University of Alberta

Regional and Local Controls of Surface Water Chemistry in the Boreal Plain and Shield Transition of Canada

by

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Abstract

The Western Boreal Forest exhibits complex hydrogeology juxtaposed with rapid resource development. Predicting surface water chemistry to assess the influence of landuse and climate change is needed. The research purpose was to test if a global model (Gibbs), used to assess water chemistry relative to precipitation, geologic and evaporative processes can be applied to mid-continental locations; and test if regional to local scale controls of surface-groundwater interactions can be used to refine predictions where geologic processes dominate water chemistry. The global model applied to many ponds, but failed in dilute and saline ponds. Caution is necessary, as the model assumes chloride-dominated precipitation, and continental to regional scale groundwater systems influence water chemistry, independent of evaporative processes. Bedrock geology influenced ion composition, TDS and pH via mineral dissolution and scale of flow. Surficial geology influenced TDP, TDN, DOC, pH and TDS, and wetland connection influenced TDP, TDN and DOC via flowpath. To assess water chemistry and the influence of landuse and climate change, regional to local controls of surface-groundwater interactions prove valuable over the global assessment of chemistry in heterogeneous and complex landscapes.

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Completion of this thesis would not have been possible without the love, support and patience of my wife, Leah Hrab and our daughters Rory and Avery. My family has endured an absent husband and father working on his thesis for far too long, and I promise to make up for it.

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Acronyms

AET – Actual Evapotranspiration

ANOVA – Analysis of Variance

BMP – Best Management Practice

BP – Boreal Plain

BS – Boreal Shield

DOC – Dissolved Organic Carbon

DUC – Ducks Unlimited Canada

ET – Evapotranspiration

FHLU – Fundamental Hydrologic Landscape Unit

GE – Gross Evaporation

GPS – Global Positioning Satellite

MWL – Meteoric Water Line

NMS – Nonmetric Multidimensional Scaling

OLF – Overland Flow

P – Precipitation

PE – Potential Evaporation

SRD – Saskatchewan River Delta

TDN – Total Dissolved Nitrogen

TDP – Total Dissolved Phosphorus

TDS – Total Dissolved Solids

WBF – Western Boreal Forest

Chapter 1

Introduction

1.1 Western Boreal Forest

The Western Boreal Forest (WBF) is rapidly changing due to forestry, oil and gas exploration and extraction, agriculture, and climate change (AEP, 1998). A large portion of the Boreal Plains of Canada consists of peatland-wetland-pond complexes, which cover up to 50% of the landscape (Kuhry et al., 1993, Vitt et al., 1995). These complexes provide critical breeding, staging and molting habitats for North American waterfowl and waterbirds. The response of Western Boreal lakes and wetlands to future drier conditions, and potential water quality impacts as influenced by enhanced resource activity, cannot be effectively assessed without a better understanding of the natural variability of pond or lake hydro-chemistry. Hydrological controls will further influence water quality and are responsible for maintaining the ecological integrity of ponds or lakes at both the local and the regional scale. The WBF experiences a sub-humid climate and is characterized by a heterogeneous glacial landscape with large variability in surficial and bedrock geology which results in complex surface and groundwater interactions. This results in an array of processes and thus large variability in surface water chemistry composition, concentration and nutrient status. Therefore, a baseline inventory of surface water chemistry is needed to assess the influence of climate change or landuse.

Currently, more research is needed on the processes controlling either the hydrologic function or the spatial variability of nutrient and solute chemistry of wetland-ponds in the WBF, and to assess or predict current impacts of landuse and climate change to develop models for assessing the susceptibility of wetland-ponds (Buttle et al., 2000). The location, movement, and chemical characteristics of water are fundamental to many water-resource related issues, therefore a conceptual framework for designing data networks, syntheses, and research is needed based on the hydrologic system (Winter, 2001). Understanding the natural spatial variability of water chemistry in relatively pristine ponds and lakes is required for effective interpretation of the effect of disturbance within any hydrogeological setting. Estimates of probable background chemistry can be useful in assessing the relative susceptibility of wetland-ponds to eutrophication or siltation following disturbance (Nip, 1991).

The study area is located within the Boreal Plains and transition to the Boreal Shield of Manitoba and Saskatchewan (Figure 1.1). Typically, the Boreal Plain (BP) and Boreal Shield (BS) of Saskatchewan and Manitoba experience a mid-continental climate and are the transition between wet and dry boreal and prairie regions, thus a range of climate controls on surface water chemistry may occur. Precipitation (P) is generally equal to or less than gross evaporation (GE) within the BP. Variability of climate within the BP will consequently influence dominant flowpaths of water and consequently dominant mechanisms influencing surface water chemistry (Gibbs, 1970). The BP of Saskatchewan and Manitoba exhibits complex geology, and at a continental scale, changes in near surface bedrock are dramatic over short distances. The variability of geology can influence the concentration and composition of surface water chemistry via dissolution of parent material (Moser et al., 1998). The BP consists of deep heterogeneous glaciated deposits that result in complex groundwater interactions which further complicates surface water hydrology and thus chemistry (Devito et al., 2005). As mentioned previously, peatland-wetland-pond complexes cover up to 50% of the BP of Canada and have also been shown to influence surface water hydrology and surface water chemistry (Moser et al., 1998). There is a need to predict the variability in background surface water chemistry to assess the influence of landuse and climate change and develop best management practices

1.2 Background Information

The Gibbs (1970) model has been used at the global scale to explain the variability of surface water chemistry (Wetzel, 1983, Jorgensen and Vollenweider, 1989). Dominant processes influencing surface water chemistry were explained by the interaction of climate and geology. The three major mechanisms identified by this empirical model consist of the atmospheric precipitation process, the rock dominance process, and the evaporation-crystallization process. The original model was applied to major lakes and rivers around the world and an envelope of points were observed when the ratio of Na/(Na+Ca) and Cl/(Cl+HCO_3) were plotted against their associated measures of total dissolved solids (Figure 1.2).

The first of three mechanisms used to describe surface water chemistry was atmospheric precipitation. Regionally, these were humid areas where P greatly exceeded potential evaporation (PE) (P>PE), and the potential to produce overland flow and reduce the residence time of soil water interactions was increased. The second mechanism described by Gibbs was the rock dominance mechanism. This mechanism is generally dominant in areas of moderate precipitation or moderate potential for producing overland flow (P=PE). Therefore it is hypothesized that geologic dissolution controls the salinity and composition of these waters. The third mechanism, the evaporation-crystallization mechanism was typical of regions that experience a very dry climate where there is little or no potential for runoff (P<PE).

Regional variability of surface water chemistry within the major mechanisms identified, and specifically in surface waters that fall within the rock dominance mechanism where P is generally equal to PE (continental Canada), is not addressed in the global model. Therefore, further understanding of the hydrologic cycle as it interacts with geology is needed and thus the interaction of atmospheric precipitation, surface water and groundwater can be used to further explain water chemistry variability within geologic dominated regions.

The need for a broad scale classification of a hydrologic response unit was initially presented by Winter (2001). Devito et al. (2005) argued that a broad scale classification of catchments was required to generalize dominant hydrologic processes before relying on topographic hydrologic boundaries that have become common practice and can be easily defined by land managers. A hierarchical classification was presented to generalize the dominant controls of water cycling and develop a conceptual framework to determine the dominant component of the hydrologic cycle to determine the scale of interaction that should be considered. This framework consisted of a hierarchy of factors nested within each other to characterize the relative importance of different scales and types of hydrologic interactions ranging from local to regional interactions. The orders in which these factors influence hydrologic flowpaths were presented as climate, bedrock geology, surficial geology, soil type and depth and lastly topography. These different hydrologic flowpaths will consequently influence dominant mechanisms influencing surface water chemistry.

1.3 Thesis Objectives and Format

The objectives of this research are:

1) to acquire a baseline inventory of the natural variability of relatively pristine surface water chemistry in a site bordering the Canadian Boreal Plain and Shield;
2) to test whether the Gibbs model can be applied to ponds in a continental climate and complex geology of the WBF, and identify the applicability of the model;
3) to define natural areas for management in the region; and
4) to test whether surface water chemistry can be related to hydrological controls of scale and flowpath, and to determine which scale and which landscape unit best predicts surface water chemistry of the Canadian Boreal Plain and Shield.

