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University of Alberta

#### The Influence of Groundwater Flow on Phosphate Dynamics in Three Riparian Wetlands Surrounding an Outwash Lake in Northern Alberta

by

Zabrina Gibbons



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science

in

Environmental Biology and Ecology

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#### Abstract

Shallow groundwater flow was monitored in a discharge, transition and a recharge riparian wetland of an outwash lake and was sampled for SRP, Fe<sup>2+</sup>, Redox, DO, pH, EC, Ca and DOC concentrations to determine the influence of flowpath on biogeochemistry and SRP sink source behaviour. Large groundwater volumes bypassed the discharge riparian wetland causing it to have little influence on P retention. Infiltration of dilute water, low redox and low pH of the riparian peat in the transition and recharge riparian wetland resulted in increased P mobility and may be a potential source of P to the lake and groundwater. Alternatively, pH and Ca were high in clays and groundwater outside the riparian zone and limited SRP export from the peatlands. The control of the mobility of SRP was found to be a complex relationship of precipitation reactions, sediment adsorption and desorption, vegetation, microbes and the influence of water chemistry.

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## 1 Introduction

#### 1.1 Study Area

The Western Boreal Forest (WBF) in Canada is one of the largest forested regions in the world and contains abundant wetlands that support a wide array of biota. Recently, the Boreal Plains ecozone of the WBF has experienced accelerated development in forestry, oil and gas-well exploration and extraction (AEP, 1998). Such large-scale disturbance has the potential to impact wetlands and lakes in the area by altering their hydrologic regime and nutrient generation capability (Bedford, 1999; Likens et al., 1977). Wetlands and lakes of the Boreal Plain may be particularly sensitive to changes in nutrient loading because they are shallow and P-rich (Cooke and Prepas, 1998; Vitt et al., 1995). Therefore, understanding the controls and functions on nutrient dynamics of Boreal Plain wetlands is paramount for effective natural resource management and landuse planning.

The climatic and geological characteristics of the Boreal Plains are unique compared to the Boreal Shield. The Boreal Plain has a sub-humid climate with generally low topographic relief, is underlain by thick heterogeneous P-rich glacial deposits (Klassen, 1989) and is characterized by a poor surface drainage network and numerous isolated ponds and associated peatlands of glacial origin (National Wetlands Working Group (NWWG), 1988). The average annual precipitation is often less than annual potential evaporation (Woo and Winter, 1993), which leads to reduced runoff and landscape hydrologic linkages. In contrast, the Boreal Shield is humid and has shallow till with granitic bedrock that result in lower nutrient concentrations and biotic productivity (Winter and Woo, 1990). Since the complex geology and sub-humid climate of the Boreal Plain may prevent accurate extrapolation of study results from the Boreal Shield, the Hydrology, Ecology and Disturbance (HEAD) project was initiated to investigate the hydrological and ecological functioning of Boreal Plain wetlands in the Utikuma Research Study Area (URSA) of Northern Alberta.

The URSA encompasses a 50 km<sup>2</sup> area that is representative of the Boreal Plain and includes wetland complexes in three different landforms, a topographic high-stagnant ice moraine, a lowland clay plain and a sandy glacial outwash plain. Due to the low

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hydraulic conductivity of clay till, the wetland complexes of the moraine and clay plain have limited interaction with regional groundwater flow systems (Ferone and Devito, 2004), and on an annual basis are more influenced by evaporation and precipitation than by groundwater. Steep water table gradients and large fluctuations in hydraulic head are characteristic of low permeability silty-clayey till (Winter and Rosenberry, 1995). Thus, groundwater interaction is minimal in the fine-grained textured soils of the moraine and clay plain. Increased groundwater and surface water interactions were found in the coarse-grained deposits in glacial fluvial landforms of the URSA compared to the finegrained till soils of the URSA (Smerdon et al., In Press). This was also found in the coarse-grained soils of the sandhills of Nebraska, where water table gradients were relatively uniform due to their direct connection with the groundwater system (Winter et al., 2001). These expected increases in surface and subsurface interactions may affect the nutrient dynamics of riparian wetlands in coarse-grained sediments but, to date, studies are limited. Within the framework of the HEAD project, this study investigated the relationship between hydrogeology and SRP dynamics in three riparian wetlands on coarse textured deposits of the Utikuma Research Study Area (URSA), in Northern Alberta.

#### **1.2 Riparian Wetlands**

Riparian zones are vegetated strips of land located between aquatic and terrestrial systems and have the potential to regulate fluxes of nutrients between uplands and surface water (Devito et al., 2000b; Gregory et al., 1991; Hill, 1996). Riparian wetlands act as nutrient sinks in some areas and can influence water quality of adjacent water bodies or connected surface waters (Burt and Haycock, 1996). The effectiveness of riparian wetlands to store nutrients has been shown to vary between landscapes (Devito et al., 2000a; Emmett et al., 1994; Lockaby et al., 1999), where wetlands can also function as nutrient transformers (Brinson, 1993; Devito and Hill, 1997), and as nutrient sources to adjacent aquatic systems (Raisin et al., 1999; Uusi-Kamppa and Ylaranta, 1992). The ability of riparian wetlands to control nutrient fluxes, such as phosphorus, is governed by their hydrologic and geologic setting (Devito et al., 2000a; Devito et al., 1989; Ferone,

2

2001). Thus, there is a need to understand the hydrology of a riparian wetland in order to understand its biogeochemical functions and nutrient dynamics.

## **1.3 Phosphorus Interactions**

Phosphorus does not have a gaseous phase, so it will remain within the soil-plantbiomass pool unless it is dissolved or physically exported from the riparian zone (Burt and Haycock, 1996). Phosphorus can occur as soluble and insoluble complexes in both organic and inorganic forms in soils (Mitsch and Gosselink, 2000). The principal inorganic form of phosphorus is orthophosphate (SRP or  $PO_4^{3-}$ ). Two processes that control the concentration and mobility of inorganic phosphorus in soil are the solubility of phosphorus-containing minerals, which is controlled by redox and pH, and the fixation or adsorption of phosphate ions on the surface of soil particles, which is controlled by the anion exchange capacity of the soil (Brady and Weil, 1999).

Phosphate ( $PO_4^{3-}$ ) is not directly altered by changes in redox potential but is affected by reactions with iron, manganese, and sulphide, which is influenced by redox potential (Mohanty and Dash, 1982). Prolonged anoxic conditions can reduce the iron in these complexes from ferric ( $Fe^{3+}$ ) to ferrous ( $Fe^{2+}$ ) iron, making the iron-phosphate complex much more soluble (Patrick and Khalid, 1974). This can release phosphate into solution (Brady and Weil, 1999) (Figure 1). The specific redox potential at which chemicals are stable, in either reduced or oxidized state, is pH dependent because it determines the inorganic form of phosphorus that is present (eg.,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ ) (Mitsch and Gosselink, 2000). Of the inorganic phosphorus, calcium phosphate minerals, such as apatite and hydroxy apatite, predominate in most alkaline soils (pH greater than 8.0), while iron and aluminium hydroxy phosphate minerals, such as strengite and vivianite, predominate in acidic soils (pH less than 6.0) (Brady and Weil, 1999) (Figure 1). Thus, if pH or redox conditions change, phosphates can be released into solution.

A major proportion of phosphorus in wetlands is tied up in organic litter and peat in inorganic sediments (Mitsch and Gosselink, 2000). Thus, organic forms of phosphorus, such as sugar phosphates, inositol phosphates and phospholipids, can be released during decomposition and mineralization (Mitsch and Gosselink, 2000). Retained phosphorus may later be released from soil and vegetation as dissolved phosphorus, when plants decompose or conditions change, and exported to surface waters (Vought et al., 1994). It is therefore important to know the properties of the soil to understand the dynamics of phosphorus within the riparian zone.

Hill and Devito (1997) showed that the seasonality of phosphorus release was related to hydrology and geologic setting. Variable phosphorus dynamics in wetlands have been linked to redox controls on phosphorus solubility (Ann et al., 2000; Bayley et al., 1985; Serrano et al., 1999). Water table position may not influence phosphorus concentrations directly but may, for example, affect the redox conditions, which may indirectly influence phosphorus mobility (Mohanty and Dash, 1982). Under reduced peat conditions and mid range pH, phosphorus solubility is enhanced (Ann et al., 2000), and therefore dominant hydrologic flowpaths can strongly influence phosphorus retention versus export within a catchment (Raisin et al., 1999). Thus, there is a need to understand the hydrology interaction of geochemistry and the influence of water table fluctuations in a riparian wetland to determine whether or not it will function as a sink or source of phosphorus.

#### 1.4 Influence of Flow on Nutrient Dynamics in Riparian Wetlands

Current forest management practices usually leave a designated riparian zone adjacent to waterways in order to mitigate nutrient export to aquatic systems exacerbated by disturbance. Riparian zones and wetlands will only function as nutrient buffer zones if water actually flows through the riparian wetland. Hydrologic pathways ultimately control the flux of sediments and nutrients into and across a wetland (Burt and Haycock, 1996). Furthermore, riparian lithology and its influence on surface and subsurface flow can influence nutrient transformation and transport to connected surface waters (Bern, 1998; Carlyle and Hill, 2001; Devito et al., 2000b; Hill, 1996). Therefore, one must understand how water flows through a riparian wetland before one can fully understand the nutrient dynamics in a riparian wetland.

Water may flow beneath a riparian wetland in highly permeable substrates, such as sand or gravel, and flow directly into the water body or hillslope preventing interaction of water with the riparian zone, except briefly at the water-sediment interface (Burt and Haycock, 1996). Water can also flow over the surface of a riparian wetland during spring melt when the peat is frozen, preventing interaction of water with the peat and preventing the riparian zone from functioning as a buffer zone (Woo and Winter, 1993). Thus, it is important to understand the flow paths in a riparian wetland in order to determine the effectiveness of nutrient storage and release.

Considerable interaction between groundwater and surface water occur in riparian wetlands, and numerous flow systems can be present. Dominant linkages to the wetland will control the timing and magnitude of groundwater and surface water flow inputs, the degree of interaction with the underlying sediments, and the chemistry of source waters (Brinson, 1993; Hill and Devito, 1997; Roulet, 1990). Size and scale of a groundwater flow system (eg., local vs. regional) will influence the concentration of solutes and the dominant forms of chemical species imported into the riparian wetland (Hayashi et al., 1998b; Winter, 1989). Riparian wetlands receiving groundwater from a larger flow system will reflect the geochemistry of longer flowpaths (e.g., increased salinity) (Freeze and Cherry, 1979) and the underlying geologic material (LaBaugh et al., 1998). In contrast, wetlands influenced by local flow systems reflect shorter flowpaths, near surface chemistry and more dilute water than regional flow systems (Winter et al., 1999). As a consequence, it is important to understand the types of flow and dominant linkages in a riparian wetland, to better understand the wetland environment and its nutrient dynamics.

Groundwater flow to a wetland can be very complex, particularly in hummocky terrain. For instance, ponds, lakes and streams may be areas of groundwater recharge, discharge or both (Winter, 1990). In a discharge zone water will flow from the hillslope, to the riparian wetland, and then into the lake (Winter, 1990). In this case any incoming nutrients and minerals may flow through the peat before reaching the lake. In a recharge zone, water will flow from the lake, to the wetland, and then into the hillslope and the riparian wetland will reflect chemical signatures of the lake (Marin et al., 1990).

A riparian wetland is a dynamic system and the direction of flow can also reverse, from a recharge to a discharge function, for example, depending on the season and magnitude of water inputs (Devito et al., 1997; Siegal, 1981; Siegel and Glaser, 1987). These dynamic flow conditions can have important implications for chemical transport and biogeochemical transformations (Brinson, 1993; Devito and Hill, 1997; Hayashi et al., 1998b; LaBaugh et al., 1997). Flow reversals are usually localized and can be caused by focused recharge of precipitation (Hayashi et al., 1998b), bank storage (Winter, 1999), mounding (Anderson and Munter, 1981), infiltration of meltwater and rainwater (Anderson and Munter, 1981), and evapotranspiration from plants (Hayashi et al., 1998a; Winter and Rosenberry, 1995). The sponge-like properties of peat (Boelter and Verry, 1977) may also influence local flow paths within the peat in conjunction with those discussed previously. Seasonal and annual patterns of groundwater movement can have implications for the biogeochemical function of wetland systems (Devito and Hill, 1997; Waddington and Roulet, 1997b). There has been little research of flow reversals in riparian wetlands adjacent to high permeability uplands, such as sand and its effect on wetland chemistry.

#### 1.5 Objectives

The overall objective of this study is to investigate how the linkages between hydrologic flowpath, riparian lithology and biogeochemical processes influence SRP dynamics in a riparian wetland of a lake in coarse-grained outwash sediments of the WBF of Northern Alberta. This thesis compares the spatial and temporal variability of SRP in three riparian wetlands of varying flow regimes in order to provide baseline information on the natural controls of SRP availability and increased knowledge of the surface/subsurface connections between groundwater and peat in coarse-textured deposits. My approach involved the analysis of spatial and temporal patterns of groundwater flow and pore water SRP concentrations in relation to redox, pH, ferrous iron, and calcium concentrations within the riparian zone. Specific objectives and hypotheses (**H**) are:

1) To determine the seasonal and spatial variability of water table fluctuations in a discharge, a transitional and a recharge riparian zone within an outwash lake

H1: Water-table fluctuations in the upland and riparian zone will be dynamic, both spatially and temporally, thus the hydrologic function will differ in relationship to lake-groundwater interactions and water table position in the riparian zone.

