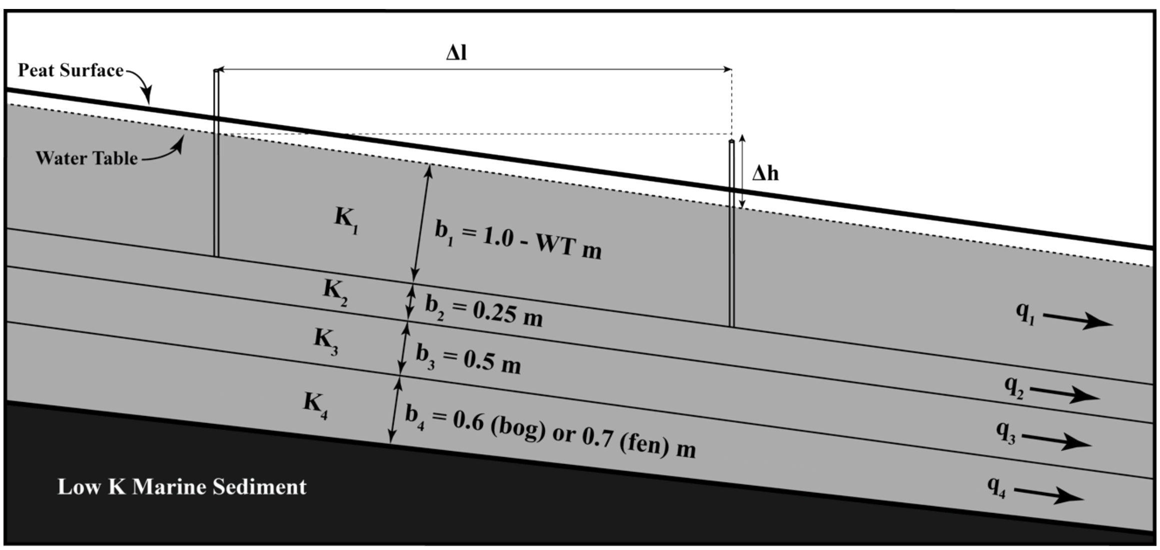

Figure 3.2. Simplified schematic diagram showing the four-layered peatland runoff model used to calculate per unit width water and solute fluxes along the BF and FT transects. Each layer (1 through 4, denoted by the subscript) is assigned a thickness (b) and corresponding hydraulic conductivity (K). Thickness in layer 1 in the bog and fen, and K in the bog, is related to the position of the water table relative to the peat surface based on continuous water level data.

Table 3.1. Values of layer thickness (b), spatially averaged (± standard deviation) hydraulic conductivity (K), mean (and range) of the hydraulic gradient (dh/dl), and seasonal mean concentrations of dissolved organic carbon (DOC), total mercury (THg), and methylmercury (MeHg) assigned to each layer for the bog and fen. Thickness and K values for layer 1 are dependent on the position of the water table relative to the peat surface (WT). *These values represent the mean (and range) hydraulic gradients for the study period. Actual hydraulic gradients are calculated from continuous logger data at hourly intervals.

Layer (i)	**Thickness (b, m)**	**K ($m\ s^{-1}$)**	**dh/dl***	**DOC ($mg\ L^{-1}$)**	**THg ($ng\ L^{-1}$)**	**MeHg ($ng\ L^{-1}$)**
Bog						
1	1 – WT	$0.0044e^{0.053(WT)}$		31.0 ± 3.6	2.02 ± 0.58	0.073 ± 0.021
2	0.25	6.4×10^{-6} ± 5.4×10^{-6}	-0.0021	33.8 ± 1.8	1.16 ± 0.53	0.056 ± 0.034
3	0.50	3.4×10^{-5} ± 4.0×10^{-5}	(-0.0019 to -0.0022)	31.3 ± 2.1	0.78 ± 0.40	0.012 ± 0.012
4	0.60	1.4×10^{-6} ± 7.0×10^{-7}		23.2 ± 0.9	0.41 ± 0.39	0.023
Fen						
1	1 – WT	3.6×10^{-3} ± 9.5×10^{-6}		9.2 ± 1.1	0.90 ± 0.15	0.033 ± 0.022
2	0.25	9.4×10^{-6} ± 3.6×10^{-6}	-0.0015	9.3 ± 0.8	0.26 ± 0.35	0.025
3	0.50	6.2×10^{-6} ± 5.9×10^{-6}	(-0.0010 to -0.0017)	8.7 ± 0.5	0.29 ± 0.35	0.013 ± 0.005
4	0.70	4.6×10^{-8} ± 1.6×10^{-8}		8.1 ± 0.8	0.49	0.051

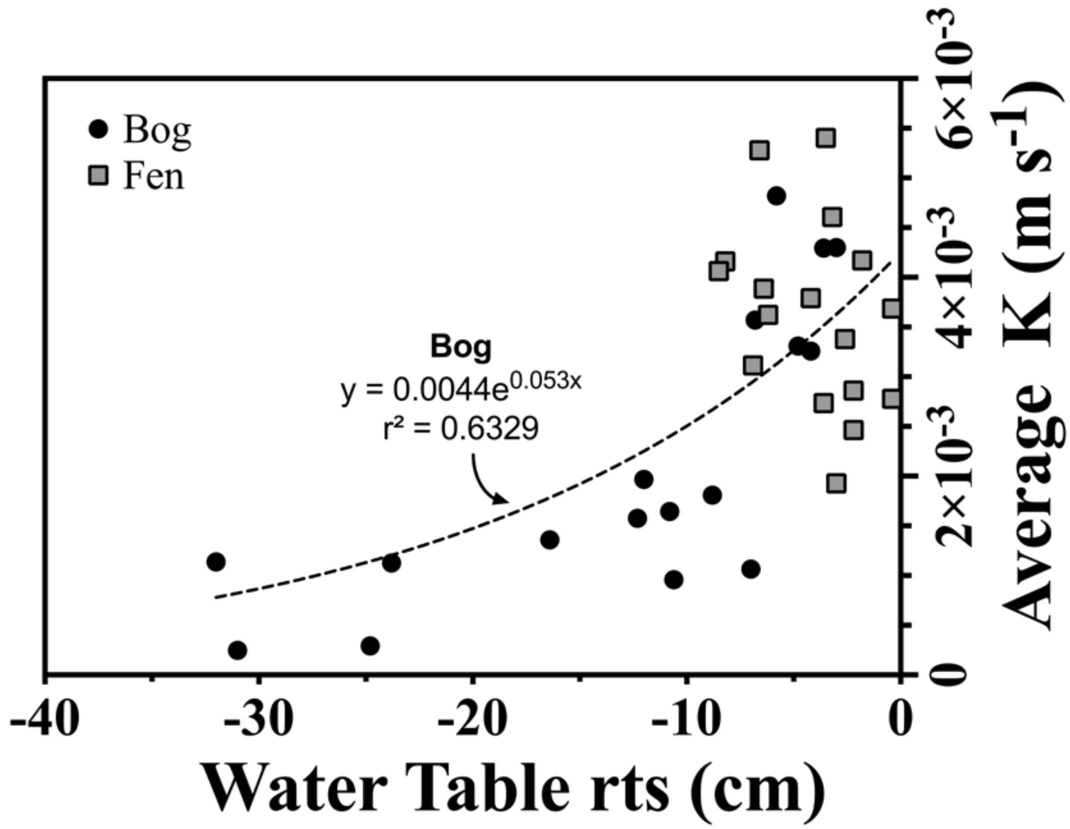

Figure 3.3. Measured effective hydraulic conductivity (K) values in uppermost 1 m layer of peat from bail tests done on fully-penetrating groundwater wells in the bog (black circles) and fen (grey squares) at varying positions of the water table relative to the peat surface (r.t.s.) for the 2011 field season.

The unit width (w = 1 m) groundwater discharge rate for the snow and ice free season (May 15 to October 19, 2011; 157 days) was calculated for each layer (i) of thickness (b) within the peat profile using Darcy's Law, Equation 3.1:

$$\boldsymbol{Q_i = -K_i b_i \frac{dh}{dl}} \qquad \textbf{Equation 3.1}$$

where Q is discharge per unit width ($m^3\ s^{-1}$), K is the saturated hydraulic conductivity of the peat layer ($m\ s^{-1}$), and dh/dl is the unitless hydraulic gradient determined from the elevation of the water table between wells. Hydraulic gradients were calculated on an hourly basis from continuous logger data.

The total discharge of water (Q_t, $m^3\ s^{-1}$) through all four layers in the peat profile is calculated by summing the discharge from each individual layer, i (i = 1 – 4), using Equation 3.2:

$$\boldsymbol{Q_t = \sum_{i=1}^{4} Q_i} \qquad \textbf{Equation 3.2}$$

The total volume of water (V_t, m^3) conducted through the peat profile for the study period (t, s) is calculated using Equation 3.3:

$$\boldsymbol{V_t = Q_t \times t} \qquad \textbf{Equation 3.3}$$

The unit area (1 m^2) change in the water balance for the duration of the study period for both the bog and fen was estimated using Equation 3.4:

$$\boldsymbol{\Delta S = P - ET - R \pm \xi} \qquad \textbf{Equation 3.4}$$

where ΔS is change in storage, P is precipitation, ET is evapotranspiration, R is runoff, and ξ is the residual tern (all in mm). Change in peatland storage was estimated as the mean difference in water table position at wells in the BF and FT transects between the start and end of the study period.