This thesis follows a paper format style and has been organized into four chapters. Chapter 2 includes the applicability of the Gibbs model to continental regions such as the WBF (Gibbs, 1970). In regions where geology dominates, greater resolution is required to assess spatial variability in surface water chemistry. Chapter 3 examines regional to local controls of hydrologic scales of flow and flowpath and their influence on surface water chemistry. Chapter 4 presents a general summary and conclusions of the previous two chapters and management implications of the research conducted.

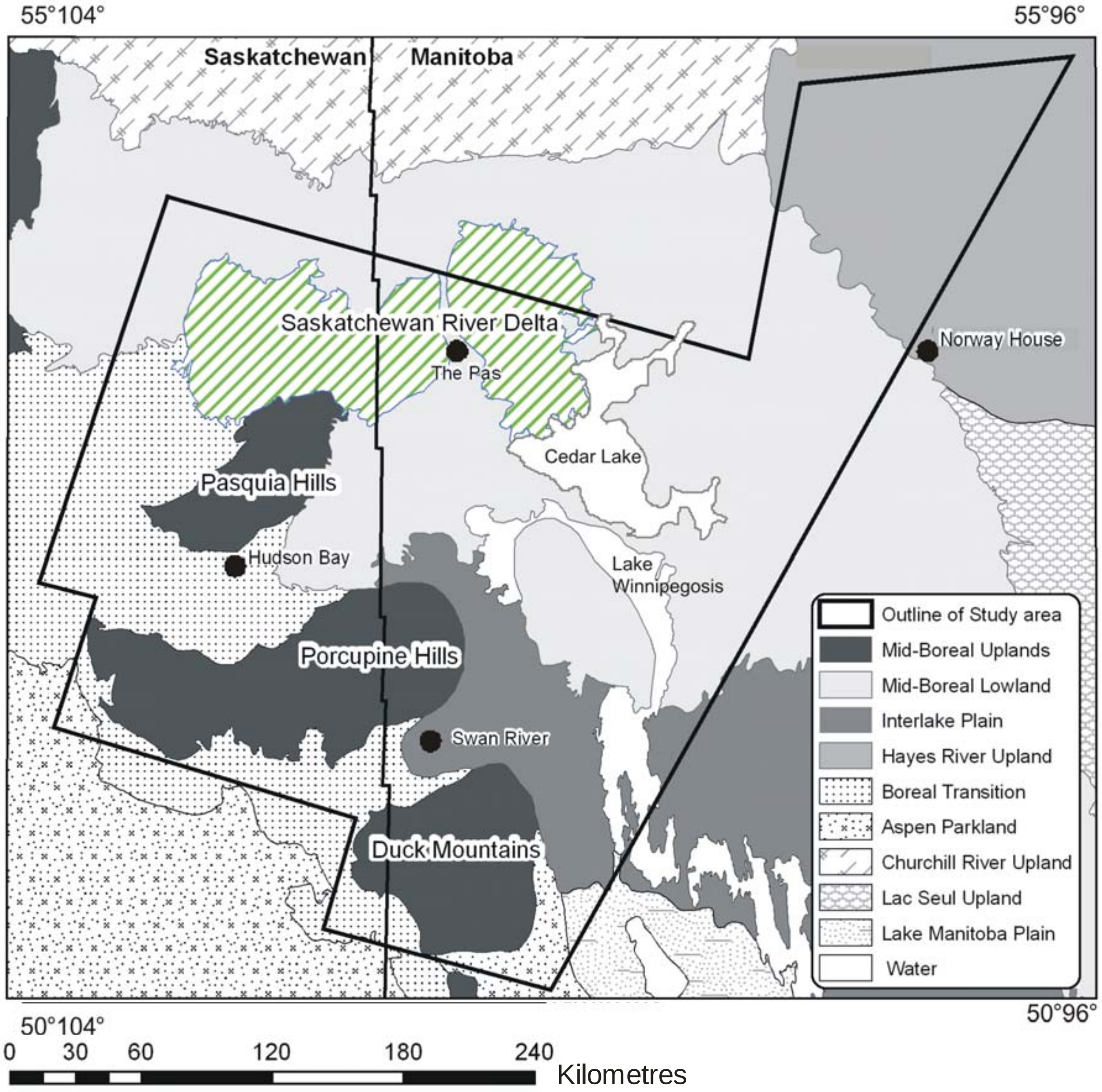

Figure 1.1. Spatial location of all ecoregions and key communities of the study area. Areas of ecological interest are also marked on the figure (Saskatchewan River Delta, Pasquia Hills, Porcupine Hills and Duck Mountains).

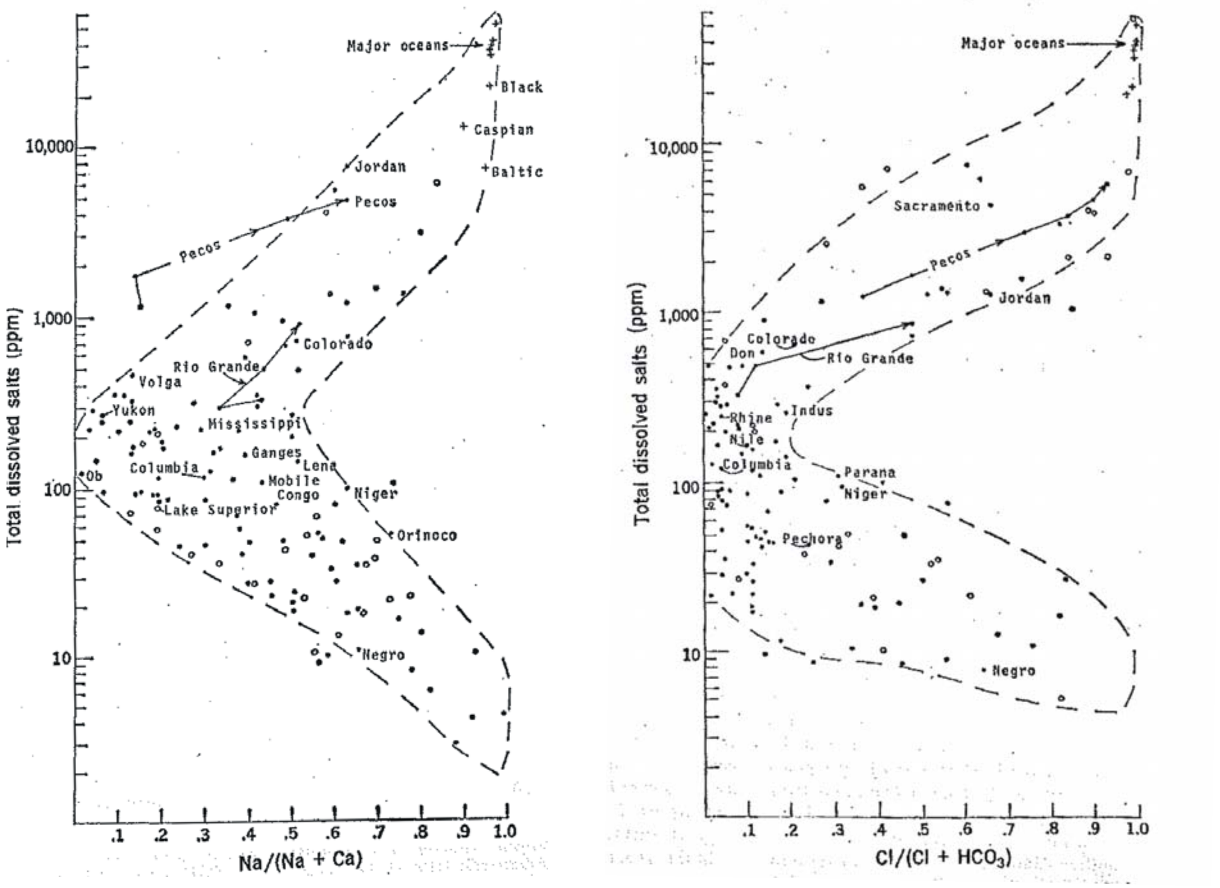

Figure 1.2. Variation of the weight ratio Na/(Na+Ca) and Cl/(Cl+HCO3) as a function of the total dissolved salts of the world surface waters. Modified from Gibbs (1970).