**H2:** Variability in water-table in the riparian zone will be more of a function of local versus regional groundwater flow rather than recharge/discharge function.

 To investigate the spatial and temporal variability of SRP in the riparian zone with varying hydrologic regimes in the discharge (T1), transitional (T2) and recharge (T3) riparian zones.

**H3:** SRP concentrations in the riparian zone will be higher during the spring and fall due to runoff and plant senescence.

**H4:** Highest concentrations of SRP will be associated with organic sediments of the riparian zone because a major proportion of phosphorus in wetlands is tied up in organic litter and peat in inorganic sediments (Mitsch and Gosselink, 2000).

 To investigate how different sources of water to the riparian zone, including precipitation, surface water and groundwater, influence the chemistry and SRP dynamics within the riparian zone.

H5: Significant water will flow through the riparian sediments and result in the transformation of SRP within the riparian zone. Groundwater inflow will affect peat anoxia and chemistry, which will affect SRP transformation and transport in the riparian zones.

**H6:** Groundwater will not flow through the riparian zone and SRP mobility will be most influenced by interaction with local flow regimes.

 To determine the role of the riparian zone in buffering SRP concentrations in varying groundwater flow regimes. H7: Groundwater interaction will influence whether the riparian zone is a source or sink of SRP. If groundwater flows through the riparian zone the riparian zone will retain SRP (controlled by soil adsorption, vegetation uptake,  $Fe^{2+}$  precipitation in aerobic zones).

**H8:** Organics in the riparian zone are a source of SRP (either to the lake in the discharge or to the groundwater in recharge), which is a combination of low buffering of organics, increased mineralization causing mobilization in aerobic areas, and  $Fe^{2+}$  reduction and mobilization of SRP.

5) To determine the biogeochemical control on P mobility in riparian zones with varying flow regimes.

**H9:** P mobility (transformation and transport) is controlled by redox environment and Fe<sup>2+</sup> in organics (riparian zone) and in the mineral substrate (groundwater).

**H10:** Redox in organic riparian sediments has little influence on P mobility in calcareous substrate, and it is thus Ca and pH controlled.

## 2 Methods and Materials

#### 2.1 Utikuma Research Study Area

The study lake (Lake No. 16) is located (56°6'N, 116°32'W) approximately 370 km North of Edmonton, Alberta at the Utikuma Research Study Area (URSA) (Figure 2). The URSA is located in the Mixedwood Boreal Plains Ecozone of Northern Alberta, at the transition between the Middle and High Continental Boreal Subregion (NWWG, 1988). The region has low relief and is characterized by three dominant landforms: 1) rolling to undulating hummocky disintegration moraines comprised of layers of silts, sands and gravels in clayey/silty till 2) lacustrine plains with extensive peatlands over clay and 3) glacial outwash areas of predominantly coarse-grained sand and gravels (Toth, 1978; Vogwill, 1978). The coarse-textured glacial deposits represent the primary aquifer units in the area; the hummocky moraine uplands areas represent groundwater recharge areas (Ceroici, 1979; Siegal, 1981; Tóth, 1978; Vogwill, 1978). The surficial glacial sediments of the broad region around the URSA include glaciofluvial, glaciolacustrine, and moraine deposits, which are underlain by the Smoky Group shale unit of the Upper Cretaceous period (Ceroici, 1979; Vogwill, 1978). Surface water from the Utikuma watershed drains into the Wabasca River tributary and eventually into the Peace River Basin (Vogwill, 1978).

Generally in the URSA, forest vegetation consists of trembling aspen (*Populus tremuloides*), balsam popular (*Populus balsamifera*), white spruce (*Picea glauca*) and jack pine (*Pinus banksiana*) in well drained areas, with black spruce (*Picea mariana*), tamarack (*Larix laricina*) paper birch (*Betula papyrifera*) and alders (*Alnus sp.(rugosa, tenuifolia, sinuata*)) in poorly drained areas. Poorly drained areas are prominent in this region, with wetlands covering 25 to 50% of the landscape, which include blanket peatlands, basin peatlands and pond-peatland complexes (NWWG, 1988).

The URSA is located approximately 150 km south of the discontinuous permafrost zone (Woo and Winter, 1993). Long term mean annual temperature for the Slave Lake meteorological station (approximately 100 km south of the URSA) is 1.7°C and mean summer (July) and winter (January) temperatures are 15.6°C and -14.5°C, respectively (Environment Canada, 2004). Annual precipitation and potential

evapotranspiration (PET) for the study area roughly balance: 503 mm and 517 mm respectively (Environment Bothe and Abraham, 1993; Canada, 2004). However, PET exceeds precipitation in most years, where infrequent wet years occur on a 10 to 15 year cycle (Ferone and Devito, 2004). Winter (November-March) snowfall is typically less than 100 mm/year, and represents less than 25% of the total annual precipitation (Marshall et al., 1999).

#### 2.2 Previous Investigation

A previous study (Smerdon et al., In Press) investigated the interaction of groundwater and surface water in the outwash sediments of Lake 16. Groundwater springs were observed along the east shore during the winter of 2001, thus groundwater interaction was inferred. A total of 70 piezometers were installed at 41 locations around and within the lake between 2000 and 2002 to determine the groundwater and surface water interactions. The study lake was found to be well connected to local and intermediate groundwater flow systems and locations of the discharge, transition and recharge zones were established. This study further investigates groundwater and surface water interactions on the local scale in the riparian zone and its affect on nutrient dynamics.

#### 2.3 Study Lake

The 39 ha lake (URSA No. 16) is situated on a glacial-fluvial outwash plain approximately 663 m above sea level (Figure 3). (Elevations reported in this study are relative to an assumed benchmark determined from maps; however, a recent survey suggests the elevations reported here are 20 m higher than the correct elevations for this region). Lake 16 is situated in the centre of a series of lakes, separated by eskers of sand and gravel, with Lake 17 to the southeast and Lake 5 to the northwest (Figure 3). On July 15, 2002 Lake 17 was 2.36 m higher than Lake 16, which was 1.91 m higher than Lake 5 suggesting flow from Lake 17, through Lake 16, to Lake 5 (Figure 4). There are no visible surface inflows to the study lake; however, springs are present on the southeast shore. A small outflow, a 1 m wide channel on the northwest side of the lake, flows into an adjacent fen where surface water subsequently recharges the local groundwater system.

The study lake is situated in a surficial hummock-and-hollow topography, consisting of glacial fluvial deposits and ice-contact sediments on the southeast edge of the lake (Fenton et al., 2003). The ice-contact, esker sediments are poorly sorted and range in size from sand to cobble, while the outwash sediments are stratified sand and gravel, with some silt (Ceroici, 1979; Fenton et al., 2003). Absence of surface flows and the presence of highly permeable surficial deposits, suggest a dominance of groundwater flow (Smerdon et al., In Press).

The lake basin is on average 4.4 m deep, lined with finer-textured silt and siltysand, and has filled with gyttja to an approximate depth of 1.5 m below the mean lake level (Smerdon et al., In Press). Most of the lake basin is open water, but tall emergent reeds and floating macrophytes have developed in shallow areas. Three transects of piezometers were installed perpendicular to a 10 to 30 m wide riparian peatland located between the lake and the sandy aspen upland that surrounded the entire lake.

#### **2.4 Transect Descriptions**

Three transects of piezometers were installed in a suspected discharge (T1), transition (T2) and recharge (T3) zone to observe three different groundwater-riparianlake interaction zones. The discharge transect (T1) was installed in a suspected groundwater discharge area, near the observed springs, located near the southern edge of the lake (Figure 3). The transition transect (T2) was located on the western edge of the lake near an assumed transitional area, a suspected hinge-line between the groundwater discharge and recharge zone (Figure 3). The recharge transect (T3) was located on the northwest side of the study lake in a suspected groundwater recharge area (Figure 3).

The dominant mineral soil of the three transects was coarse-grained sand (Smerdon et al., In Press), which was overlain by organic soils of various thickness. The discharge transect (T1) had the thinnest organic layer and the narrowest riparian zone, which was approximately 10 m wide and consisted of approximately 0.3 m of dark brown mesic organics and underlain by coarse-grained sand (Figure 5). Clumps of sedges (*Carex* spp.), grasses and mosses occurred near the lake, which succeeded into alder (*Alnus* spp.), birch (*Betula* spp.) and willow (*Salix* spp.) near the edge of the upland. The upland was dominated by aspen (*Populus* spp.) and birch. The upland had a 10 cm layer of decaying leaf litter (LFH), which was underlain by fine-grained sand to a maximum core depth of 4 m.

The riparian zone of the transition transect (T2) spanned a distance of approximately 40 m and consisted of a 20 m wide wet open fen near the lake and a 20 m wide dry open fen closer to the upland, which were separated by alder (Alnus spp.) (Figure 6). Lake sediments consisted of 1 m of flocculent gyttja, which was underlain by fine-grained grey sand that contained organics and approximately 10 to 20% clay at 2 m below the surface. The vegetation of both the wet open fen and the dry open fen consisted mostly of sedges (Carex spp.) and brown moss (Amblystegium serpens) with a few reeds (*Phragmites* spp.) and cattails (*Typha latifolia*) in the wet open fen and willow (Salix spp.) and hummocks and hollows of peat in the dry open fen (Whitehouse, 2004, per comm). The peat of the wet open fen was approximately 0.60 m deep and consisted of fibric peat, composed predominantly of decomposing sedge roots and vegetation, while the peat of the dry open fen was mesic and ranged from 0.60 to 0.80 m in depth varying between hummocks and hollows. Mineral soils underneath the wet and dry open fens consisted of fine-grained sand that also contained silt closer to the peat/mineral interface. The aspen upland had an average of 0.10 m of leaf litter (LFH) above coarsegrained sand that contained some layers of gravel.

The recharge transect (T3) was located near the outflow at the northwestern side of the lake in a suspected groundwater recharge zone. Organic lake sediments adjacent to the riparian zone consisted of gyttja that became more compact at 2.4 m below the surface and overlaid a sand layer (Figure 7). A 15 m wide wet open fen, similar to that found in T2, was located next to the lake and was composed of sedges (*Carex* spp.) and brown moss (*Amblystegium serpens*) with cattails (*Typha latifolia*). The peat in the wet open fen was the deepest of the three transects and consisted of fibric to mesic peat in the top 0.30 m and a layer of mesic to humic peat underneath. Mineral soils underneath both the lake and wet open fen organic sediments consisted of 1.0 to 2.0 m of fine-grained sand and a sandy/silty clay layer that transitioned to lacustrine clay/till at 3.3 to 3.5 m below the surface. Willows (*Salix* spp.) and birch (*Betula papyifera*) separated the wet open fen from a 40 m wide conifer swamp, which was dominated by black spruce (*Picea mariana*) with an understory of *Sphagnum* and other moss hollows situated among hummocks of Labrador tea (*Ledum groenlandicum*). The upper 0.60 m of peat was fibric, underlain by 0.30 m of mesic to humic peat that overlain a silty/clayey sand mixture. Aspen dominated the eastern slope of the upland while jack pine grew near the crest and the western slope of the upland.

#### 2.5 Precipitation and Evaporation Measurements

Precipitation measurements were made from November 2001 to October 2003 incorporating the hydrologic years November 2001 to October 2002 and November 2002 to October 2003. Annual precipitation was determined with a weight-recording rain gauge, located 10 km west of the study lake (near URSA Lake No. 206) (Figure 2). Summer precipitation at Lake 16 was measured using a bulk rain gauge in 2002 and both a bulk rain gauge and a tipping bucket rain gauge (Jarek model 4025) in 2003. Both gauges were located on the southern edge of the lake (Figure 3). The difference between the cumulative rainfall between May and September from the weight-recording gauge and the measurements made at the study site was 10 mm (Smerdon et al., In Press). Snow depth and the snow water equivalent (SWE) were measured in the centre of the lake during March of both 2002 and 2003, before snowmelt began.

Precipitation samples were collected in a polyethylene bag that lined a plastic container (0.31 x 0.178 m diameter) during the summer of 2002, which was placed on a wooden stand located near the bulk rain gauge. Bags were rinsed with distilled deionized water (DDW) and were collected as soon as possible following rainfall. Electrical conductivity (EC) and pH of samples were measured within 24 hours of sampling and the remaining water sample was then filtered immediately following pH and EC readings.

Evaporation from the lake was measured with a Class A evaporation pan located near the southern edge of the lake (Smerdon et al., In Press). The pan was installed in the

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spring shortly after spring melt and was taken up in the fall before freeze up. Water levels were maintained within 0.1 m of the top rim, were recorded continuously with a transducer-datalogger device, and were confirmed with weekly to monthly manual measurements.

#### 2.6 Surface Water Measurements

Water level fluctuations of the lake were determined using staff gauges (stainless steel rulers attached to angle-irons) anchored in the mineral soil and level-surveyed annually. A total of two staff gauges were installed at the study lake: one near the southern shore near the precipitation gauge (inflow staff gauge); and one located on the northern edge of the lake near the surface outflow (outflow staff gauge) (Figure 3). Staff gauges were also located in each of the two adjacent lakes (Figure 2). Summer lake elevation was also monitored continuously with a transducer-datalogger device (Global Water model WL-14) in a stilling well attached to the inflow staff gauge (Figure 3). These continuous measurements were confirmed with periodic manual measurements from the inflow staff gauge. Movement of 0.15 to 0.20 m at the outflow gauge (caused by ice heaving) was observed between the fall of 2002 and the spring of 2003, and was corrected for in subsequent stage measurements.