Solute fluxes (J) over the study period (Equation 3.5), were calculated by multiplying the total volume of water moving through each peat layer by the average seasonal concentrations (C) of DOC, THg or MeHg for each peatland type and layer as outlined Table 3.1. Advection is assumed to be the dominant solute transport process in groundwater, and diffusional and dispersion processes are assumed to be negligible. Conservative transport behavior was assumed for all solutes. Potential errors to solute fluxes were estimated by calculating the minimum and maximum solute fluxes by incorporating the uncertainties of K and C assigned to each layer.

$$\boldsymbol{J = V_t \times C} \qquad \textbf{Equation 3.5}$$

The net ecosystem carbon balance (NECB, g C m^2 y^{-1}, Equation 3.6) was calculated for the bog and fen using estimates of annual CO_2 and CH_4 fluxes, based on eddy flux measurements at the site:

$$\boldsymbol{NECB = NEE - CH_4 - DOC} \qquad \textbf{Equation 3.6}$$

where NEE represents net ecosystem exchange (i.e., net CO_2 flux, g C-CO_2 m^2 y^{-1}), CH_4 represents carbon lost as methane gas (g C-CH_4 m^2 y^{-1}) and DOC represents export of dissolved organic carbon via groundwater (g C m^2 y^{-1}). Estimates of NEE and CH_4 fluxes for the study period were provided by Elyn Humphreys (Carleton University) and the

MOE. The calculated seasonal fluxes of water, solutes, NEE, and CH_4 for the study period are assumed to be equal to annual fluxes, since appreciable snow cover, a thick frost layer, and low wintertime temperatures (<20 °C) likely hinder significant exports of water and solutes, as well as minimize atmospheric exchange of H_2O, CO_2 and CH_4.

The propagation of uncertainties for the water and carbon balances was accomplished using Equation 3.7:

$$\boldsymbol{\delta X = \sqrt{(\delta a)^2 + (\delta b)^2 + (\delta c)^2 + \cdots (\delta z)^2}} \qquad \textbf{Equation 3.7}$$

where δX is the uncertainty of some quantity X (*e.g.*, NECB) , associated with the combination of sums and differences of quantities (a, b, c, *etc.*), and their respective uncertainties (δa, δb, δc, *etc.*).

3.3 Results

3.3.1 Hydrology

The unit area (per 1 m^2) water balance calculated for the bog and fen for the duration of the study period is presented in Table 3.2. Total annual precipitation for 2011 (657 mm) was slightly less than the long-term average for the region (~700 m). During the study period, the site received 443±44 mm (72% of annual total) of rain (Figure 3.4), with more than half (282 mm) of that falling during five major storm events throughout the season. Given that interception from above-ground vegetation is likely minimal and spatial variability in rain and snow inputs over the small ~5 km^2 subwatershed is negligible, we assigned a conservative uncertainty of 10% to the precipitation estimate for the study period (Winter, 1981). Evapotranspiration was the dominant water loss pathway at the site, accounting for losses of 276±28 and 289±29 mm for the bog and fen, respectively, during the study period. ET over the study period accounted for >99% of the total annual measured ET at both sites. Mean seasonal (± standard deviation) rates of ET during the study period were comparable at both sites (Figure 3.4), but slightly higher in the fen (1.85 ± 0.96 mm d^{-1}) than in the bog (1.77 ± 0.87 mm d^{-1}). Rates of ET peaked in June at nearly ~3.8 mm d^{-1} at both sites, coinciding with increases to daily air temperatures (data not shown). During extended periods of high rainfall, rates of ET decreased significantly, sometimes approaching zero.

Table 3.2. Estimates (± uncertainty) in mm for individual components of the bog and fen water balances for the study period (May 15 – October 19, 2011), including change in storage (ΔS), precipitation (P), evapotranspiration (ET), runoff (R).

Site	ΔS (mm)	P (mm)	ET (mm)	R (mm)	ξ (mm)
Bog	29±14	443±44	276±28	73±13.7	-64.3±55.7
Fen	23±11	443±44	289±29	55.7±0.3	-75.3±54.0

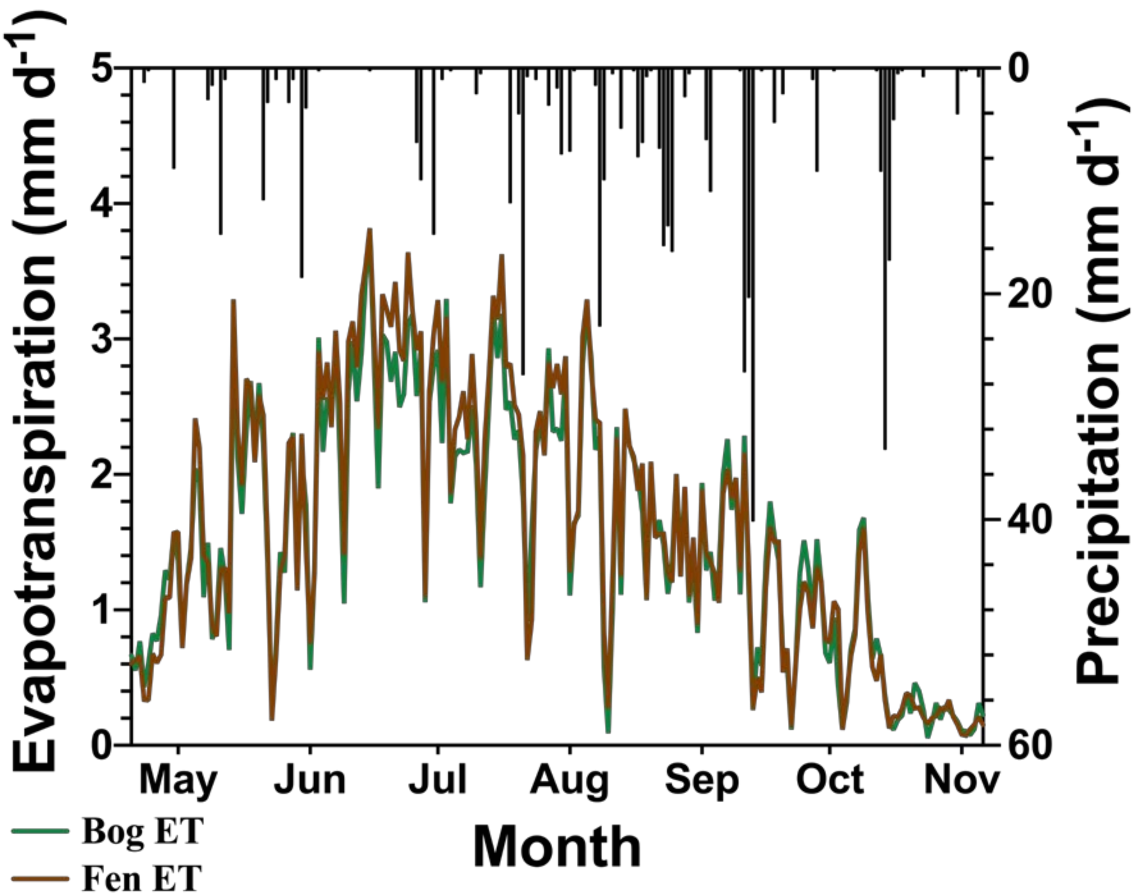

Figure 3.4. Total daily precipitation (P) and evapotranspiration (ET) for the bog and fen (in mm d^{-1}) for the duration of the study period. Data courtesy of C. Charron, Ontario Ministry of the Environment.

A positive change in storage was measured over the study period in both the bog (29±14 mm) and fen (23±11 mm), due to a net increase in water table position in October as compared with May (Figure 2.3B). The uncertainty in the change in storage is represented as the standard deviation of the water table elevations in wells.

Runoff was estimated by calculating the flux of water through the peat profile at the BF and FT transects using the 4-layer peat model (Figure 3.2). Total modeled runoff for the study period was 73±13.7 and 55.7±0.3 mm for the BF and FT transects, respectively. The relatively higher K (10^{-3} m s^{-1}) in layer 1 accounts for more than 99% of total runoff at both the bog and fen. This is not a realistic representation of the physical processes at the site, since it is likely that only the topmost (highest K) portion of layer 1 is actively transmitting water through the peat column. Our method of K testing in the shallow peat did not allow us to discretize runoff into thinner sections within the 1 m portion of the profile. The error in runoff was estimated by calculating groundwater discharge using the lowest and highest values of hydraulic conductivity at each layer based on the mean±standard deviation of K for the bog and fen.

The residual water balance term reflects the unaccounted hydrological inputs and outputs, as well as the discrepancy (or error) in the estimates. The calculated residuals (± propagated errors) for the bog and fen are -64.3±50.4 and -75.3±47.9 mm, respectively. The negative values indicate that there is still a small portion of hydrological outputs that have not been accounted for, but the relative magnitude of the residual (relative to hydrologic inputs) is moderate (14.5% and 17.0% for the bog and fen, respectively).

3.3.2 Dissolved Organic Carbon and Mercury Chemistry

Contoured monthly concentrations of pore-water DOC for the BF and FT transects are shown in Figures 3.5 and 3.6, respectively. Overall, concentrations of DOC are generally higher and more variable throughout the study period along the BF transect (7.4-67.2 mg L^{-1}) than in the FT transect (5.8-18.4 mg L^{-1}). Patterns of DOC in the BF transect are complex and show zones of elevated concentrations (>50 mg L^{-1}) at 50-100 and 325-400 m along the transect, which correspond to ridges, and hummock-dominated surface features. Pore-water samples taken near pools and hollows (200-300 m along the transect) correspond to lower DOC concentrations (<25 mg L^{-1}). Generally, levels of DOC gradually decrease from ~30 to 10 mg L^{-1} at the distal end of the BF transect as the bog transitions into the fen. Changes to mean DOC concentrations in the bog between May and August 2011 are only significant (>2 mg L^{-1}) in the first meter below the peat surface, with an increase from 21.8±6.1 to 37.7±8.2 mg L^{-1} at the water table, 27.6±5.9 to 35.1±5.5 mg L^{-1} at 0.5 m, and 33.1±17.3 to 35.2±18.1 mg L^{-1} at 1.0 m. Large inputs of precipitation to the site in September and October resulted in the dilution and flushing of pore-waters, leading to lower DOC concentrations in October samples which were 27.2±5.1, 30.7±3.2, and 31.7±24.2 mg L^{-1} at the water table, 0.5 m, and 1.0 m below the peat surface, respectively. A larger pool of water located within the bog water track that was sampled in October contained 25.2 mg L^{-1} DOC.