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Chapter 2
Characterization of Anomalous Water Chemistry in a Geologically Heterogeneous Landscape

2.1 Introduction

The Western Boreal Forest (WBF) is rapidly changing due to forestry, oil and gas exploration and extraction, agriculture, and climate change (AEP, 1998). A large portion of the Boreal Plains of Canada consists of peatland-wetland-pond complexes, which cover up to 50% of the landscape (Kuhry et al., 1993, Vitt et al., 1995). These complexes provide critical breeding, staging and molting habitats for North American waterfowl and waterbirds. The response of Western Boreal lakes and wetlands to future drier conditions, and potential water quality impacts as influenced by enhanced resource acquisition or development, cannot be effectively assessed without a better understanding of the natural variability of wetland hydro-chemistry. The susceptibility of surface water ponds and lakes to land use and climate change will be influenced by natural variation in local to regional hydro-ecological process (Winter 2001, Devito et al. 2005).Therefore, a baseline inventory is needed to assess the influence of anthropogenic or natural disturbances surrounding wetlands.

The Saskatchewan River Delta (SRD) is the largest inland freshwater delta in North America, covering approximately 9500 km^2. The SRD is rich in biodiversity providing important habitat for hundreds of species of birds, mammals and fish, and also important for traditional hunting and trapping (DUC, 2006). The SRD experiences extreme water control by hydro-electric dams above and below the lower delta. Understanding of local to regional connectivity of ponds and wetlands within the SRD is critical to fully assess and manage the integrity of wetland and river ecosystems.

Typically, the Boreal Plain (BP) and Boreal Shield (BS) of Saskatchewan and Manitoba experience a mid continental climate and is the transition between wet and dry boreal and more arid prairie regions. Precipitation (P) is generally equal to or less than potential evaporation (PE) within the BP. Variability of climate within the BP will consequently influence dominant flowpaths of water and consequently the dominant mechanisms influencing surface water chemistry

(Gibbs, 1970). Specifically the BP of Saskatchewan and Manitoba exhibits complex geology, and at a continental scale, changes in near surface bedrock are dramatic over short distances. The variability of geology can influence the concentration and composition of surface water chemistry via dissolution of parent material (Moser et al., 1998). The BP consists of deep heterogeneous glaciated deposits that result in complex groundwater interactions which further complicates surface water hydrology and thus chemistry (Devito et al., 2005). As mentioned previously, wetlands cover up to 50% of the BP of Canada and have also been shown to influence surface water hydrology and surface water chemistry (Moser et al., 1998).

Wetland and aquatic ecosystem losses through land use changes and resource extraction have resulted in the recognition that management must occur at larger spatial scales to satisfy the multiple demands on the world's resources. This recognition has led to the development of landscape management perspectives globally which vary in scale and process for addressing environmental issues in relation to water quantity. This project addresses natural processes and their influence on surface water quality of shallow open water wetlands or ponds, potholes and lakes, hereafter referred to as ponds. The question remains as to which models should be used and which landscape features can be used to generalize water chemistry across complex regions, such as the interaction between climate, regional and local scale processes.

2.1.1 Methods of Assessing Water Chemistry at a Regional Scale

Recent interest in water quality management has led researchers to address the heterogeneous nature of the environment surrounding bodies of open water (Omernik et al., 1987). It has long been recognized that terrestrial processes can influence the state of an adjacent body of water (Summer et al., 1990, Wetzel, 1983). Globally, variables such as physiography, soil characteristics, and human land use have been found to be major drivers in determining water quality (Johnson et al., 1997). These variables are often heterogenous throughout the landscape and frequently do not conform to any easily delineated boundaries such as watersheds. Although watersheds are commonly used for this purpose, they may not represent hydrologic boundaries in all landscapes. Specifically, the assumption that topography defines hydrologic boundaries may be limited in the WBF (Devito et al., 2005).

An approach researchers have taken to generalize water quality throughout a region has been by defining lake order as presented by Strahler (1964). This has been used as a metric to analyze the effect of a cumulative drainage network and infer flow to limnological features. Lake order, analogous to stream order, is based solely on geographical information and is simple to measure (Riera et al., 2000). Lake order has been used to understand the spatial orientation of both physical and biological variables of lake districts in Wisconsin, U.S.A. and in South Central Ontario (Riera et al., 2000, Quinlan et al., 2003). The relationships between lake order and a number of physical and chemical variables were found to be significantly related in both regions. However, these studies were conducted on simple homogeneous hydrogeologic settings, and require hydro-chemical assumptions similar to topographic catchment studies based in Eastern Canada. There may be some difficulty in incorporating these methods to the deeper surficial deposits and more complex groundwater flow systems of the WBF.

The ecoregions concept (Wiken, 1986 and Omernik, 1987) has also been used to relate the spatial distribution of the environment to discriminate between lakes of different water quality (Jenerette et al., 2002). These studies show that the large-scale spatial distribution of ecosystem types is more complicated than that suggested by the current ecoregion boundaries and are unable to explain the variability between aquatic systems. Ecoregion classification systems also have some restrictions as ecoregion boundaries show regions of distinct ecosystems, but not characteristics that can be transferred to other regions globally.

Alternatively, the natural evolution of groundwater chemistry has been related to flowpath and flowlength, and thus the groundwater inputs to surface water will influence surface water chemistries (Chebotarev, 1955, Tóth, 1999). Typical environmental effects and conditions resulting from the action of groundwater moving through different flow systems (local, intermediate and regional) will result in systematic changes in the dominant groundwater ion facies from bicarbonate through sulphate to chloride. The location of ponds within the discharge areas of these flow systems will influence surface water chemistries.

2.1.2 Gibbs Model

The Gibbs global model has been used at the global scale to explain the variability of surface water chemistry (Wetzel, 1983, Jorgensen and Vollenweider, 1989). Dominant processes influencing surface water chemistry were explained by the interaction of climate and geology. The three major mechanisms identified by this empirical model consisted of the atmospheric precipitation process, the rock dominance process, and the evaporation-crystallization process. The original model was applied to major lakes and rivers around the world and an envelope of points were observed when the ratio of Na/(Na+Ca) and Cl/(Cl+HCO_3) were plotted against their associated measures of total dissolved solids (Gibbs, 1970).

The first of three mechanisms used to describe surface water chemistry was atmospheric precipitation. Regionally, these were humid areas where P greatly exceeded potential evaporation (PE) (P>PE), and the potential to produce overland flow and reduce the residence time of soil water interactions was increased. Waters were typically low-salinity waters controlled by the amount of dissolved salts present in precipitation. Within the model, precipitation chemistry is typically described as having relatively higher proportions of both sodium and chloride as a result of salts cycled from the ocean. These waters generally consisted of tropical rivers in Africa and South America, where the rate of supply of dissolved salts is very low from thoroughly leached areas and the amount of rainfall is high.

The second mechanism described by Gibbs was the rock dominance mechanism. This mechanism is generally dominant in areas of moderate precipitation or moderate potential for producing overland flow (P=PE). Therefore it is hypothesized that geologic dissolution controls the salinity and composition of these waters. These waters were described as being more or less in partial equilibrium with the surrounding material of their basins. In general these waters were calcium-bicarbonate rich, and displayed relatively moderate measures of salinity.

The evaporation-crystallization mechanism was typical of regions that experience a very dry climate where there is little or no potential for runoff (P<PE). These waters ranged from calcium-rich moderate salinity waters to sodium-rich high salinity waters, a result of the evaporation-crystallization process. The change in composition towards the sodium-rich high salinity waters was attributed to be a function of evaporation, which increases salinity and the precipitation of calcium-bicarbonate (Feth and Gibbs, 1971). This resulted in waters with a relatively high proportion of both sodium and chloride.