#### 2.7 Groundwater Measurements

#### 2.7.1 Installation of Piczometers

A total of 36 piezometers and 6 wells were installed perpendicular to the lakeshore to monitor groundwater flow at the lake-wetland-hillslope interface. Three to four piezometers nests, each containing 3 to 5 piezometers and 1 well, were installed in each transect, excluding transect 1, which had 2 nests and 2 wells located in the hillslope. At least one piezometer nest was installed in each distinct vegetation zone. Piezometers were installed in the organic layer, in the underlying mineral substrate and at the interface. Additional piezometers were installed in each different type of mineral soil and organic layer observed during coring. Wooden boardwalks were constructed at each transect to minimize surface disturbance while water levels and samples were collected. Data from one well and two piezometers (P8-W, 2B, 1A) that were part of another study on this lake (Smerdon et al., submitted), are also used in this thesis (Figures 5, 6, & 7).

Piezometers and wells were installed using a 0.05 and a 0.019 m diameter handauger and were constructed from 0.05 m, 0.025 m, or 0.019 m internal diameter plastic PVC pipe, which was screened at the bottom 0.15 or 0.30 m and wrapped in filter cloth to prevent influx of small sediment particles. Piezometers were named with respect to transect number (Discharge =1, Transition = 2, Recharge =3), location from the lake (1 is closest to lake, 5 is furthest from lake), and piezometer depth (cm) below ground. Piezometers installed in the hillslope (T1-3-200, T1-4-400, T2-5-360 and T3-5-280) were constructed with 1 m long screens, which allowed them to act as wells. Bentonite was used to seal some piezometers (2B, 1A, T2-2-170, T2-3-140 and T2-4-140) installed prior to the start of this study (Smerdon et al., In Press). The remaining piezometers were pushed to the desired depth because of the soft nature of the organic soil. Piezometers were also driven into the mineral soil using a hammer to the final depth.

#### 2.7.2 Lithology

Lithology was determined from soil samples collected (0.3 to 4.0 m depth) during hand auguring of piezometer core holes. These data were added to the lake-groundwaterstudy (Smerdon et al., In Press), which used both a hand bucket auger and a portable solid-stem auger power drill. Cores from deep piezometers (up to 30 m depth) installed in the upland areas were obtained from the HEAD database. Manual texturing was used to characterize soil texture in the field, which was later calibrated to particle size analysis (Smerdon et al., In Press).

Saturated hydraulic conductivity (K) values for 19 piezometers in representative lithologies and peat of the three transects were determined from bail tests conducted on piezometers using the Hvorslev (1951) method. In fibric peat near the edge of the lake, piezometers that filled too rapidly to perform bail tests were assumed to have a high hydraulic conductivity (K >  $10^{-3}$  m/s).

#### 2.7.3 Groundwater Flow Determination

Groundwater levels were measured biweekly during 2002, and monthly during 2003. Water levels were measured manually with a dipmeter water level indicator and were confirmed by pressure transducers installed in eight piezometers surrounding the lake (Smerdon et al., In Press). Hydraulic heads and groundwater levels were used to create a flow diagram for each sampling date. Equipotential lines were drawn between points using triangulation and linear interpretation. Piezometers and wells were surveyed once per year to quantify piezometer movement. Three seepage meters were also installed near the southeast edge of the lake, which were used to estimate the influx of groundwater (Smerdon et al., In Press) and collect samples of groundwater discharge. A minimum change of 0.03 m in hydraulic head was chosen in order to guard against slight measurement errors and piezometer movement that could produce false recharge-discharge conditions.

#### 2.8 Water Chemistry

#### 2.8.1 Water Sampling Procedures

Piezometers in the three transects were sampled weekly to bimonthly in 2002 and monthly in 2003 during the ice-free season (14 times in 2002 and 4 times in 2003). Piezometers and wells were purged 24 hours before sampling by completely draining, where possible, or by removing 2 to 3 volumes of water. Sample water was collected using a 3-way valve and a 60 mL syringe that was attached to pre-rinsed tubing to prevent contact with air and degassing of oxygen. Acid washed bottles were rinsed three times with sample water, filled, and stored in a cooler to prevent degassing due to warmer ambient air temperatures.

Ferrous iron (Fe<sup>2+</sup>) was determined immediately on-site using a HACH DR-890 Colorimeter. Variance of ferrous iron concentrations was determined by sampling three times. Smaller syringes (5 to 20 mL) were used to dilute the sample when Fe<sup>2+</sup> concentrations were greater than 3 mg/L. Temperature, dissolved oxygen (DO) and redox potential were measured on-site using a MultiLine P4 Universal Pocket Meter. These were measured by inserting the probe directly inside the piezometer at screen

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depth or immediately from a pre-rinsed bottle if water levels were deeper than the length of the probe (3 m) or if piezometer diameter was smaller than the probe (0.02 m). DO data from bottles and redox values from 2003 were not included in the analyses due to large differences between DO values in piezometers and bottles, and redox values collected with a different meter in 2003. EC and pH were determined 12 to 24 hours following sampling using the MultiLine P4 Meter. Differences between field EC and lab EC values measured 12 to 24 hours later were less than 5%. EC from decanted water was usually determined within 24 hours for cloudy samples that required settling.

#### 2.8.2 Chemical Analysis of Water

All water samples were analyzed for soluble reactive phosphorus (SRP) and total dissolved phosphorus/ total phosphorus (TDP/TP) concentrations. The analytical measure of biologically available orthophosphates is sometimes called soluble reactive phosphorus (SRP), although the equivalence among soluble reactive phosphorus, exchangeable phosphorus, and orthophosphate is not exact. However, SRP is often used as indicators of the bioavailability of phosphorus (Mitsch and Gosselink, 2000), and was used in this study to determine biologically available phosphorus or phosphate ( $PO_4^{3-}$ ).

One sample per month was also analyzed for total dissolved iron (TDFe), major cations including calcium, magnesium, sodium, potassium,  $(Ca^{2+}, Mg^{2+}, Na^+, K^+)$  and occasionally dissolved organic carbon (DOC). Bicarbonate (HCO<sub>3</sub><sup>-</sup>), Sulphate (SO<sub>4</sub><sup>-</sup>), and Chloride (Cl<sup>-</sup>) were also measured occasionally and were used in geochemical modeling.

Samples to be analyzed for SRP were filtered immediately (less than 24 hours) following sampling events through 0.45 µm Millipore<sup>™</sup> filter paper and frozen until analysis. Tests done within the laboratory, comparing the results of frozen versus nonfrozen SRP methods, found an error of less than 5% (Ferone, 2001). Samples for TDP and cations analyses were also filtered through 0.45 µm Millipore<sup>™</sup> filter paper, but were kept refrigerated at 4°C until analysis. All other water samples were filtered within 24 to 48 hours of sampling with the exception of samples to be analyzed for TP, which were not filtered. DOC samples were filtered through Gelman<sup>™</sup> GF/C paper and stored with unfiltered TP samples at 4°C until analysis. Cation samples were acidified with 2 to 3 drops of nitric acid (50% HNO<sub>3</sub>).

SRP was analyzed within two months of sampling according to the method of Murphy and Riley (1962). TP and TDP were digested and analysed after Menzel and Corwin (1965) as modified by Prepas and Rigler (1982), within two months of sampling. DOC was analysed using the Total Organic Carbon (TOC)/ Combustion Infrared Method (Greenberg, 1992) using Ionics Model 1505 Programmable Carbon analyzer. Cations were analysed by atomic absorption spectrometry (Perkin Elmer 3300 Atomic Absorption Spectrometer). All water chemistry analysis was performed at the University of Alberta Limnology Laboratory.

#### 2.9 Soil Nutrient Analysis

#### 2.9.1 Extractable Pools of Phosphate and Bulk Density

Soil samples were collected in 5 representative areas of vegetation along the transition transect (T2) to determine extractable pools of phosphate and were correlated to water sampled from adjacent piezometer nests. Soil transect 1 (S-1 = T2-5) was located in the sandy aspen upland near T2-5 and contained aspen with some birch trees. The understory consisted of feather moss and low-lying shrub species. Soil transect 2 (S-2 = T2-4) was located in a black spruce swamp approximately 10 m north west of T2-4 and was representative of the conifer swamp in T3. The hummock-and-hollow understory was composed of spruce needles along with feather moss, Sphagnum moss, Labrador tea and reindeer lichen, growing on the hummocks. Soil transect 3(S-3 = T2-3)was located in the dry open fen adjacent to nest T2-3 and consisted of sparse alders and larch. The top layer of organic material contained feather moss with less Sphagnum moss, while the lower layer consisted of a fibric to mesic peat. Soil transect 4 (S-4 = T2-2) was located in the wet open fen next to nest T2-2 dominated by sedge hummocks and brown moss hollows. The peat was very fibric and contained many sedge roots. The fifth soil transect (S-5 = T2-1) sampled the gyttja, or the lake sediment near the lake piezometers (nest T2-1).

In each of these zones, two depths were sampled from 5 locations in each of the 5 representative transects (approximately 0 to 0.10 and 0.10 to 0.20 m). These 5 locations were spaced 5 paces apart from each other in a straight-line perpendicular to T2. The soil cores were collected using a 0.10 m bulb core with the exception of lake sediment, which was collected using a plastic tube  $(0.83 \times 0.04 \text{ m diameter})$  pre-rinsed with lake water. Soil samples were stored at 4°C in Ziploc<sup>©</sup> bags and soil extractions were conducted within 24 hours. In the aspen hillslope transect (S-1), the leaf litter was collected as a sample (usually 5-10 cm) and the underlying mineral soil was collected as the deeper core to a depth of 10-15 cm. Gyttja samples (S-5) were collected as two cores in each of the five locations in May 2002, one from the top flocculant gyttja and the bottom core collected from the bottom mineral gyttja. Due to difficulty in sampling gyttja, samples were collected as one core (for a total of five samples) for July and August 2002.

For each core, sub-samples of approximately 5 g of fresh organic soils and 10 g of fresh mineral soils were shaken in 125 mL plastic cups with 50 mL of potassium chloride (2M KCl) for 1 hour. This was performed 3 times during the summer to determine seasonal variation in phosphate concentrations. Extracts were gravity filtered using Whatman No. 42 filter paper and frozen until the time of analysis. Extracts were analyzed for SRP according to the methods described in the preceding section.

Bulk density was determined by dividing the mass of the sample after oven drying by the original sample volume (Fetter, 1994).

#### 2.9.2 Adsorption/Desorption Laboratory Experiment

Soils from transects T1 to T3 (Figure 5, 6, & 7) were frozen at -21°C for one year and used in phosphorus adsorption/desorption tests. Techniques for analysis were a modification of the methods described in Hill (1982), Lyons et al (1998), and Ferone (2001). Sediment samples were air dried for one week in a soil drying room in Department of Renewable Resources Soils Laboratory at the University of Alberta (23 to 24°C, approx 35 to 40% humidity (Molina-Ayala, 2004, per comm)), ground and passed through a 2 mm sieve. The soils were then sub-sampled for 0.15 g of dry weight, which was placed in 15 mL of DDW for the aerobic experiment or in DDW and Resazurin dye for the anaerobic experiment. Solutions were not adjusted with 0.01M CaCl<sub>2</sub>, in order to evaluate the potential for P release directly into overland flow (Hill, 1982; Hooda et al., 2000). Types and numbers of bacteria were not determined and pH was not measured.

#### 2.9.2.1 Anaerobic and Aerobic Experiment

A 0.001% solution of redox indicator dye Resazurin was used to determine the redox potential of the solution. This purple dye turns clear at less than -111 mV and pink at less than -51 mV, which is the same range as iron is reduced to ferrous iron. To ensure anaerobic conditions, Erlenmeyer flasks of DDW and Resazurin dye solutions were boiled, sparged with N<sub>2</sub> and then added to 20 ml glass tubes that were also sparged with N<sub>2</sub> gas. A 14 mL solution of DDW and dye was measured into 20 mL glass test tubes, which were sparged and then sealed with a cap containing a rubber middle to allow for syringe injection of liquids. 0.1 mL of NaS was added to mineral soil only, to lower the redox to allow the Resazurin to turn pink (Peat water cleared without any addition of NaS). Test tubes were then shaken for 12 hours on a back and forth shaker table at 200 rpm to allow the soils to reach reduced conditions. Following 12 hours, 0.15 mL of chloroform was added, and the tubes were shaken for another 24 hours to allow time for the chloroform to reduce the activity of bacteria and thus prevent phosphorus uptake by bacteria. Following this 36 hour period 1 mL of various concentrations of phosphorus  $(KH_2PO_4)$  was added to the test tubes with a syringe to produce concentrations of 0  $\mu$ g/L, 20 µg/L, 50 µg/L, 100 µg/L, 250 µg/L, 500 µg/L, 1000 µg/L and 2000 µg/L. Test tubes were then shaken at 200 rpm for 18 hours, centrifuged to remove fine particles and then gravity filtered using pre-rinsed Whatman No. 42 filter paper. Samples were immediately analyzed for orthophosphate (SRP) according to techniques described earlier.

Fourteen millilitres of DDW was added to 50 mL glass Erlenmeyer flasks containing 0.15 g of soil and were covered with aluminium foil. 0.15 mL of chloroform was added and the flasks were then shaken on a circular motion shaker table for 24 hours. One millilitre of the same concentrations of phosphorus as used in the anaerobic experiment was added and the flasks were then shaken for 24 hours. Soil and water solutions were filtered and analyzed as in the anaerobic experiment.