Along the length of the FT transect, DOC concentrations are generally much lower (<15 mg L^{-1}) and show no discernable spatiotemporal patterns or stratification through the peat profile. Samples taken over the study period from large ponds at Fen+650S and Fen+450S exhibited similar concentrations of DOC (8-10 mg L^{-1}) to those found in peat pore-waters (data not shown). Variability in DOC concentrations within the fen is also less pronounced (standard deviations are typically 1-3 mg L^{-1}), as compared to the bog. However, mean DOC concentrations at the surface in the fen did increase significantly over the growing season, from 7.6±0.3 mg L^{-1} in May to 12.3±2.4 mg L^{-1} in August, and then decreasing to 8.2±1.9 mg L^{-1} in October. Water samples taken from a rivulet in the Trib 5 riparian zone (at the terminal end of the ribbed fen) ranged between 7.2 to 11.0 mg L^{-1} throughout the study period.

Dissolved organic carbon in samples from piezometers installed at depths between 0.5 and 1.4 m into the marine sediment (at Fen+800N) ranged between 7.6 and 14.1 mg L^{-1} (data not shown). Concentrations of DOC in Trib 5 increased steadily from 12.5 mg L^{-1} in the spring to 20.0 mg L^{-1} in October (data not shown). A seepage face delivering water directly to Trib 5 from between the organic and marine layers was sampled periodically throughout the study period, and was found to contain levels of DOC between 8.9 and 17.7 mg L^{-1}, which were elevated as compared to pore-water samples from the ribbed fen.

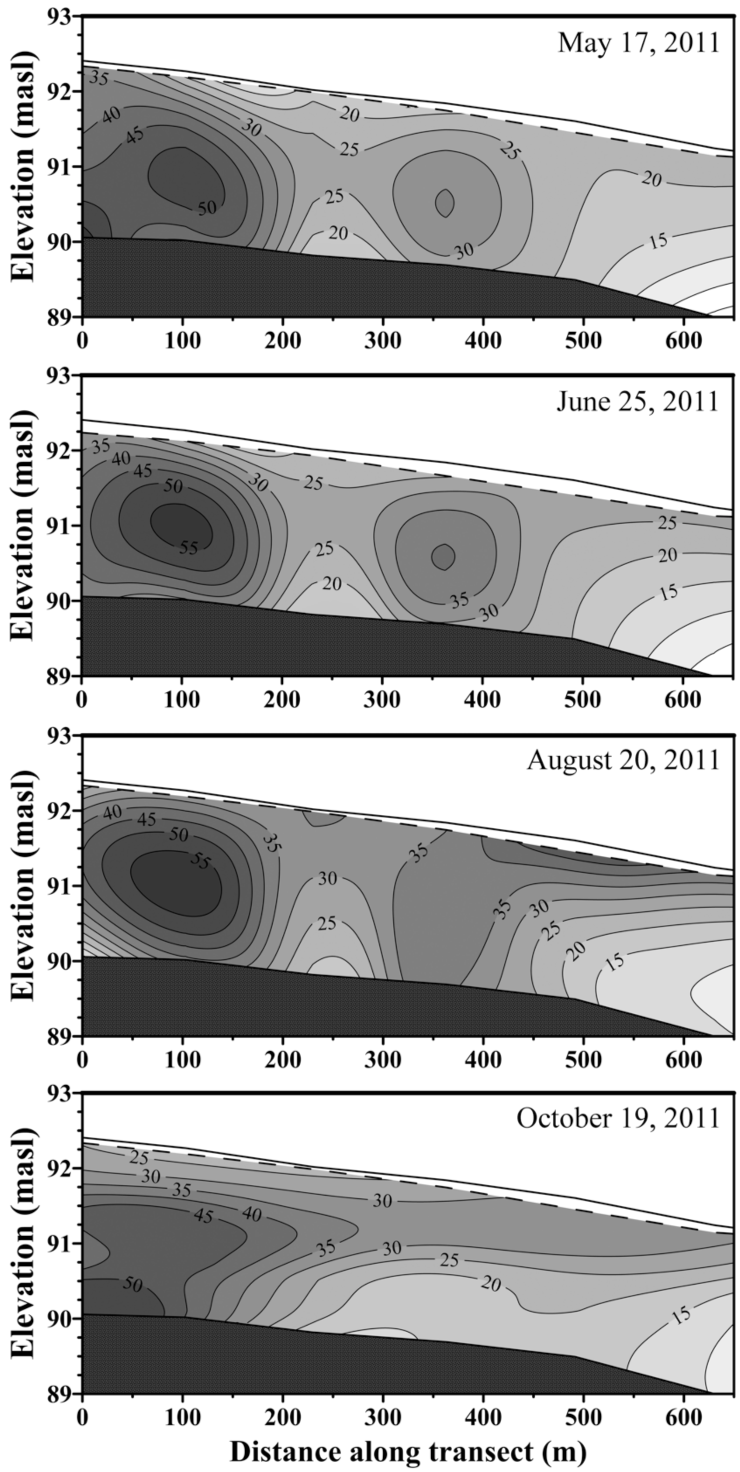

Figure 3.5. Vertically exaggerated (75x) cross sections of the BF transect showing interpolated DOC concentrations (mg L^{-1}) on May 17, June 25, August 20, and October 19, 2011. Contours are shown every 5 mg L^{-1}. The uppermost dashed and solid lines show the water table and peat surface, respectively. The dark speckled layer under the peat represents the low K marine sediment.

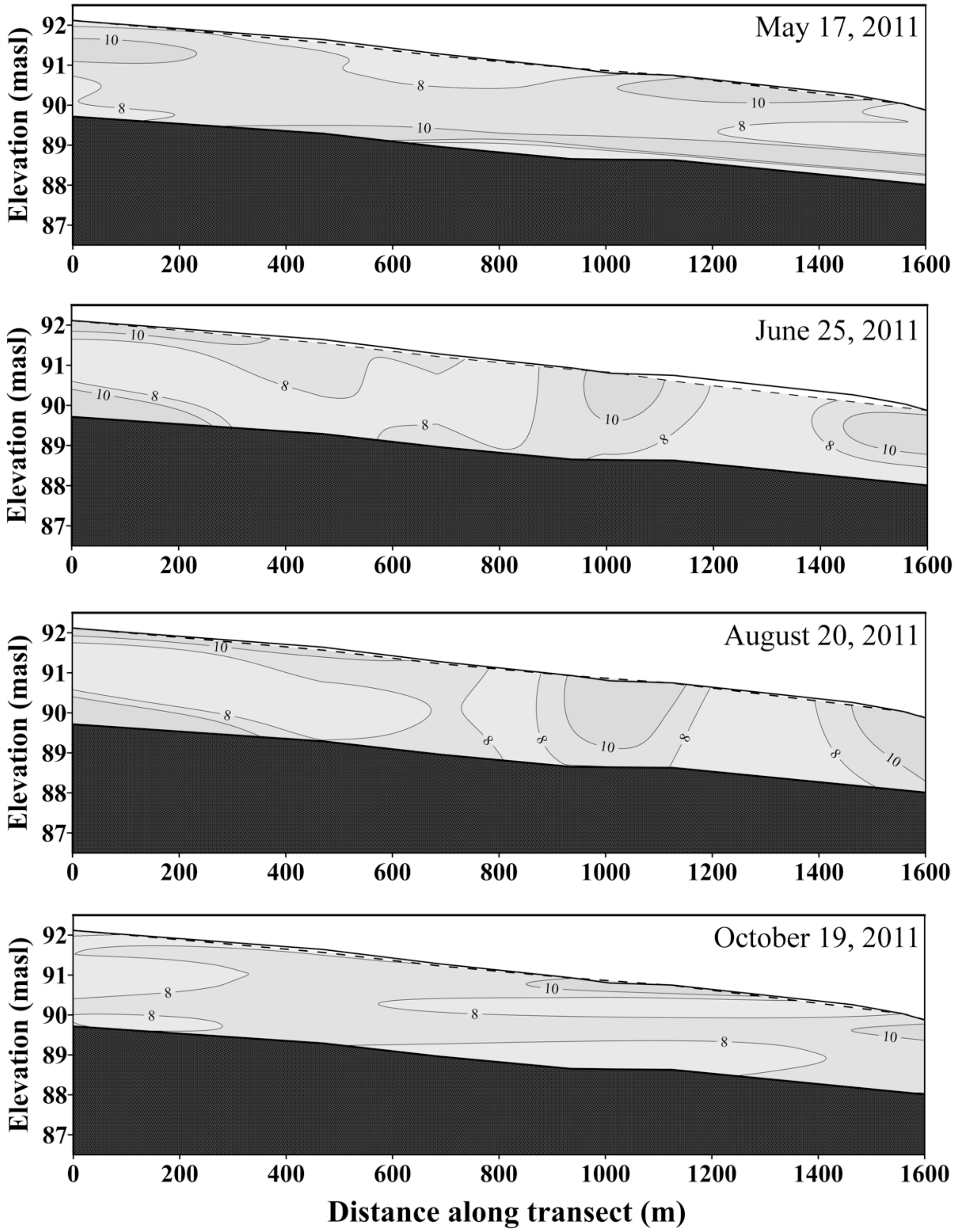

Figure 3.6. Vertically exaggerated cross sections (80x) of the FT transect showing interpolated DOC concentrations (mg L^{-1}) on May 17, June 25, August 20, and October 19, 2011. Contours are shown every 2 mg L^{-1}. The uppermost dashed and solid lines show the water table and peat surface, respectively. The dark speckled layer under the peat represents the low K marine sediment.

Overall, mean seasonal concentrations of THg in pore-waters throughout the peat profile were relatively low at both the BF (1.55±0.99 ng L^{-1}) and FT (0.71±0.76 ng L^{-1}) transects, with some samples containing trace (<LOD) levels, while some as high as 3.70 and 4.30 ng L^{-1}, respectively. Concentrations of MeHg were typically <10% THg, and often not more than 5% THg. In the BF transect, mean seasonal concentrations of MeHg were 0.052±0.051 ng L^{-1} with one sample as high as 0.201 ng L^{-1}. Mean seasonal MeHg concentrations in the FT transect were similar to those in the BF transect (0.037±0.052 ng L^{-1}), and one sample exceeded 0.25 ng L^{-1}.