The model is currently still a topic of debate, and its validity is continually addressed since it was first presented in 1970 (Kilham, 1990, Eilers et al., 1992, Blakar and Hongve, 1997, Ramos-Escobedo and Vazquez, 2001). Extrapolations of the model to the interior of continents, which often have arid to sub-humid climates and heterogenous geology and complex surface groundwater interactions is also lacking. The Gibbs model indicates a wide variability in surface waters as influenced by heterogeneity in geology, and does claim to provide predictive capabilities in these regions. Greater resolution of controls may be required in these regions.

There are a number of studies that show that many natural waters do not conform directly to the envelope of rivers and lakes presented by Gibbs. Eilers et al. (1992) focused on the inapplicability of the Gibbs model as it applies to dilute lakes, and found that local variations in hydrologic flowpaths and local soils and geology can easily modify surface water chemistry outside the envelope proposed by Gibbs. They report that many lakes deviate from the expected distribution due to low weathering rates in certain geologies that result in extremely dilute lakes, and relatively high base-cation production of sodium and magnesium compared to calcium, and strong precipitation dominance without substantial marine influence. These findings and others by Kilham (1990) also found that although the model applies well to large lakes and rivers of the world, it's applicability to smaller lakes and wetlands have been questioned. Wu and Gibson (1996) found that larger watersheds tended to average regional variations in geology and flowpath, and consequently showed more consistency with the model, while smaller lakes were influenced more by local variations in flowpath through soils and geology. Changing the shape of Gibbs model to a more calcium-bicarbonate type of water rather than a sodium-chloride type of water with respect to the atmospheric precipitation mechanism was suggested because much of the rain falling in the interior of the continent originated from inland waters with a Ca-HCO_3 signature. Sodium and chloride dominanted precipitation was only likely to be important near the coasts and along a few major storm tracks over weather-resistant rock (Kilham, 1990).

Further, evolution of groundwater, and its role in influencing concentration and composition of surface waters was not considered in the original model. The importance of groundwater in influencing lake and wetland chemistry is becoming well documented (Toth 1999, Winter 2001,). In contrast to evapoconcentration controls on surface water composition, length and time along groundwater flow paths can result in similar evolution of water chemistry and influence surface water connected to local, intermediate or regional groundwater discharge (Chebotarev, 1955, Toth, 1999). Therefore, further examination of surface water chemistry in inter-continental regions in relation to control produced by heterogeneity of geology and scale of groundwater influence are required.

2.1.3 Objectives

The objective of this research is to test the applicability of the Gibbs model and develop additional metrics to determine background spatial variability in surface water chemistry of the inter-continental Boreal Shield and Boreal Plain regions. This region is a transitional landscape between glaciated scouring and deposition regions, resulting in large heterogeneity in bedrock and surficial geology, and complex surface and groundwater interactions at local to regional scales (Winter 2001, Grasby and Betcher, 2002). This transitional region is home to a number of wetland-pond complexes including the SRD, important to local as well as continental species diversity, including waterfowl and other migrating birds. This region is experiencing both climate change as well as rapid and wide spread disturbance from multiple land use such as agriculture, forestry and oil and gas exploration and extraction.

Specific objectives of this research are:

1) to acquire a baseline inventory of the natural variability of relatively pristine surface water chemistry in a site bordering the Canadian Boreal Plain and Shield;
2) to test whether the Gibbs model can be applied to shallow ponds of the WBF, and identify the applicability of the model;
3) to define natural areas for management in the region; and
4) to develop a conceptual model to assess the natural range and dominant controls of chemistry within the ponds of the WBF.

2.1.4 Hypothesis

A baseline inventory and characterization of dominant processes influencing surface water chemistry as it varies across the landscape is needed to assess future influence of disturbances on the WBF. Approximately 1/3 of Canada experiences climatic conditions where P is equal to PE and thus surface waters should be geologically controlled (LaBaugh et al., 1998). As shown in Table 2.1, historical data show that the general water balance within Central Manitoba and Saskatchewan experiences a slight water deficit, where gross evaporation (GE) exceeds P by 90 mm to 200 mm throughout the study area, the exception is in the northeast where P slightly exceeds GE (Environment Canada, 2001). The Gibb’s model has not yet been applied to water chemistry data sets of the WBF of Canada; however, surface waters in the study area should be driven by the rock dominance mechanism and potentially trend slightly towards the evaporation-crystallization mechanism, as P and GE are relatively the same throughout the study area. According to Gibbs, their positions within the rock dominance grouping should be dependent on the relief, climate, and the composition of soils and geology of each basin. There is also a transition in geology of the study area, and ranges from easily weathered limestone, dolomite and shale of the Boreal

Plain to granite bedrock of the Boreal Shield. Therefore, surface waters should vary from low to moderate salinities and be dominated by both calcium and bicarbonate, while their positions within the envelope should vary with geology. Alternatively, the location of surface waters within the hierchical set of local, intermediate and regional flow systems will result in systematic changes in the groundwater ion facies from bicarbonate through sulphate to chloride, and thus be reflected in surface water chemistry (Tóth, 1999). Ponds located at flow system terminuses can result in increased salt contents of soils. Saline marshes can occur in situations where wetland conditions and intensive salt supply coincide (Tóth, 1999).

2.2 Methods

2.2.1 Study Area

This research was conducted in cooperation with the Western Boreal Division of Ducks Unlimited Canada (DUC). The study area is one of a number of areas within the WBF where DUC has conducted waterbird inventories and water chemistry surveys, to be used to evaluate the use of wetlands by waterfowl and other wetland-dependent waterbirds (Bell et al., 2003, Bell et al., 2005). The study area encompasses a 97,500 km^2 area of the Boreal Plains and Shield ecozone (Figure 2.1). The latitude and longitude of the northeast corner and southwest corner of the study area are 96^{o}50'W, 54^{o}58'N and 103^{o}50'W 52^{o}01'N, respectively.

Areas of ecological interest within the study area consist of three regional uplands (Pasquia Hills, Porcupine Hills, and the Duck Mountains) that are currently experiencing harvesting and agricultural pressure. Straddling the Manitoba-Saskatchewan border, the Saskatchewan River is Canada's fourth longest river. The Saskatchewan River Delta (SRD) is thought to be one of the most important wetland areas in North America. It is considered to contain the most important wetlands for breeding waterfowl (IBA, 2006). Resource activities within the SRD also include a number of hydroelectric dams situated above and below the delta.

2.2.1.1 Ecoregions and Climate

Within the Boreal Plain ecozone there are a number of notable features within the study area (Figure 2.2). The Pasquia Hills, Porcupine Hills, and the Duck Mountains are located within the Mid-Boreal Uplands ecoregion with the Boreal Transition ecoregion bordering the south edge of the regional uplands. The organic plains west of Lake Winnepegosis are found within the Interlake Plain ecoregion. Also, within the Boreal Plain, the SRD is an ecologically important ecosystem of Saskatchewan and Manitoba and is located within the Mid-Boreal Lowlands ecoregion. Within the Boreal Shield ecozone, organic deposits northeast of Lake Winnipeg are found within the Hayes River Upland ecoregion.

General climate data for communities within the study area are summarized in Table 2.1. The region experiences a mid-continental climate with long, warm summer days and cold winters. Continental seasonal January and July temperatures respectively range from –18°C to –22°C and 17°C to 18°C (Environment Canada, 2001). Annual precipitation within the study area ranges from 413 mm in Hudson Bay, Saskatchewan to 523 mm in Norway House, Manitoba. In general, GE exceeds P (-237 mm in Hudson Bay, Saskatchewan) with the exception of the northwest corner of the study area where P exceeds GE (+79 mm in Norway House, Manitoba).

2.2.1.2 Bedrock Geology and Rock Type

The bedrock geology of the study area consists of eight formations based on genesis (Table 2.2). As geology may influence surface water chemistry composition and concentration, bedrock units were grouped based on similar mineralogical rock types and similar weathering rates.

Near surface bedrock units were identified throughout the study area using the Geological Highway Map of Manitoba and The Atlas of Saskatchewan (Corkery, 1987, Fung, 1999). The geological map of Saskatchewan was at a 1:2,750,000 scale, while the geological map for Manitoba was at a 1,000,000 scale. While a number of different formations were present that relate to different ages of deposition and rock mineralogy, the number of actual rock types was quite low and have been classified as, dolomites/limestone, shale/dolomite mix, shale, sandstone, and intrusive granite (Table 2.3).