Equilibrium phosphorus concentrations (EPC values), the dissolved phosphorus concentrations at which there is neither adsorption or desorption by the sediments (Hill, 1982; Lyons et al., 1998), were evaluated from P adsorption isotherm by plotting the amount of P sorbed ( $\mu$ g P g-1 dry soil) vs. the final P concentrations following shaking (Hill, 1982). Logarithmic trend lines were applied to aerobic phosphorus sorption isotherms to determine final equilibrium phosphorus concentrations (EPC) (Brady and Weil, 1999), while exponential trend lines were applied to anaerobic sorption isotherms.

#### 2.10 Geochemical Modeling

Geochemical modeling was performed using a hydrogeochemical model PHREEQC for windows, version 2.8 (Parkhurst and Appelo, 2002) to determine the partitioning of phosphorus between aqueous species and complexes. Median chemical parameters, including NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SRP, SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Si, Alkalinity, pH, redox, DO and temperature, from representative sites were used for geochemical modeling. Representative sites included the lake, seepage meters, the sandy upland, peat, gyttja, and clay. Further modeling was performed to evaluate the possible influence of changes in redox and pH on SRP concentrations and to illustrate differences in substrate type (Peat vs Sand) with high (800 µg/L) and low (20 µg/L) SRP concentrations. Low SRP peat (T2-2), high SRP peat (T2-3), and the low SRP sandy upland T1-3 were modeled with low (-200 mV) and high redox (200 mV) and low (4.00) and high (8.00) pH.

Geochemical models assume equilibrium conditions but in the field, especially where there is mixing of groundwater and freshwater, equilibrium conditions are not often present. Geochemical models do not account for adsorption and desorption reactions in the soil and there may also be limitations to SRP values used in this model due to the interference from high DOC concentrations in some piezometers.

#### 2.11 Statistical Analysis

Empirical relationships between physical parameters and soluble reactive phosphorus dynamics within the riparian zone were tested using scatter plots and linear regressions. Linear regressions were used to determine linear relationships between SRP, pH, EC, DO, Redox, Ca, Fe,  $Fe^{2+}$ , and DOC. Assumptions of normality and homogeneity of variance were not met, so linear regressions were performed using logtransformed data. Graphs show raw data while all reported  $r^2$  values are from logtransformed data. All correlations and descriptive statistics (e.g., sample means, medians, standard deviations (SD) etc.) were calculated using Systat, version 10.2 (Systat Software Inc., 2002).

## **3** Results

#### 3.1 Spatial and Temporal Variation of Flow

#### 3.1.1 Atmospheric Fluxes

Total annual precipitation from November 1 to October 31 was 283 mm and 370 mm for 2002 and 2003 respectively (Figure 8). Precipitation in each of these hydrologic years are below the long-term climate normals (1961-2000) of approximately 502.7 mm for Slave Lake, Alberta (Environment Canada, 2004). Most precipitation (50 to 60%) occurred between May and June of both years (177 mm in 2002, 202 mm in 2003). Most daily precipitation events were less than 10 mm for 2002, with one storm greater than 20 mm (Figure 8). During 2003 there were four storms greater than 20 mm. Snow water equivalent (SWE) of the lake centre was 44 mm in 2002 and 83 mm in 2003, while SWE of the aspen hillslope was 51 mm in 2002 and 128 mm in 2003.

Cumulative lake evaporation was 336 mm in 2002 and 465 mm for 2003 (Smerdon et al., In Press). During 2002, precipitation minus evaporation was -53 mm while in 2003 it was -95 mm. Long term average potential evaporation is 517 mm (Bothe and Abraham, 1993; Marshall et al., 1999).

#### 3.1.2 Seasonal Surface Water Level Fluctuation

During 2002, lake water levels dropped over the early summer to reach lowest levels in mid-summer (Figure 8). Water levels fluctuated with July-September rainstorms, indicating that spring and fall rain was important for regulating lake water levels. Whereas in 2003, initial water levels in spring were lower and dropped during May and June in response to evaporation. As in 2002 water levels fluctuated with summer rains, with peaks in early August and mid-September. Summer water level fluctuations were greater in 2003, reflecting higher summer rainfall. Lake water levels also increased proportionally to precipitation events in 2003, usually immediately. Lake levels rose 46 mm following a 32 mm storm on June 23, 29 mm following a 30 mm storm on July 13 and 64 mm following 4 days of rain in August, which totalled 60 mm.

#### 3.1.3 Spatial and Temporal Patterns in Flow

Arithmetic averages of hydraulic conductivities (K) for representative substrates surrounding the study lake are reported in Table 1. Most of the mineral soils of the study lake are composed of sandy substrates, which have average hydraulic conductivities of  $5.6 \times 10^{-5}$  m/s. Sandy areas with a higher proportion of silt, have a K of  $6.8 \times 10^{-6}$  m/s, whereas the finer textured till associated with the recharge transect (T3) are estimated to have a K of  $1.6 \times 10^{-7}$  m/s (Table 1).

Temporal patterns of water levels in piezometers and wells located in the riparian wetland and sandy upland of the three transects studied were similar to patterns observed in lake water levels (Figure 9), except water level fluctuations were higher in the upland wells (from 0.15 to 0.24 m). Water levels were higher during the spring of 2002 and steadily decreased over the summer, and again were lower during the spring of 2003 but steadily increased over the summer of 2003.

Within the long term lowering of lake water level the remainder of this analysis will focus on a drying date (represented by data from August 12, 2002), and a wetting date (represented by data from July 14, 2003). On August 12, 2002, the lake was at one of its lowest levels for 2002 and was preceded by two weeks of minimal precipitation, thus, representing a drying trend. A 30 mm storm occurred before July 14, 2003 and

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measured water levels were some of the highest observed in 2003, thus representing a wetting trend. Thus, the largest variations in groundwater flow observed during the twoyear study period are represented by these two dates.

Hydraulic heads in the discharge transect (T1) showed upward flow towards the lake, suggesting a groundwater discharge area. Seepage meters also consistently discharged to the lake and fluxes varied between  $5.0 \times 10^{-8}$  and  $3.0 \times 10^{-6}$  m/s over the duration of this study (Smerdon et al., In Press). The water table in the upland of T1 was consistently above the lake level for the duration of the study period (Figure 9a). On August 12, 2002 water levels in T1 were 0.50 m higher in the upland (T1-3-200) and 0.06 m higher in the riparian zone (T1-2-50) than the lake level (Figure 9a). Water levels were also higher in the upland on July 14, 2003 and all water levels were 0.08 to 0.20 m higher than observed on August 12, 2002 (Figure 10). The flow in the discharge transect (T1) was largely towards the lake with consistent upward flow near the shore and mounding in the upland observed on the wetting date.

The hydraulic gradients between the upland, riparian zone and the lake in the transition transect (T2) varied very little (Smerdon et al., In Press) (Figure 9b). Hydraulic heads in the upland (nest 2B, approximately 100 m from the lake) were consistently higher (0.13 to 0.36 m) than the lake, suggesting slight flow towards the lake; however regional flow analyses also indicated that groundwater flow was parallel to the lake (Smerdon et al., In Press). Hydraulic head measurements on the drying date (August 12, 2002) indicated there were vertical upward flow and some flow from both the lake and upland to the riparian zone (Figure 11a). On the wetting date (July 14, 2003) there was also slight upward flow in the riparian zone (T2-3, Figure 11b), although gradients indicated mounding in the upland, which caused a reversal in flow towards the lake. The observed vertical upward flow from bottom mineral soil, local recharge from surficial riparian zone illustrate the transient nature of flow in this transitional transect.

Recharge was more accentuated in the recharge transect (T3) compared to the transition transect (T2) with dominant flow towards the upland and with frequent reversals during wetting periods (Figure 9c). Water levels in piezometer 1A, located

approximately 410 m from the lake adjacent to in T3, were consistently 0.8 to 0.9 m below the lake level (Figure 9c) indicating regional recharge that moved laterally and vertically downward from the lake towards the upland. Water levels in the riparian zone (T3-2-W and T3-3-W) were similar to lake elevation on August 12, 2002, while water elevations in and near the upland (T3-4-W and T3-5-280) were below lake elevation (Figure 12a), which also supported the movement of water from the lake towards the upland. Conversely, on the wetting date (July 14, 2003) water levels in the upland and in the conifer swamp (nest T3-4) were higher than lake levels, which caused a reversal in flow towards the upland and the lake (Figure 12b). Thus, the reversal of flow during the wetting date was caused by mounding of water in the hummock-and-hollow conifer swamp, which created a hydraulic depression between the upland and the riparian zone and local flow towards the lake.

Electrical conductivity (EC) fluctuated very little during the study period and can be used to support hydrometric data. Overall, highest EC values were observed in groundwater located near the lake and lowest values were located in the upland of the three transects studied (Figure 13). Highest conductivity values were observed for piezometers installed in clay and ranged from 800 to 1200  $\mu$ S/cm. EC's associated with deeper piezometers installed in sand ranged from 300 to 600  $\mu$ S/cm, lake water ranged from 130 to 240  $\mu$ S/cm, and precipitation ranged from 10 to 33  $\mu$ S/cm. Considering the variation of these distinct zones EC values can be used to interpret the source of water entering the riparian zone.

Median EC values in T1 ranged from 280 to 610  $\mu$ S/cm and were highest in the groundwater springs near the lake, in deeper flow systems and lowest in the upland (T1-3) (Figure 13a). EC values suggest that more dilute water originated from the adjacent hillslope and mixed with higher EC, deep flow originating from Lake 17 (Figure 13a).

Electrical conductivity values at T2 were the lowest of the three transects studied with median values ranging from 52 to 410  $\mu$ S/cm (Figure 13b). Highest EC values were located near the lake (nest T2-1) and in deeper groundwater underneath the upland (2A), which was similar to deep groundwater at T1 (Figure 13b). The lowest values were located in and near the break in slope of the upland (nests T2-4 and T2-5) and in surficial

peat deposits, where hydraulic heads showed recharging surface water into and below the peat (Figure 13b).

Highest EC values were observed in the recharge transect (T3), with median values ranging from 58 to 1200  $\mu$ S/cm (Figure 13c). EC values followed a similar pattern to those found in the transition transect (T2) with the highest EC values occurring near the lake and within the deeper till deposits, and the lower values found in and near the toe of the upland and surface of the peat. Dilute EC values in the riparian zone also suggest that the peat is recharging the groundwater with a more dilute source of water. These EC values indicate that water near the lake and within till deposits is more concentrated than water in the upland and both types of water meet near the conifer swamp (nest T3-4).

## 3.2 Spatial and Temporal Variation of SRP

## 3.2.1 Spatial and Temporal Variation of SRP

Soluble reactive phosphorus (SRP) concentrations varied little seasonally relative to spatial variation; however, some elevated concentrations were observed following precipitation events (Figure 14). SRP concentrations of rain in 2002 were higher than all SRP concentrations observed in T1 (Figure 14a), which were the lowest of the three transects studied. SRP concentrations entering the discharge transect (T1) in groundwater were lower than or equal to the lake during the study period. SRP concentrations in the upland (T1-3) were higher than in the riparian zone and were highest during July and August of both years, which coincided with increased precipitation events. Concentrations on August 12, 2002 ranged from 3 to 6  $\mu$ g/L in the riparian zone and were slightly higher in the upland (10  $\mu$ g/L in T1-3, Figure 15a). Concentrations showed similar patterns on July 14, 2003, ranging from 4 to 6  $\mu$ g/L in all piezometers except for in the upland (T1-3), which increased to 63  $\mu$ g/L (10x higher) (Figure 15b) and corresponded with low EC values.

Most median SRP concentrations in the transition transect (T2) were less than 100  $\mu$ g/L and were generally less than precipitation, except in the dry open fen (T2-3-60 and nest T2-3), which had consistently high concentrations (approximately 1000  $\mu$ g/L) for the

duration of the study period (Figure 14b). SRP patterns were similar during the drying and wetting dates with highest concentrations located near the middle of the dry open fen (nest T2-3), and lowest concentrations located in the upland and near the lake (Figure 16). SRP was more likely to be transported to the lake on the wetting date as reversals caused water to flow towards the lake and the upland, originating from high SRP areas associated with peat in the riparian zone.

In the recharge transect (T3) SRP concentrations in piezometers closer to the lake (T3-3-290, T3-1-250) varied the most, and were usually highest following precipitation events (Figure 14c). SRP concentrations were highest in the conifer swamp, (nest T3-4) and lowest in piezometer nests closest to the lake for the duration of the study period (Figure 15). Most SRP concentrations were lower on the wetting date (July 14, 2003), except for higher concentrations in the upper peat near the edge of the conifer swamp (T3-3-30) (Figure 17). The upland well (T3-5) was dry on August 12, 2002 and could not be sampled; however the SRP concentration was 100  $\mu$ g/L on July 9, 2002. Conditions in 2002 were too dry to allow surface pooling and thus prevented the collection of surface water samples from the peat.