Figures 3.7 and 3.8 show depth profiles of mean peat pore-water THg and MeHg concentrations, respectively, for both transects throughout the study period. There is a clear decrease in concentrations of THg with depth at all sites (Figure 3.7), with a 2-4x difference in concentrations between the surface and deepest piezometers. Shallow pore-water THg concentrations in the bog are >2 ng L^{-1}, but <1 ng L^{-1} at the contact between peat and the marine sediment. In the fen, surficial concentrations of THg are slightly lower (1-2 ng L^{-1}), and there is little differentiation with depth past 1.0 m. THg variability is much more pronounced in the bog, particularly in 0.5 and 1.0 m piezometers and in samples taken in October, whereas the fen shows very little variability with depth and throughout the season. Temporal changes to THg are apparent, with a slight increase in mean concentrations at each depth in the peat profile at both the BF and FT transects throughout the season. However, variability between individual samples is high which makes it difficult to assess whether seasonal changes to pore-waters are significant or simply an artifact of variability and low sample numbers (n=1 to 4 at each depth).

Depth profiles of MeHg in pore-waters at both sites (Figure 3.8) show similar decreasing concentrations with depth, with the exception that that some samples from the 0.5 m piezometers show higher levels of MeHg than those found at the water table. Mean monthly MeHg concentrations in the BF transect are between 0.1-0.2 ng L^{-1} at the surface and 0.5 m, and decrease below 0.1 ng L^{-1} at greater depths. Similar levels of MeHg are found in the FT transect, but with slight increases in concentrations at depths greater than 1.0 m below the peat. Variability in MeHg is high at the surface, 0.5, and 1.0 m piezometers. As with THg, temporal trends in MeHg are masked by large inter-nest variability, but in general, MeHg concentrations at the surface and 0.5 m increase by a factor of 1-2 over the growing season.

Mercury concentrations at other locations in the study site (data not shown), namely open pools of water, and surface waters near the fen-tributary transition zone, are similar to those found in peat pore-waters along the BF and FT transects. THg concentrations in larger ponds in the study site ranged between 3.43-4.46 ng L^{-1} in the bog and 0.60-1.64 ng L^{-1}in the fen. MeHg was also very low in bog (<LOD to 0.0081 ng L^{-1}) and fen ponds (<LOD to 0.0037 ng L^{-1}). Concentrations of THg and MeHg in the marine sediment were slightly lower and more temporally consistent then in the peat, 0.29-1.51 ng L^{-1} and 0.044-0.166 ng L^{-1}, respectively. Samples taken from a rivulet flowing from the riparian zone portion of the fen into Trib 5 (n=4 for duration of study period) were also low in THg (0.54 to 1.05 ng L^{-1}) but elevated in MeHg (0.010 to 0.163 ng L^{-1}). These high levels of MeHg were not reflected in Trib 5 surface waters, which were found to contain approximately half the concentrations as compared with the rivulet (0.024 to 0.075 ng L^{-1}). THg concentrations in Trib 5 were between 0.84 and 1.25 ng L^{-1}, slightly higher than concentrations in the rivulet.

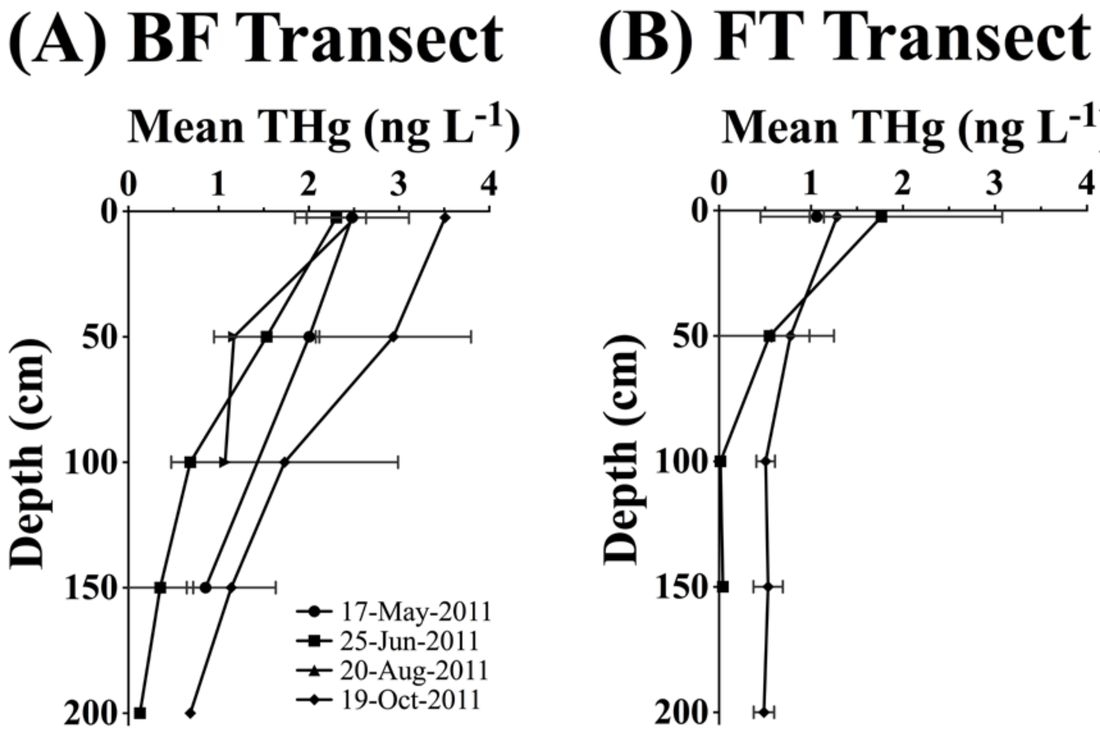

Figure 3.7. Depth profiles of mean total mercury (THg) pore-water concentrations in the BF and FT transects for the study period. Samples from the peat surface were obtained from 0-5 cm below a seasonally fluctuating water table, but are all shown as 2.5 cm below the peat surface for consistency. Error bars indicate standard deviations of arithmetic means.

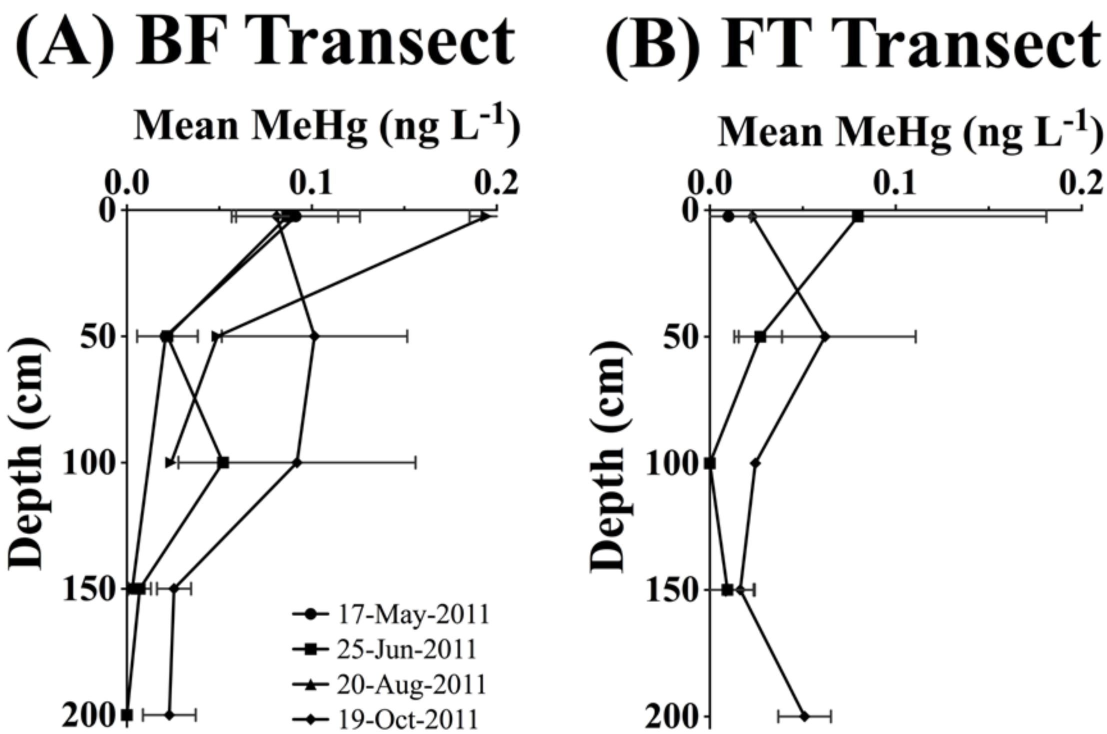

Figure 3.8. Monthly depth profiles of mean methyl mercury (MeHg) pore-water concentrations along the BF and FT transects. Samples from the peat surface were obtained from 0-5 cm below a seasonally fluctuating water table, but are all shown as 2.5 cm below the peat surface for consistency. Error bars indicate standard deviations of arithmetic means.

No strong relationships between THg and DOC were observed in either the BF or FT transect (Figure 3.9). DOC in the fen generally did not vary by more 2-4 mg L^{-1} with depth and over the study period, yet THg concentrations did exhibit a relatively large range of concentrations (<LOD and ~ 2 ng L^{-1}). In the bog, DOC varies greatly with depth and over the study period, but even higher DOC concentrations (>40 mg L^{-1}) can have low associated levels of THg.