The near surface bedrock of the west to southwest portion of the study area consists of upper and lower Cretaceous shale and sandstone (Fung, 1999). These sedimentary rocks underlie the three regional uplands within the study area (Pasquia Hills, Porcupine Hills, and Duck Mountains) (Figure 2.3). Devonian shale, a dolomite mix and Silurian dolomite/limestone are situated in the east to northeast portion of the study area and underlie the Saskatchewan River Delta, and the organic plains west of Lake Winnepegosis (Fung, 1999). The northeast portion of the study area is situated on the Boreal Shield. This unit is comprised of

Precambrain intrusive rocks and is covered by a thin layer of clay rich lacustrine sediments (Corkery, 1987).

A summary of the formation names and rock types within the study area is shown in Table 2.2. The lower Cretaceous sandstones and shale from the Swan River Formation generally consist of quartzose sandstone, kaolinitic shale and minor lignite (Fung, 1999). The major formations from the upper Cretaceous are the Riding Mountain, Favel and Vermillion Formations. The Riding Mountain Formation generally consists of soft greenish bentonitic shales, while the Favel and Vermillion Formations consist of carbonaceous shales (Fung, 1999). The middle Devonian basal red shales, limestones and dolomites are from the Dawson Bay Formation. The upper Devonian Souris River Formation also consists of red shales with argilaceous and high calcium limestone and dolomite. The lower Silurian Cedar Lake Formation consists of micrimitic, fossiliferous, stromatolitic and bistromal dolomite with sandy agrillaceous marker beds. The upper Ordovician sedimentary rocks are from the Stonewall Formation and consist of fine-grained dolomite (Corkery, 1987). The Precambrain intrusive rocks of the study site are generally comprised of tonalitic gneiss and minor amphibolite, layered migmatitic gneiss, and anorthositic gabbro (Corkery, 1987).

2.2.1.3 Surficial Geology, Vegetation and Land Use

The study area is composed of a mosaic of glacial deposits typical of the Western Boreal Plain. These glacial deposits vary in particle size from region to region and are presented on Figure 2.4. The following surficial geology and vegetation descriptions are summarized from Environment Canada (2005).The Mid-Boreal Lowland ecoregion which includes the SRD is a relatively flat, low lying region with extensive wetlands covering the area. The area is covered almost entirely by level to ridged glacial till that can extend on the order of tens of kilometers, lacustrine silts and clays and extensive peat deposits. The poorly drained bogs and fens are covered with tamarack and black spruce, while the mixed deciduous and coniferous forest is characterized by closed stands of trembling aspen and balsam poplar with white and black spruce and balsam fir.

The Mid-Boreal Uplands ecoregion is covered by kettled to dissected, deep, loamy to clayey-textured glacial till, lacustrine deposits and inclusions of coarse, fluvioglacial deposits. Vegetation consists of closed stands of trembling aspen and balsam poplar with white and black spruce and balsam fir. Poorly drained fens and bogs are covered with tamarack and black spruce. The Boreal Transition ecoregion is characterized by hummocky to kettled plains covered by calcareous, glacial till and significant inclusions of relatively level lacustrine deposits. Vegetation includes closed stands of trembling aspen with secondary quantities of balsam poplar. Poorly drained sites are usually covered with sedges, willow, some black spruce and tamarack. The Interlake Plain ecoregion consists of broadly ridged, extremely calcareous glacial till and by shallow, level lacustrine sands, silts and clays. The vegetative cover consists of a closed cover of tall to low trembling aspen with secondary quantities of balsam poplar and open stands of tall jack pine occur on dry sandy sites. The Hayes River Upland ecoregion is comprised of upland surfaces covered with discontinuous deposits of ridged to hummocky calcareous loamy till. Thin clayey lacustrine deposits cover a large part of the till deposits, especially in the low-lying areas. These lacustrine deposits are in turn, often overlain by shallow to deep peat materials. Fluvioglacial moraines and eskers are locally prominent.

Land-use within the study area consists of forest harvesting in the three regional uplands, agriculture associated with the lowlands surrounding the regional uplands, oil and gas production and hydroelectric power related to the Saskatchewan River. Hunting, trapping, and traditional aboriginal activities also occur throughout the area.

2.2.2 Sampling Design

Two-hundred and ten shallow pond or pothole wetlands, hereafter refered to as ponds, were sub-sampled for water chemistry from a total of six-hundred and eighteen DUC waterbird survey ponds (Friedt and Smith, 2004). The DUC waterbird survey ponds were randomly sampled within ecodistricts. The ponds sampled for water chemistry on the Boreal Shield were not a subset of the DUC waterbird survey ponds and were selected based on accessibility on foot.

To address the question of the influence of geology, ponds were selected from the DUC waterbird survey ponds to incorporate all bedrock geologic types observed in the area. The final distribution of ponds sampled within bedrock and surficial geologic units is summarized in Table 2.3. The number of ponds sampled largely represents the % area covered by each geologic unit. There are five dominant bedrock units identified within the study area (Figure 2.3). To address interaction of surficial geology and bedrock geology, the study area was further stratified by a total of four different surficial deposits (Figure 2.4). Of the five bedrock types present in the study area, approximately ten ponds were selected from each surficial geological unit. Surficial geologic units were not all present within each of the bedrock units and in some cases there were not ten ponds to be sampled within surficial geologic units. Ponds overlying organic deposits were assigned to the nearest surficial deposit.

2.2.3 Water Chemistry

2.2.3.1 Water Chemistry Sampling

A one litre grab sample of water was collected from the middle of the open water area of each pond. Sampling was conducted off the mounted inflatable floats of a 206 Jet Ranger helicopter from July 26th to August 1st 2003. In the summer of 2004 (July 25th to July 29th) ponds sampled from the Boreal Shield were accessed by land. In 2004, water samples were collected within 2 m of the pond edge. For all water samples, water was collected from approximately 20 to 30 cm below the surface. ArcView 3.2a software and the moving map extension Track Analyst, combined with a global positioning system (GPS) were used as a navigational tool to locate each pond. A TM scene was used with Track Analyst to ensure that the correct ponds were sampled by using predefined Latitude and Longitude coordinates. The water chemistry survey crew consisted of a pilot, a navigator, and a person to collect a water sample, characteristics of the vegetation surrounding the pond, water color, depth and secchi depth of the pond.

Perishable parameters (i.e., soluble reactive phosphorus, ammonium and nitrate) were filtered through a Millipore membrane filter (pore size-0.45 μm) and frozen within 8 hours of sampling until analysis. The pH and conductivity of the pond waters were measured within 8 hours of sampling using a Fischer Scientific Accumet 925 pH meter and an Oakton Con 300 conductivity meter, respectively. Water samples were packed in ice filled coolers and shipped to the University of Alberta Limnology lab and received within 72 hours. A subset of 118 pond water samples were shipped to the University of Calgary Isotope Science Laboratory for deuterium/hydrogen isotope analysis.

2.2.3.2 Water Chemistry Analysis

A full suite of dissolved anions (negatively charged) and cations (positively charged) were analyzed to allow for a complete ion charge balance, and general measure of water quality for each pond. Major cations sampled included sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}). Cations were measured on a Perkin Elmer 3300 Atomic Absorption Spectrometer while water samples were processed using the methods presented by Stainton et al. (1977). Major anions sampled consisted of bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}), sulfate (SO_4^-), and chloride (Cl^-). SO_4^- and Cl^- were measured on a Dionex DX600 Ion Chromatograph and were processed using methods presented by EPA (1993). Alkalinity and pH were measured using the Alkalinity (2320)/ titration method (Greenberg et al., 1992). Total dissolved solids (TDS) concentrations were calculated by summing the major anions and cations.

For this study, water samples with an ionic charge balance error of less than plus or minus 10% were utilized. All ions were converted to milli-equivalents and the difference between the sum of cations and sum of anions was divided by the total sum of anions and cations. A total of four ponds were removed from this analysis as their ionic charge balance errors ranged from 15% to 27%.