SRP concentrations of the lake (2 to  $10 \mu g/L$ ) did not vary as much as SRP concentrations in piezometers and were generally low for the duration of the study. Thus, possible flushing of SRP to the lake from the transition (T2) and the recharge (T3) transects was not reflected in lake concentrations. Alternatively, SRP concentrations of the groundwater entering the discharge transect (T1) were similar to lake concentrations, which suggests an influence of groundwater on SRP dynamics of the study lake. The highest concentrations of SRP were located in the riparian peat, approximately 15 to 20 m from the toe of the upland, in the transition (T2) and recharge transects (T3). The lowest SRP concentrations were observed in the discharge transect (T1), and the upland and lake margin areas in the remaining transects. Generally, highest SRP concentrations were associated with peat deposits, moderate SRP concentrations were associated with groundwater.

TDP patterns were similar to SRP patterns with highest concentrations found in the riparian zones of the transition and recharge transects (Figure 18). TDP concentrations were higher in the lake, especially in the spring compared to SRP concentrations (Figure 18). SRP were unexpectedly greater than TDP in 21% of the water samples (n=456) likely due to analytical error and interference from organic matter in some samples.

#### 3.3 Correlations Between the Mobility and Location of SRP

### 3.3.1 Biogeochemical Correlations of SRP Concentrations

#### 3.3.1.1 Redox and Dissolved Oxygen

Redox measurements in all pore and groundwater sampled in the three transects were less than 200 mV. Median redox potential values were highest near and within the upland, and lowest near the lake in the three transects (Figure 19). The lowest median redox potential values of 2002 were observed in the discharge transect (ranging from -25 to 54 mV), while the highest redox values (ranging from 58 to 150 mV) were observed in the transition transect (T2). Seasonally redox values in T1 were highest during the spring and fall and lowest during the summer (data not shown). Conversely, redox values in T2 and T3 were lowest in the spring and fall and highest following summer rain events, increasing by 40 to 50 mV, when surface water recharge was apparent (data not shown). A threshold relationship was observed between SRP and redox as SRP concentrations greater than 0.2 mg/L occurred between redox potentials of 0 to 150 mV (Figure 20).

Median dissolved oxygen (DO) concentrations showed a similar pattern to redox, with more oxygenated water occurring near the upland and in surficial peat and less oxygenated water near the lake and within the peatland in the three transects studied (Figure 21). Median DO values ranged from 0.06 to 0.80 mg/L, 0.10 to 0.70 mg/L and 0.10 to 0.70 mg/L for the discharge, transition and recharge transects respectively. Highest DO values were observed in the lake and ranged from 11.50 to 13.30 mg/L. DO values showed a threshold relationship to SRP, with SRP concentrations greater than 0.25 mg/L occurring at DO measurements less than 2 mg/L (Figure 22).

## 3.3.1.2 <u>Iron</u>

Seasonally, ferrous iron ( $Fe^{2^+}$ ) concentrations fluctuated little and followed similar patterns to EC values, with lowest concentrations observed in the upland and highest concentrations observed near the riparian zone and lake edge (Figure 23). Concentrations in the discharge transect (T1) were mid-range of the three transects studied, ranging from 4 to 13 mg/L, with highest concentrations occurring near the lake and in the seepage meters (Figure 23a). Lowest  $Fe^{2^+}$  concentrations were observed in the transition transect (T2), ranged from 1 to 10 mg/L, and were highest near the gyttjawetland/sand interface (Figure 23b). Highest  $Fe^{2^+}$  concentrations were observed in the recharge transect (T3), ranging from 1 to 27 mg/L, with lowest concentrations observed in the upland and highest concentrations occurring in the wet open fen, gyttja and clay near the lake (Figure 23c).

Overall, Fe<sup>2+</sup> showed distinct patterns between transects with lowest redox and mid-range Fe<sup>2+</sup> concentrations in the discharge transect (T1), highest redox potentials and lowest Fe<sup>2+</sup> concentrations in the transition transect (T2) and mid-range redox and Fe<sup>2+</sup> concentrations observed in the recharge transect (T3) (Figure 24). The relationship between SRP and ferrous iron showed distinct patterns observed between transects (Figure 25). Lowest concentrations of SRP and moderate Fe<sup>2+</sup> concentrations were observed in the discharge transect (T1), while high SRP and lowest Fe<sup>2+</sup> concentrations were observed in the transition transect (T2) and highest SRP and Fe<sup>2+</sup> concentrations were observed in the recharge transect (T3). A positive linear correlation was observed between SRP and total elemental iron ( $r^2 = 0.458$ , y = 0.706 - 1.284x,  $\rho < 0.05$ , n=38) (Figure 26). Also, concentrations of SRP greater than 0.10 mg/L were only observed at sulphate (SO<sub>4</sub><sup>-</sup>) concentrations less than 2 mg/L, which suggests that sulphate, SRP and iron may be related (data not shown).

## 3.4.1.3 <u>pH</u>

The range of pH distribution throughout the transects was not extremely variable and most values were in the range of 6 to 7. Higher pH values were located near the lake while lower pH values were located in and near the upland and the peat in the riparian

zone (Figure 27). The lake had the highest pH values, with median values ranging from 8.37 to 8.81 and a maximum of 9.96 on August 13, 2002. pH values were lower in the peat and from surficial peat waters (<5.0) collected from the riparian zone during 2003. SRP concentrations showed a threshold relationship with pH, as SRP concentrations in groundwater and surface water exceeded 0.25 mg/L only when pH was between 6.0 and 7.0 (Figure 28).

#### 3.3.1.3 <u>Calcium</u>

Calcium (Ca) concentrations followed similar patterns to ferrous iron and electrical conductivity, with highest concentrations observed near the lake and lowest observed in the upland (Figure 29). Median Ca concentrations in the discharge transect (T1) were highest near the lake (95 to 100mg/L), mid-range in the riparian zone (75-80 mg/L), lowest in the upland (50 to 58 mg/L) and in the lake (21 mg/L). The lowest median Ca concentrations were observed in the transition (T2) transect, ranged from 8 to 60 mg/L, and showed similar patterns to those in the discharge transect (T1). Highest median Ca concentrations occurred in the recharge transect (T3) adjacent to the clay layer next to the lake (92 to 130 mg/L). The lowest concentrations in the recharge transect were located in the conifer swamp in nest T3-4 (26 to 64 mg/L), the same location as the highest concentrations of SRP were observed.

Calcium was found to have a strong positive linear correlation to EC ( $r^2 = 0.787$ , y = 1.078 - 1.062x,  $\rho < 0.05$ , n = 249)(data not shown). Ca concentrations also showed a threshold relationship with SRP concentrations as SRP concentrations in groundwater and surface water exceeded 0.20 mg/L only when the Ca concentrations were less than 100 mg/L (Figure 30). The relationship between EC and SRP was also similar as SRP concentrations were greater than 0.5 mg/L only when electrical conductivity values were less than 500  $\mu$ S/cm (data not shown). These correlations suggest that dilute water, likely from local recharge in peat, is associated with higher concentrations of SRP.

### 3.3.1.4 <u>Geochemical Modeling</u>

Results from geochemical modeling showed that there was sufficient Fe and Ca in all solutions modeled to precipitate with phosphate, with Ca being the most prevalent element in solution. Geochemical modeling predicted lake surface waters to be supersaturated with respect to hydroxyapatite, aragonite, calcite, dolomite, iron oxide, geothite and hematite (Table 2). The predicted precipitation of hydroxyapatite (a Ca-P mineral) in lake water may be an important factor contributing to low SRP concentrations observed in lake water. The predicted precipitate observed near the discharge transect (T1). Geochemical modeling did not predict that hydroxyapatite would precipitate out of solution in any of the other field solutions modeled. Vivianite (a Fe-P mineral) was predicted to precipitate out of solution in the water from the conifer swamp in T3, where the highest SRP concentrations were observed, which suggests that ferrous iron was playing a role in controlling SRP mobility in this location.

Results from geochemical modeling of sites comparing high and low redox, pH and SRP concentrations also suggested that pH was a controlling factor in SRP mobility in this system. Hydroxyapatite and vivianite were predicted to precipitate out of solution under high SRP and high pH conditions. Vivianite was also predicted to precipitate out of solution in the sandy site in all conditions modeled with high SRP, except at low pH (Table 2). The results did not vary between peat and sand substrates, although the peat is more likely to become acidic and had lower concentrations of Ca. Results from geochemical modeling suggest that Fe may be more important in precipitating with SRP in peat. Ca is likely more important in mineral soils and areas associated with groundwater inflow. Both Fe and Ca are more influenced by changes in pH than changes in redox.

## 3.3.2 Organic Influences on Subsurface SRP Concentrations

## 3.3.2.1 Dissolved Organic Carbon

Median DOC concentrations were lowest in the discharge transect (T1), varied the least of the three transects, and ranged from 13 to 17 mg/L (Figure 31a). Concentrations

in the transition transect (T2) ranged from 8 to 28 mg/L, with highest values occurring in the riparian zone (T2-3), congruent with high SRP concentrations (Figure 31b). Median DOC concentrations in the recharge transect (T3) ranged from 8 to 78 mg/L with the lowest values in the upland and the highest values found in the conifer swamp in nest (T3-4: 78 to 86 mg/L), the same location as high SRP concentrations (Figure 31c). Regression analysis also showed a weak positive linear relationship between DOC and SRP ( $r^2 = 0.141$ , y = 0.921 - 2.938x,  $\rho < 0.05$ , n = 103), which indicates that DOC may be a source of SRP (Figure 32). A positive linear relationship was observed between DOC and total iron ( $r^2 = 0.333$ , y = 1.213 - 1.775,  $\rho < 0.05$ , n = 23) (Figure 33), which suggests that iron is precipitating with DOC and thus freeing up SRP.

## 3.3.2.2. Extractable Phosphate Concentrations

There was little seasonal variation in extractable phosphate concentrations collected on three dates during the summer of 2002. Highest extractable phosphate values were always observed in the aspen upland with average concentrations of 40  $\mu$ g/cm<sup>3</sup> for the LFH and 35  $\mu$ g/cm<sup>3</sup> for the lower sandy A-B layer (Figure 34). Average extractable phosphate concentration in the upper fibric peat of the conifer swamp was 21  $\mu$ g/cm<sup>3</sup>, while that in the lower fibric peat was 6  $\mu$ g/cm<sup>3</sup>. Extractable phosphate concentrations steadily decreased in transects closer to the lake edge. Since extractable phosphate concentrations were highest in the aspen leaf litter and fibric peat deposits in the conifer swamp they are likely potential sources of SRP.

## 3.3.2.3 Adsorption/Desorption Experiment

The results of the adsorption desorption experiments produced erratic graphs that may be related to the small amounts of soil (0.15 g) used in the experiment; however, average values of the aerobic experiment provide an indication of overall patterns of equilibrium phosphorus concentrations (EPC). EPC curves for anaerobic and anaerobic experiments were similar, except the anaerobic experiment curve showed exponential trendlines, which is evidence of a precipitation curve instead of the expected adsorption curve. Thus, average EPC results from the aerobic experiment will be discussed in this thesis.

In some cases more SRP was adsorbed to sediment than was originally added to the solution, which was not expected, and may be caused by low pH of the sample that led to a release of SRP from the sediment. This suggests that SRP fixation with soil was more controlled by pH than by redox and pH should be controlled and measured in future experiments.

Mean equilibrium phosphorus concentrations (EPC) values of the aerobic experiment were highest for sand (633  $\mu$ g/L, SD = 378, n = 3) and fibric peat (340  $\mu$ g/L, SD = 243, n = 4) (Figure 35). EPC values were lowest for sand with peat (53  $\mu$ g/L, SD = 15.6, n = 5) and gyttja with clay (50  $\mu$ g/L, SD = 28.8, n = 2). These data suggest that sand and fibric peat have lower P retention capacity (higher EPC) compared to sand with mesic peat and gyttja with clay. These results correspond well to extractable P and SRP concentrations, which showed that the sand underneath the aspen leaf litter and fibric peat in the conifer swamp were potential sources of SRP.

# 4 Discussion

## 4.1 Spatial and Temporal Variation in Flow

The outwash lake is a groundwater flow-through lake that is well connected to local and intermediate groundwater flow systems (Smerdon et al., In Press), due to the lake being located in highly permeable sediments. Regional to intermediate groundwater flow from the southeast to the northwest was responsible for creating the three types of groundwater-surface water interactions observed in this outwash lake: discharge, transition, and recharge riparian zones. Flow-through lakes are dominant in highly permeable geologic settings, thus large differences in groundwater flow direction, as observed in this lake, is probably common (LaBaugh et al., 1997; Smith and Townley, 2002).

A dynamic relationship existed between atmospheric water fluxes, groundwater interaction, and surface flow, which was controlled by evaporative flux from the lake surfaces (Smerdon et al., In Press). This was expected because in permeable substrates the groundwater is regularly exposed to influences by the atmosphere and biosphere (Doss, 1993). The close relationship between evaporation and precipitation in the Boreal Plain also led to precipitation events having a large influence over surface water levels and fluctuations. As hypothesized, the three riparian zones varied in water table fluctuation and reversals, which was likely related to their position in the groundwater flow system and their dominant sources of water. Flow reversals did not occur in riparian zones that were connected to the larger groundwater flow system, but were restricted to the transition and recharge riparian zones, where peat deposits facilitated local interactions of flow.