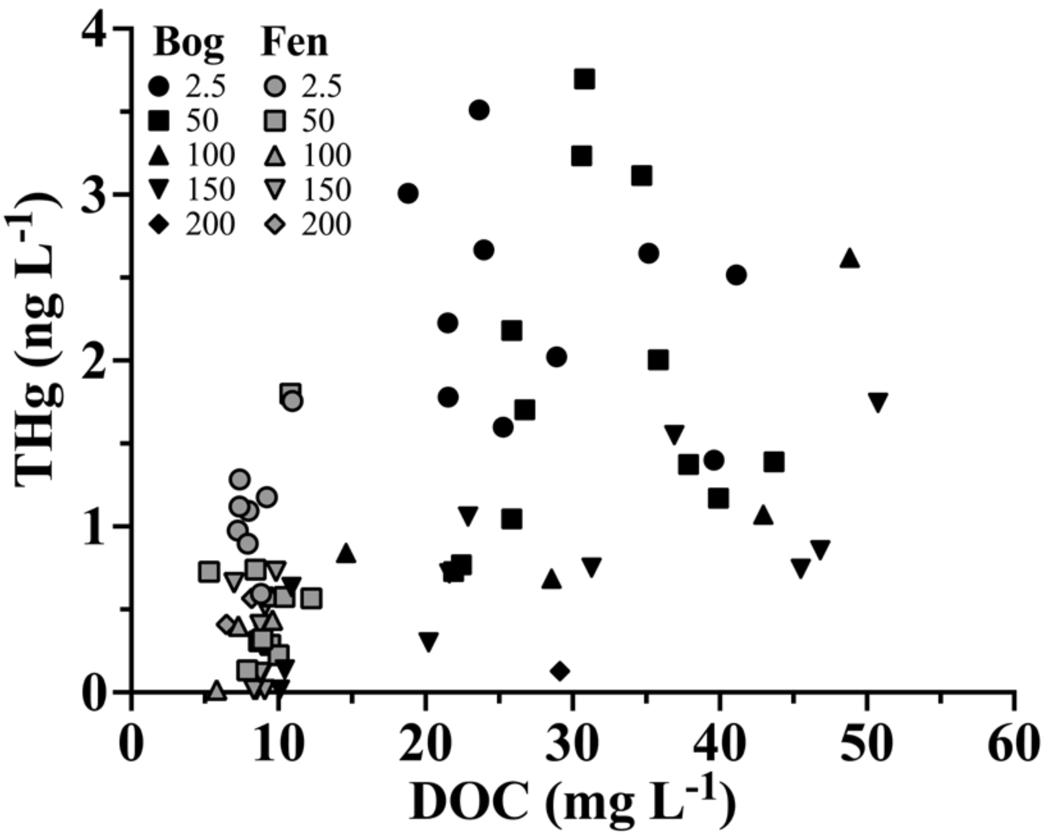

Figure 3.9. Plot of total mercury (THg) versus dissolved organic carbon (DOC) for the bog and fen for all depths.

3.3.3 Exports of DOC and Mercury

The calculated annual exports (and associated errors) of DOC from the bog to the fen, and through the fen towards the tributary, as well as annual estimates of the NECB, NEE, and annual methane fluxes are reported in Table 3.3. NEE (CO_2) was the biggest overall flux of carbon, and only significant input of carbon, into both systems, at 46.0±13.0 g C m^{-2} yr^{-1}. The bog and fen were net sources of CH_4 to the atmosphere, losing 7.0 ± 0.4 and 10.0 ± 0.5 g C m^{-2} yr^{-1}, respectively. Total exports of DOC for the snow and ice-free portion of the year were small, 2.0±0.3 g C m^{-2} yr^{-1} for the bog, and 0.5±0.1 g C m^{-2} yr^{-1} for the fen. Mean exports of DOC from the bog and fen are low when compared to other peatland systems, and only account for 5.4% and 1.4% of the NECB for each site, respectively.

Table 3.3. Estimates of the net ecosystem carbon balance (NECB), net ecosystem exchange (NEE), fluxes of methane (CH_4), and dissolved organic carbon (DOC) for the BF and FT transects, as compared to values reported for other peatlands.

Site	**NECB (g C m^{-2} yr^{-1})**	**NEE (g C-CO_2 m^{-2} yr^{-1})**	**CH_4 (g C-CH_4 m^{-2} yr^{-1})**	**DOC (g C m^{-2} yr^{-1})**
BF Transect, this study (Ombrotrophic Bog)	37.0±13.0	46.0±13.0[A]	7.0±0.4[A]	2.0±0.3
FT Transect, this study (Ribbed Fen)	35.5±13.0	46.0±13.0[A]	10.0±0.5[A]	0.5±0.1
Mer Bleue, Canada (Ombrotrophic Bog) Roulet *et al.* (2007)	21.5±39.0	40.2±40.5	3.5±0.5	14.9+3.1
Degerö Stormyr, Sweden (Minerotrophic Fen) Nilsson *et al.* (2008)	24.0±4.9	51.5±4.9	11.5±3.5	17.7±3.7
Storladen, Sweden (Permafrost Palsa Mire) Olefeldt *et al.* (2012)	44.5±16.3	50.0±17.0	2.0	3.2±0.6

[A]These values are generalized estimates provided by Elyn Humphreys (Carleton University) on behalf of the Ontario Ministry of the Environment, and not final modeled NEE and CH_4 fluxes.

Table 3.4 shows the calculated groundwater fluxes of THg and MeHg at both sites for the study period. Because of the higher runoff and overall pore-water Hg concentrations, the bog is exporting almost triple the amount of THg (132.9±45.4 ng m^{-2} yr^{-1}), as compared with the fen (50.0±8.4 ng m^{-2} yr^{-1}) per unit area. Similarly, exports of MeHg from the bog are almost twice as high as the fen per unit area, 3.4±2.8 and 1.9±1.2 ng m^{-2} yr^{-1}, respectively. The enhanced variability in runoff, and concentrations of THg and MeHg gives rise to larger uncertainty in fluxes from the bog.

Table 3.4. Mean annual groundwater fluxes of total mercury (THg) and methylmercury (MeHg) in ng m^{-2} yr^{-1} along the BF and FT transects, compared with published exports from surface waters draining wetland and upland areas. Uncertainty in mercury exports is calculated using minimum and maximum values of solute concentrations (from standard deviations of means) and runoff for each layer. Modified after Driscoll *et al.* (1998).

Site	**THg (ng m^{-2} yr^{-1})**	**MeHg (ng m^{-2} yr^{-1})**
BF Transect, this study (Ombrotrophic Bog)	132.9±45.4	3.4±2.8
FT Transect, this study (Ribbed Fen)	50.0±8.4	1.9±1.2
Northern Sweden (Lee *et al.*, 1995)	1200-1800	80-160
Ontario Wetland (St. Louis *et al.*, 1994)	600-2700	180-550
Ontario Swamp (Galloway and Branfireun, 2004)	2000-2200	180-200

3.4 Discussion

3.4.1 Calculating Runoff and Closing the Peatland Water Balance

The evaluation of the peatland water balance can provide insight into dominant hydrological processes within a catchment, and reveal whether all components of the water balance are accounted for, as well as where the largest measurement and estimations errors may exist (Winter, 1981). The final computed water balances for the bog and fen indicate a small positive change in storage for the bog (+29 mm) and fen (+23 mm) between the beginning and end of the study period. Rapid snow melt and high-frequency precipitation events in early spring and fall, respectively, resulted in high water tables rising above the average peat surface at all monitored wells. The site received 94% (657 mm) of the 30-year precipitation normal for the region, and 67% (443 mm) of the total rainfall fell during the study year, so we consider the results from this study representative of a typical water year. However, we caution that these results may not transferrable to future climate, since global climate change has already begun to influence precipitation patterns in Canada's north (Zhang *et al.*, 2000; FNSAP, 2010), and is expected to continue to increase annual precipitation (Rouse *et al.*, 1997; Moore *et al.*, 1998), especially during the winter months.

Out of all of the water budget components, precipitation was easiest to accurately quantify using a total precipitation gauge fitted with an Alter-type wind shield. Some errors in incoming precipitation may have been incurred from supplementing missing data from the Victor Mine weather station (15 km north of the study site), but an overall comparison of datasets from precipitation gauges located at or near the study site shows that daily precipitation totals are typically within 15-30% variance of each other. Snowmelt was not explicitly included in the water balance, since spatially extensive estimates of pre-melt peatland water storage and snow cover were not acquired. However, 78% (6.50×10^7 m^3) of the total annual discharge in Trib 5 occurred during the 157 day study period between May and October, which gives us confidence that we have at least captured the majority of the peatland runoff for the year, including a large portion of the remnant melt water during spring freshet.

Evapotranspirative processes are by far the largest water loss in both the bog and fen (Table 3.2), similar in magnitude to what is reported in natural and disturbed peatlands (Price and Maloney, 1994; Rouse, 1998; Waddington and Price, 2000; Lafleur *et al.*, 2005). In both bog and fen, ET water loss accounted for more than 90% of modeled annual ET for 2011, and 60% of the total incident precipitation received at the site during the study period. Evapotranspirative losses were 32-35% lower than the long-term mean annual evapotranspiration (431 mm) reported for Lansdowne House by Singer and Cheng (2002). Daily total ET rates ranged between 0.5 and 4.0 mm d^{-1}, depending on the time of year, antecedent moisture conditions, and precipitation events. The fen showed marginally higher daily rates of ET (Figure 3.4) and total ET losses, as compared to the bog, which is probably due to shallower depth to water table, lower microtopography, and higher proportion of open water pools and vascular plant cover (Oke, 1987). Uncertainty in ET measurements via eddy flux covariance techniques is assumed to be 10%, since no additional information regarding model error was provided to us at this time by the collaborators who supplied this data to us.

Total calculated groundwater runoff for the study period from the bog and fen was 73 and 56 mm, respectively (Table 3.2). This amounts to 17% of the total precipitation inputs being exported as groundwater from the bog during the study period, and 13% in fen. Because of the direction of groundwater flow paths, and neighboring position of the bog relative to the fen, the bog does contribute a small portion of groundwater to the total R in the fen. However, given the relatively small size of the bog internal water track (width = ~100 m) versus that of the ribbed fen (width = 800 m), the contribution from the bog is minimal. Runoff per unit area from the bog was consistently 20-30% higher than from the fen, but uncertainty in bog R is also greater because of increased variability in K in all layers, especially layer 1.