Inorganic and organic phosphorus and nitrogen and dissolved organic carbon were also analyzed and described in chapter 3.

According to methods presented by Krabbenhoft et al. (1994), ponds that deviate the furthest away from the meteoric water line (MWL) are undergoing larger evaporative influence as opposed to ponds that plot on or near the MWL. The deuterium hydrogen isotope analysis of water was determined by chromium reduction. Four µL of sample was injected into a chromium filled quartz reactor held at 960 °C and evacuated to ~10-3 torr . $H_{2(gas)}$ was produced and collected within 60 seconds, then sent to a dual inlet, isotope ratio mass spectrometer for analysis using methods of Freidman (1953), Coleman et al. (1982), Gehre et al. (1996), Nelson and Dettman (2001) and Donnelly et al. (2001).

The $^{18}O/^{16}O$ ratio of natural waters is determined using the common CO_2-H_2O equilibration technique in which millimole quantities of CO_2 are equilibrated with water samples under constant temperatures. Subsequently, the CO_2 is cryogenically purified and analyzed mass spectrometrically for its $^{18}O/^{16}O$ ratio. Note that this technique measures the isotopic activity of ^{18}O and not the actual ^{18}O concentration. For dilute waters, differences between isotopic activity and concentration are negligible. For saline waters and brines (TDS > 1000 mg/L), longer equilibration times were needed based on work by Epstein and Mayeda (1953), Sofer (1972), O'Neil et al. (1975) and Horita et al. (1993).

2.2.4 Additional Explanatory Variables

2.2.4.1 Gibbs Model

The boundary of the empirical model used to characterize dominant mechanisms controlling major lakes and rivers presented by Gibbs (1970), was developed by creating a layer of the existing envelope from the original paper. The boundary was then superimposed onto the surface water chemistry data collected from the study area. Therefore there is some uncertainty with the boundary, and samples close to this line should be interpreted with caution.

2.2.4.2 Riera Lake Order

Surveyed ponds were assigned lake orders according to Riera et al. (2000), where drainage order was based on the type and strength of the connection between the pond and the surface drainage network. The order of the ponds with both surface inlets and outlets were determined by the order of the stream that drained the pond, and assigned positive pond orders. Therefore, if a pond outlet has a stream order of 3, the pond would be assigned a drainage order of 3. Pond drainage order was designated using the methods of Strahler (1964) and 1:50,000 scale maps. Ponds with no permanent drainage by streams were assigned negative pond orders (Riera et al., 2000). Ponds connected to the surface drainage network only by temporary streams were assigned an order of –1, and an order of –2 was assigned to ponds connected to the drainage system developed in wetlands (marsh, swamp, fen or bog) where surface "sheet flow" appeared to occur but channelized flow was absent. A lake order of –3 was assigned to isolated ponds that appear to be hydrologically unconnected to the drainage network by surface water.

2.2.5 Statistical Analysis

2.2.5.1 Nonmetric Multidimensional Scaling (NMS)

NMS is an ordination method suited to data that are nonnormal or are on arbitrary, discontinuous, or otherwise undefined scales. This method can be used both as an ordination technique and as a method for assessing the dimensionality of a data set (McCune and Grace, 2002). NMS is an iterative search for a ranking and placement of n entities on k dimensions (axes) that minimizes the stress of the k-dimensional configuration.

Main advantages of NMS are as follows. NMS avoids the assumption of linear relationships among variables. Its use of ranked distances tends to linearize the relationship between distances measured in species space and distances in environmental space. This relieves the zero truncation problems, a common problem with heterogeneous community data sets. NMS also allows the use of any distance measure or relativization.

For this analysis PC-ORD version 4 was used to run the ordination. There were no data transformations performed on the data, however a general relativization was used on the data before the NMS ordination was run. The Sorenson (Bray Curtis) distance measure was used for the ordination. The starting configuration was produced with a random number generator. Comparing the final stress values among the best solutions assessed dimensionality of the data set and followed the methods described by McCune and Grace (2002):

- There were a total of 15 real runs, each with a random starting configuration. A real run consists of a series of solutions, stepping down in dimensionality, from the highest number of axes to one axis.
- There were then a total of 30 runs with the randomized data, where before each run the chemistry data was shuffled within columns (chemical parameters). Statistics on the final stress for each dimensionality were then accumulated.
- The best solution is defined by a specific starting configuration and associated number of dimensions. PC-ORD selects the best solution for each dimensionality as that with the lowest final stress from a real run.
- The dimensionality of the data set was then selected by comparing the final stress values among the best solutions, one best solution for each dimension. Dimensions are considered useful when they reduce the final stress by 5 or more on a scale of 0-100. PC-ORD selects the highest dimensionality that meets this criterion.

2.3 Results

2.3.1 General Water Chemistry Types

The NMS analyses indicates that 2 dominant axis explain the total variability in study pond surface water TDS, anions and cations. (Table 2.4). The first axis was positively correlated with the solutes sodium, chloride, and negatively correlated with bicarbonate. Axis 1 is also negatively correlated with calcium and magnesium to a lesser extent. The sulphate ion was the most negatively correlated ion with Axis 2, while measures of TDS weren't highly correlated with either ordination axis.

Based on the NMS ordinations, there were three major types of waters present (Figure 2.5). These types of waters consisted of a sodium-chloride type of water, a sulphate type of water and lastly, more dilute waters that were characteristically dominated by calcium, magnesium, and bicarbonate ions. These waters tended towards composition of precipitation, but still remained distinct.

The three groups of ponds with differing water chemistry were generally associated with specific geology (Figure 2.5). The piper diagram in Figure 2.6 provides further details of the composition of pond surface water chemistry. Approximately 20% of ponds sampled had water composed predominantly of sodium and chloride (Figure 2.6) and extended along the first axis in the NMS analyses (Figure 2.5). Ponds with sodium-chloride type waters overlie the lower Cretaceous sandstones, Devonian shales and dolomites, and Silurian dolomites (Table 2.4, Figure 2.5). Ponds characterized by waters with higher proportions of sulphate represented approximately 16% of the total ponds sampled and were negatively correlated with Axis 2 (Table 2.4). These sulphate type waters were typically overlying upper Cretaceous bentonitic shales, located at relatively higher elevations associated with the upland ranges within the study area. The majority of the ponds had waters characterized as having moderate to relatively dilute TDS but dominated by calcium, magnesium, and bicarbonate. These calcium-magnesium-bicarbonate type waters were located above all the general bedrock geology units sampled within the study area. However, water in ponds overlying granitic bedrock typically were associated low TDS, very low chloride concentrations, and dominated by calcium-bicarbonate.

2.3.2 The Gibbs Model

Surface water chemistry of the surveyed ponds were stratified by geology and plotted on the Gibbs model for TDS versus Cl /(Cl + HCO_3) or Na/(Na+Ca) to identify potential dominant mechanisms influencing surface waters (Figures 2.7 and 2.8). Although there is considerable variability, as expected in this region, the majority of the ponds had surface water chemistries that fell within the range predicted for waters controlled by geologic weathering or slight evaporation-crystallization in the Gibbs model. Most ponds sampled had TDS measures that ranged from 50 to 1000 mg/L and a Na/(Na + Ca) or Cl/(Cl + HCO_3) ratio that ranged from 0 to 0.6, or 0 to 0.2, respectively. This included the ponds overlying upper Cretaceous bentonitic shales, with waters dominated by sulphate that separated out in the NMS analyses and on the piper plots (Figures 2.5 and 2.6). The chemistry of waters in ponds located over granite tended to separate from other surveyed pond chemistry. These pond waters were typically dilute with very low proportions of chloride, and varying proportions of sodium (Figure 2.6). However, these waters also fell within the expected range for geological control as predicted by the Gibbs model. Controls on the variability of pond water concentration and composition that fit within the Gibbs model will be further addressed in a following chapter 3.

There were a number of ponds sampled that fell outside of the Gibbs model (Figures 2.7 and 2.8) and these will be addressed in the following sections. These consisted of three distinct groups and include: 1) dilute ponds with relatively low proportions of sodium, 2) ponds with moderate salinity waters associated with low proportions of chloride and 3) ponds with moderate to high salinities and relatively higher proportions of sodium and chloride, that plot along and outside of the ascending limb of the evaporation-crystallization portion of the model. The spatial relationship of these ponds relative to general landscape topography and bedrock and surficial geology are plotted in Figures 2.9 to 2.12.