There was a consistent influx of groundwater in the discharge transect (T1) as shown by visible springs in winter, negative vertical hydraulic gradients, and consistently discharging seepage meters (Smerdon et al., In Press). Overall, flow was from the upland towards the lake, largely bypassing the narrow riparian zone. Flow reversals did not occur in the discharge transect although local mounding did occur in the upland and may have caused some local flow away from the lake and further into the upland. This mounding was likely due to focused recharge, which is caused by precipitation infiltrating through a thin unsaturated zone adjacent to the shoreline during wet periods and during the spring (Winter et al., 1999). Increased discharge observed during the wetting period may also be due to increased recharge rates in the adjacent gravel pit. The water table was near the surface in the sandy upland toe (nest T1-3), which enhances local upland recharge and allows for large interaction between surface and groundwater (Winter and Rosenberry, 1995).

The transition transect (T2), located near the groundwater divide between the discharge and recharge zones of this flowthrough lake, had negligible vertical gradients, indicating that flow was likely perpendicular to the installed transect of piezometers. A transect of piezometers should be installed perpendicular to this transect in future studies to determine the exact gradient. Hydraulic gradients indicated there was some groundwater upwelling from below the riparian zone, but local water from the lake, the surficial peat deposits and the upland dominated the water in this transect. Low hydraulic

gradients combined with the dominance of local flow in this transect resulted in more transient flow patterns than observed in the discharge and recharge transects, suggesting increased likelihood of stagnation in transition riparian zones. Water levels in the upland toe were dynamic and groundwater mounding caused a flow reversal, which redirected groundwater through the riparian zone to the upland and the lake for the entire summer of 2003. As in the discharge transect (T1) this mounding was likely caused by focused recharge due to higher fall precipitation and snow water equivalent than in 2002 (Winter, 1999). These reversals in flow may have an important effect on local water and nutrient transport to the lake, which will be discussed in subsequent sections.

Hydraulic gradients in the upland of the recharge transect (T3) indicated downward groundwater flow and confirmed recharge conditions observed at the regional scale, although the flow rate leaving the lake was an order of magnitude lower than the movement of groundwater into the lake (Smerdon et al., In Press). Local flow reversals in 2003 caused the formation of a water table mound in the hummock-and-hollow conifer swamp, which formed a hydraulic dam and may have prevented the movement of lake water into the upland of this transect. The dominance of local flow, infiltration of precipitation and snowmelt in the upland, and recharging of new water through the hummock and hollow peat likely contributed to this reversal in flow (Winter, 1999). Decreased flow from the lake to the upland and larger accumulations of peat in this transect may have also aided in the formation of larger peat mounds and led to increased local flow to the to lake.

Differences in the types of flow reversals that occurred between the transects were amplified by differences in groundwater interaction. The constant influx of groundwater in the discharge transect (T1) and the lack of peat prevented the formation of flow reversals. Vidon and Hill (2004) also found that riparian zones linked to thicker and more extensive upland aquifers had relatively constant groundwater inputs that maintained a stable riparian water table compared to riparian zones seasonally disconnected from uplands. Riparian zones in discharge areas are therefore less susceptible to flow reversals and likely climate variations than riparian zones in transitional and recharge areas. Alternatively, the dominance of local flow, lack of groundwater influence, and deeper peat deposits in the transition and recharge transects resulted in the formation of seasonal reversals in flow. Smerdon at al. (In Press) found that groundwater mounds on the outflow of the lake were a function of the relative dominance of snowmelt recharge compared to the moderating horizontal gradient between Lake 16 and Lake 5. LaBaugh et al. (1997) found that the timing and duration of reversals were affected by seasonal and annual fluctuations in recharge by snowmelt and by rainfall. Thus, reversals in the transition and recharge zones were likely caused by the infiltration of rainwater and snowmelt dominating water flow into the upland and riparian peat.

Flow reversals may have been intensified by the internal properties of the peat, such as its capacity to retain large amounts of water, acting as a sponge (Boelter and Verry, 1977) during wet periods, and slowly releasing water during drier periods. Peatlands have been documented to generate their own local flow cells (Reeve et al., 2000) and Ferone and Devito (2004) also found that in Boreal Plains complexes, the presence of peat domes caused the formation of groundwater flow cells during wet events. In eastern peatlands isolated from regional groundwater, flow reversals have been shown to result from drought conditions (Devito et al., 1997; Fraser et al., 2001; Waddington and Roulet, 1997a). Conversely, flow reversals in Boreal Plain outwash riparian wetlands, as in the moraine and clay plain (Ferone and Devito, 2004), occurred in response to large rainfall events.

Doss (1993) showed that local flow systems developed along the margins of wetlands, located in sand, in response to evapotranspirative demands by wetlands vegetation and other climatic influences. This does not seem to be the case in this study and may be partly due to the influence of lake water levels. The large volume of water in the lake, which is closely connected to the riparian zone water levels likely helped to moderate the effects of evapotranspiration by plants.

The observed reversals in flow could play an important role in the transport of SRP, which will be discussed in subsequent sections. Riparian zones influenced by local flow will be more susceptible to climatic changes and disturbance than riparian zones more influenced by groundwater inflow.

## 4.2 Source and Mixing of Water in the Riparian Zone

Pore water and surface water chemistry (e.g., EC and pH) in the riparian zone reflected the source of water entering the riparian zone. Electrical conductivity of deeper groundwater in sand deposits ranged from 300 to 600  $\mu$ S/cm suggesting that the source of water is from longer flowpaths than the dilute water recharging in local uplands. Highest EC values, ranging from 800 to 1200  $\mu$ S/cm, were observed in piezometers installed in clay and were likely due to higher proportions of solutes or increased weathering in this type of substrate, which also suggest that the water originated from a longer or slower flowpath. These differences in EC values could also be attributed to the fact that sand is more resistant to dissolution of ions than clay substrates (Brady and Weil, 1999).

Generally, low EC values (50 to 300  $\mu$ S/cm), lower pH (<6), low redox potential and DO values, low Fe<sup>2+</sup>and low Ca<sup>2+</sup> concentration observed in the uplands and in the surficial peat reflect the infiltration of dilute rainwater and snowmelt and show that this dilute water can affect the chemistry of the riparian zone. Alternatively, highest EC, pH, Fe<sup>2+</sup>, and Ca<sup>2+</sup> associated with groundwater influx illustrate that even small inputs of groundwater will also affect the chemistry of the riparian zone. These data illustrate that varying sources of water, especially between groundwater and surface water, have a large impact on the chemistry and environment found within the riparian zone, which has the potential to influence SRP dynamics in the riparian zone.

### 4.3 Sources of Soluble Reactive Phosphorus

The distributions of SRP concentrations reflect the source of water from low SRP concentrations associated with groundwater and high SRP concentrations associated with organic layers in the upland and in the riparian zone. Highest extractable P and SRP concentrations were observed in the fibric peat of the conifer swamp, suggesting these deposits were sources of SRP to the riparian zone and to recharging groundwater. Since organics in the riparian zone are a source of SRP, the direction of water flow between the lake riparian zone and the upland determined the sink/source function of the riparian zone.

High equilibrium phosphorus concentrations (EPC's) and high pore water SRP concentrations associated with the fibric peat indicate that these soil types were less able to fix SRP. This is not surprising as soils high in organic matter generally exhibit relatively low levels of P fixation because of the presence of large humic molecules, and organic acids that compete with P (Brady and Weil, 1999). Nixon (1980) also found that the greatest proportion of the total phosphorus was in the readily available fraction in the organic-rich upper soil horizons of coastal salt marshes. High EPC associated with the fibric peat may also be due to the unique chemistry of the Sphagnum moss that makes up the fibric peat. Koerselman (1993) found that Sphagnum peat released more P and ammonium than *Carex* peat and that water chemistry, water level, and soil chemistry significantly influenced nutrient release rates in peat soils. Verhoeven (1990) suggested the generally low pH in sites with a thick Sphagnum carpet was one of the factors explaining the higher pools of labile phosphates at these sites and may be due to the increased release of organic P. Results from the adsorption desorption experiment and the extractable phosphate study agreed with the studies described above and also showed that fibric peat was a potential organic source of SRP.

High extractable P concentrations in peat and organic layers, and the correlation between SRP and DOC concentrations, suggest a relationship to organic layers. Other studies have also observed that most dissolved organic P in soil solution was associated with DOC, suggesting that this was a mechanism for leaching of P from upland soils (Donald et al., 1993; Qualls et al., 1991). Evans et al. (2000) also observed positive correlations between TDP and DOC that suggested that subsurface water flowing through the organic layer contributed more P than the mineral layers because the main source of both DOC and K was the organic layer.

High extractable P concentrations associated with the aspen leaf litter suggest that these organic layers are a possible source of SRP to the riparian zone. Xiao et al (1991) also found that P was highest in aspen, lower in mixed wood, and lowest in a conifer (black spruce) forest due to the higher decomposition rates of deciduous leaves compared to coniferous needles. Infiltration of precipitation through the leaf litter, leaching the higher SRP concentrations, is likely an important source of SRP to the recharging water. This is supported by high extractable P concentrations in the sand located below the aspen leaf litter and slight increases in SRP in the sandy upland toe of the discharge transect (T1) following precipitation events.

High SRP concentrations associated with low EC values (<500  $\mu$ S/cm), low DO, low redox potential, low Fe<sup>2+</sup>, low Ca<sup>2+</sup> (<100 mg/L), low pH (<6.0) and high DOC in peat also suggest that leaching from the surface organic layers are important sources of SRP to the riparian zone. This was also found by Evans et al. (2000) who showed that elevated TDP concentrations originated from the near-surface organic layer. Ferone (2001) and Devito et al (2000a) also showed that high P concentrations were associated with wetlands and near surface organic layers. Therefore, the potential of discharge from the peatland to the lake is influenced by the total peatland storage, but it is also limited by the connectivity of the peatland to the pond.

High EPC's associated with sandy soils suggest they have a low capacity to adsorb SRP, which may be due to the high quartz content of the sand. Quartz is inert, does not have a charge and has a much lower capacity to absorb anions than clay (Brady and Weil, 1999). Low concentrations of SRP observed in the upland sands compared to concentrations associated with fibric peat also contradict high EPC values and may be due to lack of P sources to this area and/or calcium and iron precipitation associated with ions in the groundwater.

Low SRP concentrations and EPC values associated with clay mineral soils were likely due to its positive charge and higher concentration of minerals and ions. Ferone (2001) also found till soils to have low EPC values of 59.5  $\mu$ g/L. P-fixation tends to be more pronounced and the ease of P release tends to be lowest in soils with higher clay content (Brady and Weil, 1999). Frossard and Stewart (1989) also stated that the mobility of P anions in the soil will depend on the nature of the mineral surfaces and oxide coatings because P anions are strongly adsorbed by mineral constituents such as clays and sesquioxides. Thus, the properties of clay such as its' anion exchange capacity (AEC) and its' high associated Fe<sup>2+</sup> and Ca<sup>2+</sup> concentrations are likely responsible for the low concentrations of P associated with these soils. The main sources of SRP to the riparian zone in this outwash lake were surficial organic layers predominantly from fibric peat and less from aspen leaf litter. These sources reached the riparian zone by infiltration and local recharge or precipitation water. The riparian zone was also a source of SRP and water flow may have helped to transport mobile SRP to other parts of the riparian wetland and into the groundwater system. This suggests that SRP from local sources were the most significant influx of SRP to the riparian zone.

## 4.4 Spatial and Temporal Variation of SRP Concentrations

The hypothesis that SRP levels would be higher following spring runoff and fall senescence of macrophytes was refuted. SRP concentrations did not vary seasonally as expected, but did fluctuate with precipitation events. Fluctuation of SRP in precipitation samples was also observed and may have been due to pollen and organic materials in the precipitation sample. The expected seasonal release of SRP from plants may have been masked by high concentrations of SRP present in the riparian zone; however the fact that SRP did not vary significantly seasonally suggests that plant uptake and release was not the most important factor in controlling SRP mobility in this system. Vitt et al. (1995) also found SRP concentrations in Boreal peatlands to be relatively constant throughout the season. Observed elevated concentrations of SRP associated with rain events were likely related to SRP entering the system from leaching surface P-rich organic layers. Ferone (2001) also found that P loading was greatest following high flow when a major source of P originated from peatland systems connected to local groundwater systems.

The fact that SRP concentrations were a magnitude higher in the hummock-andhollow peat of the transition (T2) and recharge (T3) transects, than in the discharge transect (T1), suggests an influence of groundwater flow on SRP mobility. Low concentrations of SRP associated with the incoming groundwater were likely due to the higher concentrations of ions present in these waters that were able to precipitate with SRP. This was also observed by Verhoeven (1990) who found that low inorganic P pools and low P mineralization associated with fens in groundwater discharge areas were probably caused by the precipitation of phosphates with Ca, Mg, Fe and Al compounds that were supplied by the inflowing groundwater. In addition groundwater that entered the discharge zone likely originated from southeast at lake 17, where visible marl deposits suggest high Ca concentrations, which would have precipitated with SRP present, further reducing SRP concentrations in the outgoing groundwater. Devito et al. (2000a) examined lake position within groundwater flow systems and also showed the importance of deep groundwater in moderating inter-annual change in TP loading and lake concentrations on the Boreal Plain. Alternatively, the dilute water from recharging precipitation and melt water in the transition (T2) and recharge (T3) transect contained fewer ions in solution to bind with P than in the concentrated water near the lake and upwelling groundwater. High P concentrations were also found near the interface of dilute water and more concentrated groundwater reflecting their differences in chemistry.

Increased groundwater flow in the discharge transect (T1) may have prevented the colonization of peat-forming plants and accumulation of organic matter (Earle et al., 2003). Since riparian peat was found to be a source of SRP, the thin deposits of peat in the discharge transect prevented the build-up and storage of SRP. Increased fluctuations of the water table due to reduced groundwater inputs in the transition and recharge zones resulted in the accumulation of deeper peat deposits, which resulted in a larger source of SRP contributing to the high concentrations of SRP associated with these substrates.