Our calculated water fluxes are lower than what has been reported for most northern peatlands, and only comparable to the 154 mm of runoff from the 204 km^2 Trib 5 watershed (Trib 5 discharge divided by the watershed area), reported by Richardson *et al.* (2012) for a dry year in 2010. In comparison, total runoff from the entire Trib 5 watershed was 249 mm for the study period in 2011 (56% of incident annual precipitation). However, those estimates include contributions from other sources, namely sediment and bedrock groundwater, seepage faces, and direct inputs of precipitation. From a nested tributary study of the Nayshkootayaow River by Orlova and Branfireun (2014), we do know that peatland runoff contributes to approximately 50% of total streamflow in Trib 5. Given this, we can assume that peatland runoff accounted for approximately 125 mm for the study period, and that our estimates of runoff are off by nearly half. If we consider the residual terms and associated uncertainty in the water balance, -64.3±55.7 mm for the bog and 75.3±54.0 mm for the fen, we can account for the potential underestimated runoff.

We speculate that a portion of the error in our estimates of runoff could be due to rapidly generated runoff that occurred as surface overland flow during high enough water tables when the peat was saturated, causing pools to become connected by networks of lower lying channels. This type of runoff generation has reported for other peatlands (Woo and Heron, 1987; Holden and Burt, 2003), and would not be accounted for in our groundwater discharge model. However, microtopography in the form of hummocks, hollows and ridges in the bog and fen was observed to quickly impede any such prolonged overland flow for meaningful distances (>20 m) during the study period. Still, it is likely that we have underestimated runoff by not accounting for minor surface flows. Networks of soil pipes within the peat profile may also be responsible for rapid delivery of water from the landscape to adjacent surface waters (Holden *et al.*, 2009), however these features are often hard to find and define using conventional approaches (Holden *et al.*, 2002). We did not observe any soil pipes within the bog and fen systems.

The most important factors in the determination of groundwater runoff for these large, low-relief peatland, particularly in the uppermost portion of the peat profile, appears to be K and the position of the water table, as well as the relationship between the two. We utilized the Hvorslev bail test method for determination of K (Hvorslev, 1951), as it is a commonly accepted approach for estimating field values of K (Boelter, 1965; Chason and Siegel, 1986; Surridge *et al.*, 2005), and is simply and easily performed *in situ,* without the need to extract peat samples for more involved laboratory-based testing (Freeze and Cherry, 1979; Beckwith *et al.,* 2003; Nagare *et al.*, 2013). Given the logistical constraints imposed by working in such a remote location and the limited amount of time spent on site, it would be challenging to obtain undisturbed samples of peat for laboratory permeameter tests, especially from the fen (where surficial peat is highly compressible). Field tests of K have the added benefit of providing a much more representative estimate of K, given the larger volume of peat that is subject to the test, that may incorporate heterogeneities into the final result.

Nevertheless, reliable values of K from bail tests depend largely on the quality of the well/piezometer installation, and smearing and/or partial blockage of the well screen can introduce bias into the results in poorly developed wells (Surridge *et al.*, 2005). Wells at the site were frequently developed, and we did not observe significant variability in replicate K tests, which gives us confidence in the integrity of our wells and results. However, the build up of biogenic gas (CH_4) bubbles in the pores of peat and wells can also limit water seepage through peat (Baird and Gaffney, 1995; Beckwith and Baird, 2001). Further, the underlying mathematical models ignore the compressibility of the medium (whereas peat is a highly compressible medium) and not provide information on anisotropy (Chirlin, 1989). However, the shallower peat profiles are known to have higher values of K_h as compared with K_v (Surridge *et al.*, 2005), and in larger, undisturbed peatland complexes where vertical hydraulic gradients are small, the values of K obtained from standpipe bail tests are likely more than adequate as estimates of K_h. Regardless, a lowered measured K (compared to the “actual” K), particularly in the shallow peats, is likely responsible for our low runoff estimates.

In our model, the relatively high K peat in layer 1 was responsible for the movement of >99% of water through the peat profile, highlighting the importance of high K layers as conduits for groundwater flow. The K values obtained from the bail tests performed on the 1 m fully penetrating wells (~10^{-3} m s^{-1}) were at least an order of magnitude higher than K measured in bog and fen piezometers between 0.5 and 2.0 m below the surface, similar to K values reported for the peatlands of northern Minnesota (Chason and Siegel, 1986; Siegel and Glaser, 1987; Wright *et al.*, 1992). The larger range in unit area runoff estimates for the bog are the result of large spatial variability in K at the bog surface due to a highly fluctuating water table throughout the season. In layer 1, the effective K did show a dependence on water table position in the bog, increasing by more than a factor of 2 between the lowest (~30 cm) and highest (~5 cm) measured water tables. Such a strong relationship was not found in the fen, because the water table did not change much over the season, and the K in top ~10 cm of the fen peat was high enough that it likely obscured any small decrease of K with decreasing water table.

3.4.2 Dissolved Organic Carbon

Concentrations of DOC in peatland pore-waters at the site are within the range of those reported for bogs and fens in the Hudson Bay Lowlands (Reeve *et al.*, 1996; Glaser *et al.*, 2004; Ulanowski and Branfireun, 2013) and other boreal peatlands (Waddington and Roulet, 1997; Moore, 2003; Siegel *et al.*, 2006). Dissolved organic carbon concentrations in the bog are at least twice as high as in the fen, and exhibit much higher variability over the length of the BF transect, as well as much greater seasonal changes, particularly between spring freshet and late-summer drought. Additionally, the distribution of DOC within the peat profile along the BF transect is stratified with distinct “bulls-eye” patterning, similar to the interpolated stable water isotope cross sections in Figure 2.12. Such clear, stratified patterns of DOC are not apparent along the FT transect. These differences in the concentrations and relative distributions of DOC between the two transects, as well as the temporal changes in the shallow peat within each transect over the growing season, can be explained by an interplay between biotic and abiotic processes. Specifically, it is the different sources of organic matter, differing biogeochemical conditions (*e.g.*, pH and temperature), and dominant hydrological regimes and flow paths that influence the microbial processes and residence times at each peatland type, respectively (Chapter 2).

Along the BF transect, DOC concentrations are consistently >20 mg L^{-1} near the surface, likely due high inputs of more easily decomposable litter from ericaceous shrubs, since sphagnum litter is quite resistant to decomposition (van Breemen, 1995). However, root exudates (Fenner *et al.*, 2004) and *Sphagnum spp.* derived organic acids (Siegel *et al.*, 2006) are also likely significant sources of DOC to bog pore-waters. The microbially mediated decomposition of organic matter into smaller DOC-size fractions can occur via aerobic or anaerobic pathways, which in peatlands is largely influenced by depth to water table (Porcal *et al.*, 2009). Aerobic processes are much more efficient at net DOC production as compared with production rates in reduced, waterlogged soils (Fenner *et al.*, 2009), and a fluctuating water table is known to augment the release and mobilize DOC from the soil-matrix into peat pore-waters (Freeman *et al.*, 2001). The variability in DOC concentration in shallow peat pore-waters along the BF transect (20-60 mg L^{-1}) is likely caused by event and season-scale water table variability (~ -25 to 5 cm relative to the peat surface), as well as differential water table positions along the transect due to hummock-hollow microtopography and the larger pool-ridge sequences. DOC concentrations along the BF transect did exceed 50 mg L^{-1} at depths >1 m in some areas (darker zones at Bog+100 and Bog+360 in Figure 3.5), possibly due to transport of DOC downwards through the peat profile due to consistently minor negative hydraulic gradients. Lower concentrations of DOC (<25 mg L^{-1}) are found in close proximity to lower-lying areas in the bog, such as ponds, where *Sphagnum* mosses dominate, aboveground vascular vegetation is absent, the water table persists near or above the surface throughout the year, and the peat has higher hydraulic conductivities. Concentrations of DOC in the bog did not change at depths greater than 1 m over the study period, suggesting a decoupling of carbon pore-water chemistry at depths greater than 1 m, at least on a seasonal time scale.

Dissolved organic carbon concentrations in the fen are low (8-12 mg L^{-1}), and depth profiles of DOC are uniform along the FT transect, with little temporal seasonal changes observed even in the uppermost peat layers. Such comparatively low concentrations in the fen are somewhat counter intuitive, given that one would expect higher DOC in fen pore-waters due to the abundance of readily decomposable litter from abundant woody-vegetation, a circumneutral environment, and longer residence times (implied by lower hydraulic conductivities and gradients) (Moore, 2009; Porcal *et al.*, 2009). Rather, it seems that the consistently high water table (-10 to +10 cm relative to the peat surface) and relatively minor short and long-term water table oscillations leads to highly anaerobic conditions, which limits the production of DOC, as well as mobilization into groundwater (*Ibid*.). These much more subdued spatiotemporal distributions of DOC along the FT Transect are likely due to the uniform alternating ridge-trough microtopography and vegetation cover, and the small-to-negligible vertical hydraulic gradients in the ribbed fen. Longer, more tortuous groundwater flow paths in the >5 km long fen system may also promote better mixing and translocation of DOC throughout the system due to diffusional and dispersive processes, whereas the length of the bog may not be sufficient to promote such redistributions of solutes (Reeve *et al.*, 2001).

Dissolved organic carbon concentrations from piezometers in the marine sediment near the tributary were unexpectedly similar to fen pore-waters (~10 mg L^{-1}). We do have confidence that this is not an artifact of contamination from improper sampling procedures, since wells were developed regularly before samples were obtained and great care was taken during piezometer installation ensure well integrity was maintained. We speculate that there may be some movement of DOC from the overlying peat strata into the marine sediment, likely via diffusional processes since the low K (10^{-7} m s^{-1}) calcite sediments should impede advective movement of solutes into the marine sediment itself (Reeve *et al.*, 2000). Additionally, the organic carbon may be derived from an entirely different source than peat, perhaps relic organic matter from the Tyrell Sea, or derived from the gravel-sized pieces of charcoal that were recovered from the sediment during piezometer installation. DOC was not sampled from the marine sediment under the bog, but given the similar hydraulic conductivities of peat and presumed hydrogeological uniformity of the clay, DOC concentrations would likely be comparable (Reeve *et al.*, 2000). The use of spectroscopic methods (*e.g.*, UV-vis, fluorescence, and FTIR) would allow for the qualitative assessment of the chemical composition of DOC from different sources (Cory and McKnight, 2005; Jaffé *et al.*, 2008), however we did not perform such optical measurements on our samples. We did attempt to use stable carbon isotopes to discern between different sources of carbon throughout the site, but the precision of our method and instrument limited the utility of such information (data not shown).