There were seven ponds in the first group with generally low TDS waters that ranged from 60 to 90 mg/L, and low proportions of sodium that ranged from 0.07 to 0.08. These ponds were located on the regional high of two of the three upland areas (Pasquia Hills and Porcupine Hills) within the study area, underlain by glacial till over Cretaceous bentonitic shale (Figures 2.9 and 2.10).

Five ponds had waters with moderate salinities that ranged from 820 to 1170 mg/L and relative low proportions of both sodium and chloride that ranged below 0.05. Spatially, these five ponds were located at the fore slope of both the Porcupine Hills and the Duck Mountains within till overlying shale bedrock (Figures 2.11 and 2.12).

There were thirty-five ponds (17% of total) with relatively higher proportions of sodium and chloride (0.4 to 0.9) , and were associated with TDS values that ranged between 200 and 20,000 mg/L that plotted along and outside of the envelope of the Gibbs empirical model (Figures 2.7 and 2.8). These waters fell within the evaporation –crystallization portion of the Gibbs model, and are grouped with ponds within the ascending limb of the Gibbs model.

The spatial orientation of ponds that correspond to the ascending limb of the Gibbs model in relation to bedrock and surficial geology is presented in Figures 2.9 to 2.12. The majority of these ponds were associated with the outcrop belt of the carbonate rock aquifer as described by Grasby and Betcher (2002), and a regionally low topographic position. Among these, approximately twenty-five of these ponds were associated with the SRD and specifically, a number of these ponds were located near the outlet of the Saskatchewan River as it opens into Cedar Lake. The remaining ten ponds were located on low lying areas west and southwest of Lake Winnepegosis. There was also one pond located on the low lying shale in the south west portion of the study area (Figures 2.11 and 2.12).

2.3.2.1 Pond Area

The relative size of ponds or lakes has been found to drive water chemistries outside of the Gibbs model, as local geology and local flowpath can easily modify surface water chemistry (Kilham, 1990). The mean size of the ponds surveyed within the study area was 182.4 hectares with a median size of

12.2 hectares. The ponds sampled ranged from 0.2 hectares to 3320.3 hectares in size throughout the study area (Figure 2.13). In general the distribution of the ponds was positively skewed and size appears to influence whether the chemistry conforms to the Gibbs model or not.

Some relationship to lake size was observed with respect to three distinct surface water chemistries that did not conform to the Gibbs model. Larger ponds were associated with moderate to higher TDS concentrations and higher sodium and chloride ratios. The ponds with relatively higher proportions of sodium and moderate to high measures of TDS had a mean and median area of 291.6 and 84.9 hectares and ranged from 2.4 to 1199.6 hectares. The ponds with relatively higher proportions of chloride and moderate to high TDS concentrations had a mean and median area of 341.4 and 97.0 hectares and ranged from 3.6 to 1497.0 hectares.

Dilute ponds with relatively low TDS concentrations and low proportion of sodium were generally small, indicating isolation. The mean and median area of ponds that fell outside the envelope with relatively low measures of TDS associated with low proportions of sodium, was 9.9 and 4.6 hectares, and ranged from 1.3 to 33.8 hectares.

Shallow ponds that had relatively low proportions of chloride associated with moderate measures of TDS were generally small with the exception of one, indicating evaporative influence. The mean and median area of these ponds was 192.7 and 6.0 hectares and ranged from 2.0 to 570.3 hectares.

2.3.2.2 Stable Isotopes and Evapo-concentration

Stable isotope relations can be used to estimate the evaporative condition of surface waters and thus indirectly if the evaporative-crystallization mechanism is influencing the chemistry of ponds of the study area (Krabbenhoft et al., 1994). Stable isotope data for selected ponds are plotted on Figure 2.14, along with the MWL from The Pas, Manitoba as presented by IAEA/WMO (2001). According to the plots of oxygen 18 versus deuterium, the majority of the ponds within the study area have undergone some evaporative influence, while a third of the ponds indicate significant evaporative influence when compared to the historical MWL (Figure 2.14a). Approximately ten ponds plot on or near the MWL and include ponds overlying the granite geology and the Saskatchewan river. The three water types that did not conform to the Gibbs model are also plotted on Figure 2.14b. The dilute waters with relatively low proportions of sodium and moderate salinity waters with relatively low proportions of chloride both plotted near the MWL and indicate little evaporative influence. The stable isotopes of the high TDS concentrations and proportionately high chloride and sodium (ascending limb) plot amongst the freshwater ponds and show no significant difference in isotopic signature between the freshwaters and saline waters. This indicates that the evaporation-crystallization process is not controlling these waters. The three ponds that exhibited a large evaporative control were magnesium-sulphate type waters overlying the shale bedrock.

The brackish to saline ponds (TDS measures >1000 mg/L) within the study area show a strong linear trend between sodium and chloride with an R^2=0.98 and slope of 1.15 (Figure 2.15). Surface waters of the study site that were characterized as freshwaters (TDS measures <1000 mg/L) had an R^2=0.77 and had a slope of 0.58.

2.3.3 Water Chemistry within the Saskatchewan River Delta

The SRD is a globally significant ecosystem of this region of the BP and BS. Given that many of the ponds have surface water with unique chemistry to the surrounding region, and of the type not consistent with geological control / influences (Gibbs, 1970), further examination of the pond waters in the SRD is presented below.

2.3.3.1 Surficial Geology

The variation in surface waters TDS, sodium and chloride within the SRD generally decreased from ponds located in the organic unit to alluvial sediments and was lowest in ponds overlying the till (Figure 2.16).

There was considerable variation in water chemistry of ponds surrounded by massive peatlands (organic units) within the SRD, with TDS, ranging from 253 to 3725 mg/L. Similarly the proportion of sodium and chloride ranged from 5.9 % to 78.1 % and 18.4 % to 97.4 % relative to the other major cations and anions, respectively. The average TDS of pond waters located in the alluvial sediments was lower than ponds located in peatlands, but with a considerable range from 72 to 2706 mg/L. However, the average proportion of sodium in pond waters located in the alluvial sediments was similar to ponds located in peatlands. The lower TDS in ponds located in alluvial sediments relative to those in peatlands was associated with a lower mean proportion of Cl, but the range was still large (0.7 % to 97.6 %). In contrast, the chemistry of waters located in till veneer on the eastern portion of the SRD were moderate in salinity (TDS 128 to 435 mg/L) and dominated by calcium-bicarbonate with low proportions of sodium and chloride, similar to the main channel of the Saskatchewan River.

2.3.3.2 Water Chemistry in Relation to the Main Channel

To further assess the role of river interactions with ponds in the SRD, the distance from a main channel was used as a measure of isolation of each pond to explain some of the observed variation in concentration and composition of pond waters (Figure 2.17). Most of the ponds had similar TDS concentrations to the Saskatchewan River showing no relationship with distance to channel. There were 35 ponds with sodium and chloride proportions exceeding that observed in the Saskatchewan River, but without a trend in distance from the main channel. The lack of trend and relatively low TDS indicate that isolation from the main channel and evapoconcentration is not the likely cause.

Mapping of direct channel or tributary connection of the pond to the major river channels showed higher concentrations of TDS and proportionately higher sodium and chloride concentrations in comparison to the ponds connected to major river channels (Table 2.5). This indicates some isolation of ponds and moderate evapoconcentration of solutes and the importance of the channel connectivity to moderating pond chemistry.

2.3.3.3 Lake Order

Lake order as described by Riera et al. (2000) was applied to the ponds of the SRD to examine the potential influence of landscape position and relative contribution of regional scale groundwater on pond surface water chemistry

(Figure 2.18). No trend was observed in the proportion of chloride. However, there is considerable variability in the trends of TDS concentration and sodium with pond order. The greatest range in TDS was found in ponds assigned an order of -2 and the range of values decreased with an increase of pond order (Figure 2.18a). Thus, the occurrence of ponds with high TDS and to some extent, greater proportion of sodium was greater with low order ponds. These represent ponds surrounded by peatlands or in groundwater spring locations.