Lower hydraulic conductivity values, correlated with the hummock-and-hollow peat in the transition (T2) and recharge (T3) transects, slowed the movement of water through the peat and, in turn, prevented the physical movement of phosphate ions. Lower hydraulic conductivity also caused increased stagnation, the lowering of redox and aided in the release and build-up of SRP in the riparian peat. Alternatively, lower P concentrations observed in the wet open fens of the transition and recharge transects were likely due to the higher hydraulic conductivity of the fibric peat, which allowed P to be flushed more easily. Slower movements of water leaving the lake in the recharge transect compared to groundwater entering the lake in the discharge transect also likely aided in the build-up of SRP concentrations in the recharge transect.

Highest SRP concentrations, observed in association with the P-rich fibric hummock-and-hollow peat in the transition (T2) and recharge (T3) transects, show that

SRP did not move far from its source. Precipitation falling on the SRP rich fibric peat facilitated P leaching into the standing water. This was also observed in a study by Damman (1978), where higher P concentrations found in the hollows and near the zone of water level fluctuation indicated P leaching from the hummocks. Reversals in the riparian zone also likely slowed the travel distance and aided in the accumulation of SRP in this area. In both the transition and recharge transects the observed seasonal flow reversals may have helped to move SRP back and forth near its source and resulted in high concentrations in one location. This agrees with findings from Ferone (2001) who found that at a finer-textured site in the same region (URSA), regular seasonal flow reversals helped to limit the distance that P was transported, and thereby influenced the formation of regions with elevated P concentrations or "hotspots" in the peatland edge littoral gyttja zone. Ferone (2001) also observed that the chemical and physical properties of the peat allowed for rapid flow responses and variable biogeochemistry observed in the riparian zone. Reeve et al. (2000) predicted that lateral flow reversals should occur in peat mounds where regional gradients were low. In Boreal Plain wetlands, peat mounds tend to develop near the lake edges, where wet and dry cycles indicate strong gradients with the surface water. Flow reversals associated with these mounds have a high potential to enhance nutrient interactions between the peat and surface water.

Low hydraulic gradients in the transition transect (T2) may have also prevented large movement of SRP, and provides supporting evidence for flow perpendicular to this transect. During low flow in the recharge (T3) transect groundwater seepage from the lake was forced to pass through the lower permeability, deeper peat, resulting in a low rate of P transport out of the system.

In this study, the influence of groundwater flow on SRP mobility was found to be more dominant than plant senescence. Groundwater influenced the chemistry, water table fluctuations in the riparian zone and in turn the formation of peat and the occurrence of flow reversals, which affected SRP build-up and transport in the riparian zone.

# 4.5 Geochemical Control on SRP Mobility

The hypothesis that SRP mobility is controlled by redox and ferrous iron (Fe<sup>2+</sup>) was not refuted because low concentrations of SRP were observed in areas of high Fe<sup>2+</sup> such as the conifer swamp in the recharge transect (T3). For a solubility-controlled solid such as vivianite, the concentration of PO<sub>4</sub><sup>3-</sup> should decrease as the concentration of ferrous iron (Fe<sup>2+</sup>) increases. Thus, Fe<sup>2+</sup> controlled PO<sub>4</sub><sup>3-</sup> during some conditions, as shown in Table 2, such as high SRP and high pH. Since Ca was predicted to precipitate with PO<sub>4</sub><sup>3-</sup> in lake surface water, it is likely an important control on SRP mobility in high pH (>7), oxidized conditions. Alternatively, low SRP concentrations due to low source of SRP, as found in groundwater, may limit these relationships.

The phosphate ion may have also been precipitating with Ca under reduced conditions and high pH, and Fe<sup>2+</sup> may have also been precipitating with humic acids, or sulphur (S). The high concentrations of DOC may have interfered with the relationship between  $PO_4^{3^2}$  or Ca and Fe and may have been responsible for the inaccuracies in  $PO_4^{3^2}$  concentrations in high DOC sites. The occurrence of high DOC concentrations with SRP and total Fe concentrations also suggest that iron may have been precipitating with humic acids instead of SRP because both humates (DOC) and P molecules compete for the same metal adsorption sites (Brady and Weil, 1999). Montigny and Prairie (1993) found that in Lake Cromwell, the cycling of P and Fe were not as tightly related as predicted by the model of Mortimer (1941) and strongly suggested that TDFe, was for the most part, bound to humic acids. Caraco et al. (1989) postulated that the formation of iron sulphides in anaerobic environments may also prevent the re-supply of Fe-oxides and the formation of Fe(III-II) oxide phosphate compounds. High concentrations of SRP observed at low concentrations of sulphate suggest that this process may have been occurring.

The strong relationship between SRP and pH than SRP and redox suggests that SRP was more controlled by pH than redox. The similarities between the aerobic and anaerobic adsorption/desorption experiment also suggests that SRP precipitation was not controlled by redox. Phosphate ions,  $H_2PO_4^{2-}$  and  $HPO_4^{-}$ , are most available and thus more mobile at a pH range from 6 to 8 (Brady and Weil, 1999). Results from this study

agree with this because highest concentrations of SRP were observed in a pH range of 6.0 to 7.0. Calcium is not affected by changes in redox potential, which may explain a stronger relationship between SRP and pH than SRP and redox potential. Geochemical modeling also showed that large changes in redox did not have an affect on SRP concentrations. Low concentrations of SRP associated with high concentrations of Ca (>100 mg/L) suggest that calcium phosphates may be precipitating under reduced conditions when ferric phosphates dissolve. This was also observed by Moore and Reddy (1994) in sediments in Lake Okeechobee where, under reducing conditions, the ferric phosphates would dissolve and calcium phosphates would precipitate.

Controls of SRP appear to be different in peatlands than the underlying mineral soils. Correlations indicated that low DO and neutral pH favoured P release in porewater. Redox potential and pH values were between the ranges required for both Fe and Ca control on SRP. Highest SRP concentrations were observed near the interface of the two sources of water, the dilute upland water and the more concentrated lake and groundwater that met in the riparian zone of the transition (T2) and the recharge (T3) transects and in the upland of the discharge transect (T1). High concentrations of SRP were observed in aerobic conditions in dilute water of upper fibric peat that had high redox, low pH, low Ca and low Fe<sup>2+</sup> concentrations, which, except for higher redox, allowed for the increased mobility of SRP. The lowest concentrations of SRP were found in areas with a pH greater than 7, low redox potential (0 to -100 mV) and highest Ca concentrations, which were observed in areas influenced by groundwater flow. Thus, the input of groundwater was important in buffering SRP in this system.

## 4.6 Role of the Riparian Zone

High concentrations and little seasonal fluctuation of SRP in this system suggests that vegetation uptake and release was minimal compared to other sources and thus was not the dominant control on SRP mobility in this outwash lake. While the redox and pH range within the peat of the riparian zone may provide the ideal environmental conditions for SRP solubility, the individual geochemistry of the sediments and the incoming water may limit the extent to which SRP will be bound or released. Physical properties of the mineral and organic soils influenced the amount of SRP adsorbed, and the amount of SRP that remained in solution. The highest concentrations of SRP were observed in soils with the highest EPC's (sand and fibric peat) while lowest concentrations of SRP were associated with soils with low EPC's (Gytta and clay, sand with mesic peat). Since highest SRP concentrations were associated with fibric organic soils of the riparian zone, the riparian zone itself was an important source of SRP. The build-up of SRP was thus higher in riparian wetlands with low hydraulic conductivity peat and low hydraulic gradients that prevented the movement of SRP out of the riparian zone

Lowest SRP concentrations were observed where Ca and Fe were the highest and suggest that, when present, Ca and Fe precipitate with SRP and remove it from solution. Ca and Fe were lowest in recently infiltrated water in the upland and surface peats, which suggests a control of chemistry by the type of water entering the riparian zone. Thus, Ca and Fe were more likely to precipitate with SRP when there were high concentrations of Fe and Ca, which occurred in conjunction with groundwater inflow and not within the dilute water of the riparian zone, the organic layers and in areas of local recharge.

The concentration of SRP present in the riparian zone depends on the inputs of water to the riparian zone and will vary with groundwater interaction. The discharge transect (T1) did not store SRP and was a potential source of SRP to the lake. However SRP exported to the lake was likely taken up immediately by algae and/or formed precipitates with high concentrations of calcium and iron present in the outwash lake. The low redox potentials, high decomposition rates, deeper peat, and local reversals observed in the transition (T2) and recharge (T3) transects led to high concentrations of SRP, causing those riparian zones to be potential sources of SRP to the lake and groundwater system. The high SRP concentrations present in the recharge zone are potential sources to groundwater aquifers.

This study shows that riparian zones are more likely to release SRP following precipitation events, which may lower pH and cause SRP to be released into solution. There is also increased movement of SRP during wet periods following dry periods when organic P is mineralized, especially in riparian zones more influenced by infiltration of rainwater than groundwater. Also, the highest SRP concentrations were found near the

edge of the lake, so any change or disturbance to this area will result in increased release of SRP from the riparian zone, especially in recharge zones where SRP will be released into the groundwater and down gradient systems.

Thus the role of the riparian zone in this system was multipurpose and varied with respect to groundwater and surface water interactions. Constant groundwater flow in the discharge transect (T1) prevented the build-up of peat and the storage of SRP thus the role of the riparian zone was minimal. The transition riparian zone flipped back and forth seasonally from being a source of SRP to the lake to a source of SRP to the groundwater system. The recharge transect (T3) had the potential to be an important source of SRP to the groundwater system and to the lake following flow reversals. Alternatively conditions in the peat allowed for the increased mobility of SRP but if SRP was exported from the riparian zone it will likely precipitate with ions present in groundwater. Thus, in this setting riparian zones are important sources of SRP and should not be disturbed, but disturbing the adjacent upland would likely have little effect unless the hydrology of the riparian zone was significantly affected.

## 4.7 Future Research

In this study, there was no one systematic control or explanation on P mobility and it was instead controlled by a combination of many factors that varied with different environmental conditions, thus a multitude of experiments and interactions are required to fully understand P mobility.

The anaerobic adsorption and desorption experiment was a preliminary experiment set up as a mini incubation in order to determine phosphorus saturation of the soil. EPC graphs showed that precipitation occurred in the anaerobic experiment instead of the expected adsorption, which suggests that redox was not the dominant control on P precipitation. In future experiments larger quantities of soil should be used, pH should be measured and an incubation experiment should be performed at both low and high pH to investigate the effects of precipitation versus redox on SRP.

High concentrations of SRP found in deeper piezometers underneath the high-P fibric peat may have been due to leaching from the surface along piezometers.

Lack of bentonite may have resulted in the movement of SRP down these piezometers, although EC values suggest that deeper water was more concentrated than surface water. Also, seals on shallow piezometers in peat may not have been adequate and hydraulic gradients are likely unrepresentative.

Groundwater flow near the toe of upland is very dynamic and piezometer nests should always be installed in this area. Future studies should also investigate the importance of organic phosphate and the difference compared to inorganic phosphate, which will aid in the further understanding of the mobility of phosphate. As well, studies examining minerals present in the mineral soil, fractionation experiments, further decomposition and mineralization studies and a phosphorus and iron budget for the lake will aid in better understanding of P mobility in this system.

# 5 Conclusions

The conclusions of the study are as follows:

## **Objective 1:**

H1: The highly permeable substrate in the outwash allowed for increased groundwater and surface water interactions. The upland hillslope and edge of the riparian zone were more prone to flow reversals than the lake edge and lake due to the close relationship between surface water and groundwater in these areas. As hypothesized, the effects of the consistent influx of groundwater in the discharge transect moderated the effects of precipitation and evaporation by preventing large fluctuations in flow and the formation of flow reversals.

**H2:** Local flow patterns caused by precipitation and evaporation were dominant in the recharge and transition transects. Reversals were caused by infiltration of precipitation into sandy upland toes and hummock-and-hollow peat and physical properties of peat.

## **Objective 2:**

**H3:** Little seasonal fluctuation in SRP suggests that plant senescence was not the dominant control on SRP concentrations in the riparian zone. Slight increases in SRP in July and August of 2003 were related to precipitation events and due to the leaching of SRP from surface organic layers into the riparian zone.

**H4:** SRP accumulated in the upper riparian zone and originated from surficial organic layers in the peat and from the aspen leaf litter. SRP accumulation in these areas were likely due to close distance to the source of SRP, physical properties of hummock-and-hollow peat, and reversals in flow.

## **Objective 3:**

H5: Minimal groundwater flowed through the deep peat deposits found in the transition and recharge transects. Local water flow was dominant in the deeper peat deposits and resulted in the transformation of SRP within the riparian zone. Local water table fluctuations caused flow reversals that aided in the build-up of SRP in the riparian zones of the transition and recharge transects.

**H6:** The influence of groundwater helped to buffer SRP inputs from dilute water originating from the aspen leaf litter and the riparian peat. As hypothesized, the groundwater entering the lake carried increased concentrations of iron and calcium ions that were important for precipitating with SRP. Highest concentrations of SRP were observed near the interface of two sources of water found in the riparian zone where dilute water recharging the upland toe and the riparian peat contained less calcium and iron ions and was thus less able to bind with SRP.