Surface water samples from rivulets and seepage faces in the riparian zone near Trib 5 exhibited slightly higher (>12 mg L^{-1}) concentrations of DOC than pore-waters along the FT Transect. We reason that such enriched DOC concentrations are the results of a much more aerobic and biogeochemically active environment and a higher abundance of litter from the larger trees and shrubs in this ~100 m transitional area between Fen+800N and the tributary (Vidon *et al.*, 2010). This may explain why Trib 5 has higher DOC concentrations than found in the ribbed fen, even after accounting for *ca.* 1:1 mixing with groundwater. Concentrations of DOC in precipitation were not measured, but values between 1 to >3 mg L^{-1} have been reported for boreal peatland ecosystems (Moore, 2003; Orlova and Branfireun, 2014).

3.4.3 Dissolved Total and Methylmercury

Generally, concentrations of dissolved THg and MeHg in peat pore-waters at the study site were lower (0.3-2.0 and 0.01-0.07 ng L^{-1}, respectively) than more southern wetlands (2-15 ng and 0.2-10 ng L^{-1}, respectively) (Branfireun *et al.*, 1999; Heyes *et al.*, 2000; Galloway and Branfireun, 2004; Mitchell *et al.*, 2008b). Low THg concentrations are expected for the HBL, given the fairly low deposition rates expected in this remote environment, particularly prior to the industrial period (Brazeau *et al.*, 2013). However, we anticipated MeHg concentrations to be much higher, given that wetlands, and peatlands in particular, are known to be efficient methylators of inorganic mercury (Branfireun *et al.*, 2005). Sulfate (SO_4^{2-}) concentrations in bog and fen pore-waters (data not shown) were consistently low (<1 mg L^{-1}), and not detected in the vast majority of samples at all sites throughout the study season.

Pore-water concentrations of THg in the bog are nearly double that of the fen at the surface and 0.5 m piezometers, which is peculiar given that both sites are adjacent to each other and should be receiving equal inputs of THg from dry and wet deposition. Additionally, concentrations of THg in HBL fen peats (~130 ng g^{-1} dry weight) tend to be 1-4x higher than in bogs (~80 ng g^{-1} dry weight) (data not shown), where the enrichment of mercury in the solid phase is likely increased due to higher rates organic matter turnover in the fens (Martini *et al.*, 2007). Given the relatively larger negative hydraulic gradients in the bog, which should translocate Hg to deeper peats, we would also expect lower concentrations at the water table as compared to the fen. However, depth profiles of THg and MeHg at the site (Figure 3.7 and 3.8, respectively) show decreasing pore-water concentration with increasing distance from the peat surface, but this trend is much more subtle in the fen than in the bog. We speculate that the enrichment of THg in bog pore-waters is driven by pH, where acidic environments promote partitioning of Hg out of the peat and into the groundwater (Gambrell, 1994).

MeHg concentrations were highest at the surface in both the bog and fen, and decreased with depth, similar to depth profiles reported by Branfireun and Roulet (1999) in a Precambrian Shield headwater catchment at the Experimental Lakes Area (Ontario, Canada). Differences in MeHg with depth are not as significant between the two peatland types mainly due to the large variability in pore-waters within the peat profile across the site. High concentrations of MeHg in shallower peats are likely due to fluctuating water dynamics that influence redox conditions, which can stimulate the production of MeHg (*Ibid.*). Variability in MeHg concentrations between nests is too high, and the number of samples is too low (n = 1-4 for each depth per sampling campaign), to draw any significant conclusions regarding the controls of MeHg production at the study site.

Peatland-fed surface waters often exhibit a strong positive relationship between THg and DOC (Galloway and Branfireun, 2004; Ravichandran, 2004), however correlations between these two solutes are small and insignificant for pore-waters sampled here (Figure 3.9), even when subdivided into different peat types and depths. It is very likely that an interplay of factors, such as transient hydrology, the quality of the peat substrate, DOC turnover in different types of peat, and non-steady state partitioning, distorts such a relationship.

3.4.4 Exports of DOC and Mercury

The export of DOC from catchments has been shown to be proportional to wetland area (Moore, 2009), so in areas with high wetland and peat cover, such as the HBL, we would expect the proportion of DOC export to also be high, relative to the overall carbon budget. However, such relationship between water chemistry and landscape elements can breakdown in northern environments were wetland cover >90%, and other variables (*i.e.*, topography) can govern DOC export (Andersson and Nyberg, 2008). It is also much more difficult to quantify the flux of DOC from a catchment when it does not contain discrete, channelized hydrological outlets, and when it is necessary to model such fluxes based on groundwater flow. Groundwater transport processes are often very difficult to accurately model, given the irregular hydrogeological properties of porous media (*i.e.*, heterogeneity and anisotropy in K, and presence of macropores), complex mass transport processes (*i.e.*, advection, dispersion, and diffusion), and often spatiotemporally limited datasets. Our generalized 4-layer runoff and transport model assumes conservative solute behavior and that advective transport processes dominate, and ignores diffusional and dispersive processes. We acknowledge the limitations of such a simple flux model, however this approach has been utilized successfully in the peatland literature to provide reasonable estimates of water and solute fluxes through the landscape (*e.g.*, Waddington and Roulet, 1997).

Despite the ubiquitous peatland cover in the region, and the high concentrations of DOC in peat pore-waters, the results from our model show that the fluxes of DOC make up a small component of the peatland NECB. Our estimates of DOC export from the internal water track feature of the bog (2.0 ± 0.3 g C m^{-2} yr^{-1}), and from the ribbed fen (0.5 ± 0.1 g C m^{-2} yr^{-1}) are 1.5-30x smaller than have been reported for northern peatlands (Roulet *et al.*, 2007; Nilsson *et al.*, 2008; Olefeldt *et al.*, 2012). The DOC flux is the smallest of three components of the carbon budget, amounting to 5.4% and 1.4% of the NECB in the bog and fen, respectively. Although flux estimates of NEE and CH_4 to and from the peatland, respectively, are still approximate, we do not expect them to change much even after the underlying models were to be refined.

Similarly, exports of mercury are also much lower when compared to estimates reported elsewhere in the literature (Table 3.2). For example, the bog exports 132.9 ± 45.4 ng m^{-2} yr^{-1} of THg into the fen, which is at least three times lower than the export from wetland catchments in the Experimental Lakes Area (600-2700 ng m^{-2} yr^{-1}) (St. Louis *et al.*, 1994), even with comparable THg concentrations. Exports of MeHg from the ribbed fen (1.9 ± 1.2 ng m^{-2} yr^{-1}) are 2-3 orders of magnitude lower than reported for wetland catchments in Ontario (180-200 ng m^{-2} yr^{-1}) (Galloway and Branfireun, 2004).

The high hydraulic conductivity of layer 1 in our model is responsible for the delivery of >99% of the solutes at both sites. The magnitude and variability of DOC, THg, and MeHg exports during the study period appears to be primarily controlled by groundwater runoff, which we estimated to be low (<75 mm) in these peatland systems, and to a lesser extent, the variability in solutes concentrations measured along the BF and FT transects. Even if we assume that the residual term in the water balance is entirely unaccounted runoff, extrapolating solute fluxes by multiplying current exports by the adjusted runoff, 137.3 mm from the bog and 131.0 mm from the fen, increases solute exports by a factor of 1.9 and 2.4, respectively. With such corrections applied, exports of DOC begin to approach values reported for subarctic wetlands (Moore, 1987; Koprivnjak and Moore, 1992; Olefeldt *et al.*, 2012). However, mercury fluxes remain low even after such an adjustment to runoff. An important caveat to consider is that although solute exports from bog and fens on a per unit area (m^2) basis are low, the overall translocation of DOC and mercury can be substantial when one considers the >300,000 km^2 areal extent of HBL peatlands.

3.5 Conclusions

Morphological and hydrogeological factors seem to govern the movement of water between the bog and fen, and the fen into the tributary. The lack of significant channelization and low lateral hydrologic gradients (<0.0025) in the peatlands of the HBL promote the export of water and dissolved solutes between peatland landscape units and to surface waters via diffuse groundwater flow. Groundwater runoff processes, and carbon and mercury dynamics in the HBL are complex, given the hydrogeological variability and micro-to-mesoscale topography in the landscape, extremely long residence times imposed by the low hydraulic conductivity organic soils ($<10^{-3}$ m s^{-1}), and constantly changing biogeochemical conditions due a highly variable climate and a constantly fluctuating water table.

Evapotranspiration is the dominant water loss pathway at the study site (~280 mm). The major control on groundwater runoff is hydraulic conductivity of the peat, given that lateral hydraulic gradients in the bog and fen are governed by topographic relief and relatively consistent over the site and throughout the year. Our estimates of runoff (73 and 55.7 mm for the bog and fen, respectively) are low compared to other northern wetlands. A negative large residual term (65-75 mm) in our water balance suggests that we have underestimated runoff by a factor of 1.4-2.5, likely caused by spatially limited peat K data. While the *in situ* bail tests did provide us with an acceptable bulk estimate of K, a lab-based approach for measuring K (*e.g.*, the modified split-container method from

Nagare *et al.* (2013)) would be advantageous in discretizing peat into thinner (*e.g.*, 5-20 cm) layers.

The concentrations and distributions of DOC in peat pore-waters are different between the BF and FT transects. In the BF transect, levels of DOC are high (15-60 mg L^{-1}), and generally increase with depth. Seasonal increases to DOC in the bog are significant in the upper 1 m of the peat profile, where concentrations nearly doubled between May and August 2011. Patterns of DOC in the bog are influenced by intermittent downward hydraulic gradients and the presence of low-lying pools of water and ridges with differing hydraulic conductivities. Fen DOC concentrations are 2-4x lower than in the bog (8-15 mg L^{-1}), and show little stratification throughout the peat profile. Large inputs of rain in the fall resulted in a sharp and sustained increase in water tables at all sites, diluting and flushing solutes from the bog and fen.

Mercury pore-water concentrations were low and exhibited high spatiotemporal variability. Concentrations of dissolved total mercury in shallow bog pore-waters were twice as high in the bog (2-4 ng L^{-1}) as they were in the fen (1-2 ng L^{-1}), the difference likely induced by differential partitioning between the peat and groundwater phases due to higher acidity in the bog. THg and DOC concentrations were poorly correlated with each other. Methylmercury in the bog (<0.2 ng L^{-1}) and fen (0.1 ng L^{-1}) pore-waters was significantly lower than values reported for other subarctic wetlands. Similar to DOC, MeHg concentrations decreased with depth, but seasonal changes were less apparent because of the large within-site variability.

The bog was shown to have consistently higher annual groundwater exports of DOC per unit area (2.0 g C m^{-2} yr^{-1}), THg (132.9 ng m^{-2} yr^{-1}) and MeHg (3.4 ng m^{-2} yr^{-1}), in comparison to the fen (0.5 g C m^{-2} yr^{-1}, 50.0 ng m^{-2} yr^{-1}, and 1.9 ng m^{-2} yr^{-1}, respectively). A combination of higher dissolved solute concentrations, hydraulic gradients, and peat permeability in the bog was responsible for the differences. However, the bog does not appear to have a measurable influence on water quality in the fen, likely because of the small size (0.51 km^2) relative to the subwatershed (4.9 km^2). The elevated levels of DOC and MeHg (relative to the fen) measured within the small channels and seepage faces of the Trib 5 riparian zone demand further investigations into the influence on water quality of these biogeochemically unique areas, which could amplify concentrations of solutes in peatland runoff solutes entering surface waters in the HBL.

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Chapter 4

4 Conclusions

This research presented in this thesis set out to enhance our understanding of natural hydrological and biogeochemical processes in the peatland-dominated landscape of the Hudson Bay Lowlands (HBL) in northern Ontario, Canada. The objectives of this study were to provide estimates of water and solute fluxes in bog-fen-tributary sequence to complement the current research projects and long-term carbon monitoring efforts occurring at the study site. This was accomplished using conventional hydrometric measurements, including regular measurements of water table and hydraulic head along two major transects, as well as campaign-based sampling of peatland pore-waters for geochemical tracers (major ions and stable water isotopes), and dissolved organic carbon and mercury chemistry.

The results in Chapter 2 showed that groundwater flow throughout the bog-fen system was dominantly horizontal and follows surface topography, confirming the conceptual models and numerical simulations of Reeve *et al.* (2000). Hydraulic conductivity was the determining factor in controlling rates of groundwater flow since hydraulic gradients remained essentially unchanged regardless of water table position. Dispersive mixing was responsible for the delivery of solutes from nutrient-rich marine sediments as suggested by Reeve *et al.* (2001), particularly in the ribbed fen system. Fine-scale patterns of vertical groundwater flow resulting from differences in surface features and periods of high and low water table were superimposed onto the predominantly lateral translocation of water and solutes through the peat. Such patterns were clearly visible in pore-water concentrations of calcium and the distribution of stable water isotopes within the peat profile, particularly in areas that exhibited consistent vertical gradients. In the ribbed fen, the strong upwards gradients and thinning of the peat strata within the distal portions of the fen transect clearly augment the redistribution of solutes from deeper layers of peat, which likely results in unique biogeochemical conditions in the riparian zone surrounding the adjacent tributary.

Water table position in the peatlands controls the amount of runoff from bogs and fens, and as well as the magnitude of hydrologic connectivity of adjacent landscape units. The tributary adjacent to the large ribbed fen exhibits threshold behavior, and responds differently to hydrological inputs to the system, based on the antecedent moisture conditions in the peatland. Large and rapid increases to streamflow are observed when the water table within the fen breaches the average surface of troughs (typically during periods of sustained water inputs such as rapid melting of snow or a sustained rain events), allowing the higher hydraulic conductivity portions of the acrotelm to conduct water rapidly through the landscape and into the stream (Quinton and Roulet, 1998). The occurrence of seasonal ground ice within the peatland can intensify runoff generation and export of water into adjacent streams, similar to the effects of permafrost on arctic wetlands (Woo, 1986). Conversely, a decrease in the elevation of the water table caused by extended periods of drought can limit runoff from the landscape as diffuse groundwater flow through lower hydraulic conductivity peats, which significantly reduces contribution to streamflow. The HBL is already experiencing unprecedented effects from climate change (Gagnon and Gough, 2010; McLaughlin and Webster, 2014), and lowering of water tables in peatlands [*e.g.*, 10-20 cm lower as predicted by Roulet *et al.* (1992)], could further limit runoff and groundwaters exports to surface waters.

The expected changes to hydrological connectivity between peatland landforms and the consequential export of solutes to adjacent ecosystems in future climate scenarios (Pastor *et al.*, 2003; Freeman *et al.*, 2004) motivated the carbon and mercury research presented in Chapter 3. Hydrology and biogeochemistry influenced the different spatiotemporal distributions of dissolve organic carbon (DOC), total mercury (THg), and methyl mercury (MeHg) in bog and fen pore-waters. Dissolved organic carbon concentrations in the bog were 2-3x higher in the bog than in the fen, and reflected the small-scale influences pools as well as vertical gradients demonstrated in Chapter 2. Total and methyl mercury concentrations were low and extremely variable in both the bog and fen, and THg did not exhibit strong relationships with DOC. A doubling in pore-water DOC, THg, and MeHg concentrations in the surface peats over the summer was followed by a significant decrease in the fall. This flushing of pore-waters during periods of high hydrologic connectivity has implications to water quality in aquatic ecosystems. Elevated concentrations of DOC and MeHg in surface waters within the fen-tributary riparian zone suggest that this are may be a hotspot for biogeochemical transformation (Vidon *et al.*, 2010), but further study is needed to confirm this observation.

A simplified 4-layered peatland groundwater model was utilized to estimate fluxes of water, dissolve organic carbon (DOC), total mercury (THg), and methyl mercury (MeHg) through the bog and fen systems for the duration ice-free season. Total groundwater runoff from the bog and fen accounted for 16% and 13% of the total hydrologic inputs respectively, with 99% occurring in the uppermost 1 m of peat. Consequently, solute fluxes were also low, as compared to other wetland-dominated systems. Exports of DOC accounted for less than 10% of the net ecosystem carbon balance, and were trumped by atmospheric fluxes of carbon dioxide and methane to and from the peatland, respectively. Similarly, exports of THg and MeHg were between 1 and 3 orders of magnitude lower than reported for other boreal peatlands. However, total annual peatland-derived solute exports for the entire HBL are still very large even when unit area exports of solutes are low, because of the vast areal extent (320,000 km^2) of this ecosystem.

The outcomes of this study are limited by the restricted spatial and temporal resolution of our hydrometric measurements, simplified groundwater models, and assumptions regarding solute transport processes. We also neglect groundwater flow during the winter, and the contribution of groundwater from the marine sediment. Future research at this site, and in the Hudson Bay Lowlands, should aim to provide better estimates of snowmelt, and quantify any overland flow occurring during wet conditions. Estimates of groundwater fluxes form the landscape could also be improved by obtaining more discrete, laboratory-based measurements of K (including measurements of anisotropy) and the utilization of more complex groundwater numerical models that incorporate the micro-to-meso-scale topography and peatland features (e.g. pools, ridges, and troughs) throughout the site.

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Glossary of Acronyms and Abbreviations

C	Carbon
C	Concentration
CEC	Cation Exchange Capacity
CH_4	Methane
CO_2	Carbon dioxide
S	Storage
DGPS	Differential Global Positioning System
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
Eh	Reduction-Oxidation Potential
ET	Evapotranspiration
HBL	Hudson Bay Lowlands
Hg	Mercury (element)
J	Solute flux
K	Hydraulic Conductivity
LOD	Limit of Detection
m	Metres
m.a.s.l.	Metres Above Sea Level
MeHg	Methylmercury
NAD83	North American Datum (1983)
NECB	Net Ecosystem Carbon Balance
NEE	Net Ecosystem Exchange
NPP	Net Primary Production
OM	Organic Matter
P	Precipitation
pH	Measure of acidity
QA/QC	Quality Assurance and Quality Control
R	Runoff
r.t.s.	Relative to Surface
s	Seconds
SRB	Sulphate Reducing Bacteria
TEA	Terminal Electron Acceptor
THg	Total Mercury
UTM	Universal Transverse Mercator Projection
WT	Water Table
ξ	Residual Term

Curriculum Vitae

Name	Thomas Ulanowski
Post-secondary Education and Degrees	University of Toronto Mississauga, Ontario, Canada 2005-2010, HBSc Chemistry and Environmental Analysis
Honours and Awards	Northern Scientific Training Program (2011, 2012) Arcangelo Rea Family Foundation Award in Environmental Research (2012) Province of Ontario Graduate Scholarship (2011-2012) Second Place, Best Student Poster, International Conference on Mercury as a Global Pollutant (2011) Best Poster (Physical Sciences), Western Research Forum (2011)
Related Work Experience	Laboratory Manager (Branfireun Lab) University of Western Ontario (2012-2013) Research and Laboratory Technician University of Western Ontario (2011-2012) Teaching Assistant University of Western Ontario (2010-2011) Environmental Technician Abacon Environmental Consultants (2006-2009)

Publications

Ulanowski, T. and Branfireun, B. Small-scale variability in peatland pore-water biogeochemistry, Hudson Bay Lowland, Canada. *Science of the Total Environment* (June, **2013**).