#### **Objective 4:**

**H7:** Higher concentrations of ions associated with groundwater flow helped to fix SRP in areas of the riparian zone most influenced by groundwater. Adsorption and desorption experiments also suggest that soil properties were important in determining the mobilization and immobilization of SRP.

**H8:** The riparian peat and aspen leaf litter were important sources of SRP and deeper deposits of peat in the recharge and transition transect allowed for build-up of high concentrations of SRP there. High concentrations of SRP were observed in aerobic conditions in dilute water of upper fibric peat that had high redox, low pH, low calcium and low iron concentrations, which allowed for the increased mobility of SRP.

#### **Objective 5:**

**H9:** P mobility was more controlled by pH than by redox. Ferrous iron was likely important in controlling P mobility in the conifer swamp.

**H10:** Calcium and pH were important in controlling SRP mobility in the lake and where calcium concentrations were high. In areas with dilute water there were less ions in solution to bind with SRP resulting in high SRP concentrations.

This study has shown that SRP mobility in riparian wetlands on an outwash plain with large interaction with groundwater is affected by groundwater-surface water interaction. The control of the mobility of SRP is a complex combination of many factors including precipitation reactions, soil adsorption and desorption, vegetation, microbes and the influence of water chemistry. The high variability of groundwater and surface water interactions observed in this outwash lake show that riparian zones exist in different environments and the role of the riparian zone will vary with these different interactions. Landscape alterations that affect groundwater and surface water interactions will affect the function of the riparian zone and in turn its nutrient dynamics. In order to predict responses of riparian zones and SRP mobility to disturbance, further research is needed in long-term studies spanning a variety of climatic conditions.

Substrate	Average	Max	Min	Std Dev	n			
Sand and Gravel	$1.0 \times 10^{-03}$	Smerdon et al. In Press						
Sand	5.6x10 <sup>-05</sup>	$1.7 \times 10^{-04}$	3.3x10 <sup>-06</sup>	6.7x10 <sup>-05</sup>	6			
Silty Sand	6.8x10 <sup>-06</sup>	$1.7 \times 10^{-05}$	2.1x10 <sup>-07</sup>	6.6x10 <sup>-06</sup>	6			
Silty Clayey Sand	2.6x10 <sup>-06</sup>	9.5x10 <sup>-06</sup>	2.3x10 <sup>-07</sup>	3.5x10 <sup>-06</sup>	6			
Till	1.6x10 <sup>-07</sup>	$1.6 \times 10^{-07}$	3.5x10 <sup>-08</sup>	8.8x10 <sup>-08</sup>	2			
Mesic Peat	8.4x10 <sup>-06</sup>	$2.0 \times 10^{-05}$	3.0x10 <sup>-06</sup>	7.9x10 <sup>-06</sup>	4			
Gyttja	3.7x10 <sup>-06</sup>	$7.0 \times 10^{-06}$	$2.1 \times 10^{-06}$	$2.7 \times 10^{-06}$	3			

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Table 1: Arithmetic average of hydraulic conductivities (K) (m/s) for representative substrates surrounding the study lake.

Site (Median Field Data)	L16	SM2	T2-2-SW	T1-3-200	T2-3-140	T3-1-350	T3-4-160	T3-6-700
Substrate Type	Surface	Springs	Surface	Sand	Peat	Clay	Swamp	Sand
Aragonite (CaCO <sub>3</sub> )	0.29	-0.28	-1.78	-1.11	-1.37	0.27	-2.2	-0.16
Calcite (CaCO3)	0.44	-0.14	-1.63	-0.95	-1.21	0.43	-2.04	0
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	0.71	-0.63	-3.34	-2.61	-3.11	0.19	-4.65	-0.63
Fe(OH)3(a)	2.71		-0.13			-3.98		
Goethite (FeOOH)	8.6		5.76					
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	18.66		13.14					
Hydroxyapatite (Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH)	0.43	-7.74	-10.96	-9.67	-8.77	-5.06	-7.61	-5.93
Quartz (SiO <sub>2</sub> )	-0.37	-0.33	-0.25	0.11	0.34	0.75	0.17	0.39
Siderite (FeCO <sub>3</sub> )	-1.2	1.28	-1.58	0.17	-0.27	I.17	-0.19	0.29
Vivianite (Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> :8H <sub>2</sub> O)	-6.77	-2.82	-8.36	-3.96	-3.49	-2.33	0.17	-4.27

) Peat versus Sand Substrates	Values used in Model		-200	200	4	8
Hydroxyapatite (Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH)		Field data	Low Redox	High Redox	Low pH	High pH
High SRP (0.73 mg/L)	Peat (T2-3-60)	-7.34	-3.44	-3.44	-23.63	1.36
Low SRP (0.02 mg/L)	Peat (T2-2-60)	-11.86	-8.84	-8.84	-29.07	_4
High SRP (0.80 mg/L)	Sand (T1-3-200)	-3.77	-2.46	-2.08	-22.57	2.27
Low SRP (0.012 mg/L)	Sand (T1-3-200)	-9.24	-7.93	-7.56	-28.04	-3.2
Vivianite (Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> :8H <sub>2</sub> O)		Field data	Low Redox	High Redox	Low pH	High pH
High SRP (0.73 mg/L)	Peat (T2-3-60)	-2.33	-0.18	-0.18	-11.67	2.23
Low SRP (0.02 mg/L)	Peat (T2-2-60)	-5.85	-4.17	-4.17	-15.68	-1.69
High SRP (0.80 mg/L)	Sand (T1-3-200)	0.03	0.74	0.36	-10.69	3.13
Low SRP (0.012 mg/L)	Sand (T1-3-200)	-3.61	-2.9	-3.28	-14.34	-0.51
Siderite (FeCO3)		Field data	Low Redox	High Redox	Low pH	High pH
High SRP (0.73 mg/L)	Peat (T2-3-60)	-0.55	0.09	0.09	-2.9	1.03
Low SRP (0.02 mg/L)	Peat (T2-2-60)	-1.13	-0.64	-0.64	-3.6	0.33
High SRP (0.80 mg/L)	Sand (T1-3-200)	0.04	0.27	0.35	-2.71	1.22
Low SRP (0.012 mg/L)	Sand (T1-3-200)	0.04	0.27	0.35	-2.71	1.23

Table 2: Saturation indices (expressed as logarithms) of a) selected field data and b) geochemical modeling comparing peat and sand. Grey shading indicates predicted precipitation.



Figure 1: Influence of pH and redox on phosphorus transformation in oxidized and reduced wetland soils. (Adapted from Moore and Reddy, 1994)



Figure 2: The Utikuma Research Study Area (URSA) in Northern Alberta. Lakes and ponds are identified by their URSA number. (Adapted from Smerdon et al, In Press). 53



Figure 3: Lake 16 study site, situated on the glacial outwash plain between Lake 17 and Lake 5, showing topography, hydrologic instrumentation, water table contours for July 15, 2002, and location of the three transects (T1 = Discharge, T2 = Transition, T3 = Recharge). Arrows are inferred flowpaths. (Adapted from Smerdon et al., In Press). 54



Figure 4: Cross section of the study lake showing the stratigraphy and water table contours for July 15, 2002. (Adapted from Smerdon et al., In Press).



Figure 5: Cross section of the discharge transect (T1) with lithology and piezometer/well screen length. The riparian zone consists of grass near the lake edge and alders near the toe of the upland. (Water table = August 12, 2002).



Figure 6: Cross section of the transition transect (T2) with lithology and piezometer/well screen depths. The wet open fen consists of sedges with cattails near the lake and with alder separating the dry open fen. (Water table = August 12, 2002).



Figure 7: Cross section of the recharge transect (T3) with lithology and piezometer/well screen depths. Cattails exists near the lake edge while birch and willow trees separate the wet open fen from the conifer swamp. (Water table = August 12, 2002).





Figure 8: Lake 16 hydrograph (m) and precipitation (mm) from May 2002 to October 2003.


Figure 9: Seasonal fluctuation in water table elevations for a) T1 b) T2 and c) T3. Dates for flow diagrams (Figures 10 to 12) are indicated along the x-axis.



Figure 10: Hydraulic heads and equipotential lines for the a) drying date (August 12, 2002) and the b) wetting date (July 14, 2003) at the discharge transect (T1). Equipotential lines are cm above 663 masl (i.e., 100 = 664.00 masl). Arrows indicate inferred direction of flow 61



Figure 11: Hydraulic heads and equipotential lines for the a) drying date (August 12, 2002) and the b) wetting date (July 14, 2003) at the transition transect (T2). Equipotential lines are cm above 663 masl (i.e., 100 = 664.00 masl). 62

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Figure 12: Hydraulic heads and equipotential lines for the a) drying date (August 12, 2002) and the b) wetting date (July 14, 2003) at the recharge transect (T3). Equipotential lines are cm above 663 masl (i.e., 100 = 664.00 masl). 63



Figure 13: Median electrical conductivity ( $\mu$ S/cm) values for a) T1 b) T2 and c) T3. Water tables shown for both the wetting (upper) and drying (lower) dates. Arrows indicate common flow between dates.



Figure 14: Seasonal fluctuation in soluble reactive phosphorus (SRP) concentrations in a) T1, b) T2 and c) T3.



Figure 15: Soluble reactive phosphorus (SRP) concentrations for the a) drying date and the b) wetting date at the discharge transect (T1). Arrows indicate direction of flow 66



Figure 16: Soluble reactive phosphorus (SRP) concentrations for the a) drying date and the b) wetting date at the transition transect (T2). Arrows indicate direction of flow.



Figure 17: Soluble reactive phosphorus (SRP) concentrations for the a) drying date and the b) wetting date at the recharge transect (T3). Arrows indicate direction of flow.



concentrations in a) T1, b) T2 and c) T3.



Figure 19: Median redox potential (mV) values for the a) 11, b) 12 and c) 13. Water tables show both wetting (upper) and drying (lower) dates. Arrows indicate common flow.

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Figure 20: Relationship between surface water and groundwater redox potential and SRP concentration in the three transects studied in the outwash lake. SRP values greater than 0.2 mg/L fall within 0 < redox < 150 mV.



c) T3. Water tables show both wetting (upper) and drying (lower) dates. Arrows indicate common flow. (\* = deleted bottle readings).



Figure 22: The relationship between surface water and groundwater DO and SRP concentration at the three transects of lake 16 grouped by substrate. SRP values greater than 2.5 mg/L fall within 0 < DO < 2 mg/L.



Figure 23: Median ferrous iron (mg/L) concentrations for a) T1, b) T2 and c) T3. Water tables show both wetting (upper) and drying (lower) dates. Arrows indicate common flow. 74



Figure 24: The relationship between surface water and groundwater  $Fe^{2+}$  (mg/L) and redox potential (mV) at the outwash lake grouped by transect.



Figure 25: The relationship between surface water and groundwater ferrous iron (mg/L) and SRP concentration grouped by transect at Lake 16.



Figure 26: The relationship between surface water and groundwater total iron (mg/L) and SRP (mg/L) concentration at Lake 16 ( $r^2 = 0.458$ , y = 0.706 - 1.284x,  $\rho < 0.05$ , n=38).



Figure 27: Median pH values for a) T1, b) T2 and c) T3. Water tables show both wetting (upper) and drying (lower) periods. Arrows indicate common flow. 78



Figure 28: The relationship between surface water and groundwater pH and SRP concentration in the three transects at Lake 16. SRP values greater than 0.25 mg/L fall within 6.0 < pH < 7.



Figure 29: Median calcium (mg/L) concentrations for a) T1, b) T2 and c) T3. Water tables show both wetting (upper) and drying (lower) dates. Arrows indicate common flow.



Figure 30: The relationship between surface water and groundwater Ca and SRP concentration for the three transects at Lake 16. SRP values greater than 0.2 mg/L fall within 0 < Ca < 100 mg/L.



Figure 31: Median DOC (mg/L) concentrations for a) 11, b) 12 and c) 13. water tables show both wetting (upper) and drying (lower) dates. Arrows indicate common flow. 82



Figure 32: The relationship between surface water and groundwater DOC and SRP concentration in the three transects at Lake 16 ( $r^2 = 0.141$ , y = 0.921 - 2.938x,  $\rho < 0.05$ , n = 103).



Figure 33: The relationship between surface water and groundwater Fe and SRP concentrations in the three transects at lake 16 ( $r^2 = 0.333$ , y = 1.213 - 1.775,  $\rho < 0.05$ , n = 23).

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Figure 34: Box plot of extractable pools of phosphorus by volume ( $\mu$ g/cm) for the five soil transects in T2. Boxes include 50% of the values and whiskers include 90% of the values. Each date represents 5 soil samples. Aspen (LFH) = Leaf litter of the aspen forest floor. Aspen (Min) = Sandy mineral soils below LFH. Con Swp = Conifer Swamp at 0-10 cm and 10-20 cm below the surface. Dry Fen = Dry open fen at 0-10 cm and 10-20 cm below the surface. Wet Fen = Wet open fen at 0-10 cm and 10-20 cm below the surface.



Figure 35: Equilibrium phosphorus concentrations (EPC's) in various sediments of Lake 16. Boxes include 50% of the values and whiskers include 90% of the values. Sand represents 3 soil samples, Fibric Peat represents 4 soil samples, Sand w Peat represents 4 soil samples and Gyttja/Clay represents 2 soil samples. Sand = two dry sands and one wet sand, Fibric Peat = upper fibric peat, Sand w Peat = Sand mixed with mesic and humic peat, Gyttja/Clay = gyttja mixed with clay in T3 near the lake.

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