2.4 Discussion

The majority of the variability in water chemistry appears at a regional level to be explained by variation in geologic processes as hypothesized by Gibbs (1970) and Wetzel (1983). However there are types of waters not explained by these models, indicating other process need to be considered. Some of the deviations from the original global model can be explained by continental scale differences in precipitation chemistry, but also complex groundwater interactions in geologically diverse regions will need to be considered. Particularly important is to consider similar chemical results from the evaporation-crystallization process originally proposed by Gibbs and interactions of ground water experiencing dissolution processes along hydrogeologic flow paths. This results in an even more complex region and further complicates management policy in a region experiencing climate change and increasing land use.

2.4.1 General Water Chemistry Types

Analysis of surface water chemistry and its influence from the underlying geology showed three types of waters were present (Figures 2.5 and 2.6). Water types characterized by high proportions of sodium and chloride were not associated with a single geologic unit. These waters were located above a number of different bedrock types and corresponded directly with the ascending limb of the Gibbs model. These findings also correspond with the spatial locations of some of the saline springs and brackish waters identified by Grasby and Betcher (2002) and will be discussed in detail in a following section. The mixing of local, intermediate and deep basin scale flow systems likely influence these waters and not a specific geologic unit.

The second major type of water was characterized by relatively higher proportions of sulphate and corresponds to a single geologic unit (Figures 2.5 and 2.6). These ponds were typically overlying upper Cretaceous bentonitic shales. High-sulphate waters usually reflect the presence of old marine sediments (Wetzel, 1983). Calcium sulphate is to be considered in such instances, although sodium-sulphate deposits can be of oceanic origin also. In addition, oxidation of gypsum and sedimentary pyrite is also a major source of sulphate and is commonly associated with shales (Cole, 1994).

Waters dominated by calcium, magnesium and bicarbonate characterized the third and final type of water, and fall within the geologically dominated portion of the Gibbs model. Geologically different catchments differ in both the release rate of elements to streams and lakes and the relative proportions that are released. However, for the major ions, the relative proportions do not differ greatly in well-watered portions of the temperate, arctic, and subtropical zones (Kalff, 2002). Calcium and bicarbonate generally dominate inland lakes and rivers of these areas, and such is the case for the majority of the ponds sampled within the study area. This type of water was found in geologic settings that ranged from Precambrian granites, Cretaceous shales, and Devonian and Silurian limestones and dolomites. Therefore, these characteristically distinct surface waters could not be associated to a single geologic unit.

2.4.2 The Gibbs Model

When ponds were applied to the Gibbs model there were no distinguishable clusters related to geology, with the exception of ponds overlying granitic bedrock (Figures 2.7 and 2.8). These were typically ponds with measures of low salinity and proportionately low chloride and varying proportions of sodium within the waters. These results coincide with others as granite is not easily weathered which results in low measures of TDS and the low proportions of chloride resembling inland meteoric waters (Krawchuck, 1998). In general waters associated with common rock types such as shale have high total ion contents with dominant ions of calcium, magnesium, sodium, and bicarbonate, and waters associated with limestone and dolomites are generally dominated by calcium, magnesium, and bicarbonate (Kalff, 2002). In comparison to results presented by Moser et al. (1998), with respect to sodium and measures of TDS, only the ponds overlying the granite bedrock showed similar proportions and concentrations (Figures 2.7 and 2.8). However, since there was large overlap of where limestone and shale ponds were found within the rock dominance portion of the model; relief and local climate may play a larger role. With respect to major anions sampled, the Gibbs model does not address sulphate concentrations, which prove to be a major anion in determining the geologic source of waters according to the results presented (Figures 2.5 and 2.6).

As mentioned previously, there were a number of ponds sampled that fell outside the Gibbs model (Figures 2.7 and 2.8). These consisted of three distinct groups and include dilute ponds with relatively low proportions of sodium, ponds with moderate salinity waters associated with low proportions of chloride and ponds with moderate to high salinities and relatively higher proportions of sodium and chloride in surface waters.

The dilute ponds with relatively low proportions of chloride were located high in the landscape overlying moderate to highly calcareous glacial deposits of the Pasquia and Porcupine Hills. These hydraulically mounded lakes that receive virtually all of their water from direct precipitation (Winter, 2001). This may result in the relatively low measures of TDS as landscape position can dictate the relative importance of the different pathways of water and solute flow (Webster et al. 1996). The relatively higher concentrations of calcium relative to sodium were likely the result of short flowpaths through calcareous till, and appear to be moving towards the inland precipitation ionic signature identified by Krawchuck (1998). These ponds were also generally small in size and may agree with findings of Eilers (1992) in that smaller lakes are more influenced by local geologic setting and flowpath. The source of the precipitation in the Gibbs (1970) model cannot be applied universally as it assumes that all precipitation is dominated by oceanic waters with high proportions of sodium and chloride ions. The continental precipitation of the continental WBF is characteristically a calcium-bicarbonate type water or a calcium-sulphate type water for the study area.

The second group of ponds, moderately saline waters associated with low proportions of chloride was located at the fore slopes of either the Duck Mountains or the Porcupine Hills. These ponds displayed conditions typical of surface waters associated with local to intermediate flow systems as defined by Tóth (1999). As these till deposits are relatively young, local flow systems are typically bicarbonate rich and have not evolved into sulphate and chloride rich waters that are indicative of longer flow systems (Chebotarev 1955). However these low chloride high TDS waters were also associated with relatively higher measures of sulphate and sodium, which agree with the hypothesis of intermediate flowpaths influencing these waters. This suggests an alternative control of surface water through mixing with intermediate groundwater flow. This may be expected or typical in complex geology such as the Canadian Sedimentary Basin.

The third group of ponds, ponds with moderate to high salinities and relatively higher proportions of sodium and chloride were associated with the outcrop belt of the carbonate aquifer, a regionally low topographic position, and near the outlet of the Saskatchewan River as it enters Cedar Lake. These ponds are associated with the outcrop belt and a hydrostratigraphic cross-section of southern Manitoba is shown on Figure 2.19. The displacement of the ponds with respect to the major cations and anions and their associated measures of TDS show that surface waters of the third group should be influenced by the evaporative-crystallization process according to the mechanisms defined by Gibbs (Figures 2.7 and 2.8). However, the study area experiences a continental climate and in general, GE does not greatly exceed P within the study area, therefore the implication that the evaporation-crystalization process is controlling surface waters is not likely (Table 2.1). Furthermore, the ponds located at the higher latitudes within the study area experience less of a water deficit in relation to the ponds of the southern portion of the study area and result in more potential to produce overland flow. The majority of the ponds located within the rising limb of the model (evaporative-crystallization mechanism) were typically in the northern half of the study area. Thus, the deficit is not large as in other "salt" lake systems (Gibbs, 1970). Contrary to Gibb's (1970) assumptions, it does not appear that these waters are experiencing large evaporative influences, which lead to waters with larger proportions of chloride and sodium.

Stable isotope results confirm that the high TDS measures and ascending limb of the Gibbs model were similar to most of the other ponds sampled, and were not the result of any large evaporative influence. Ponds that deviate from the

MWL are undergoing larger evaporative influence as opposed to ponds that plot on or near the MWL (Krabbenhoft et al.,1994). These results suggest that high measures of TDS and composition may originate from groundwater sources, rather than climate. The stable isotope results of the saline waters sampled within the study area are distinctly different from the stable isotope results typical of formation brines west of Manitoba presented by Rostron et al. (1998). Deep formation brines have undergone geothermal heating within the formation, which results in a distinctly different isotopic signature. As these high TDS surface waters within the study area share similar isotopic signatures to the freshwaters of the study area, it has been suggested that these saline springs originated as meteoric water (Grasby and Betcher, 2002) (Figure 2.14). There are two competing hypothesis presented to explain this phenomenon. Hitchon (1969) interpreted this phenomenon as a mixing of a local influx of groundwater with basin scale flows. Secondly, basin scale flows of meteoric waters from recharge sites in South Dakota which discharge into Manitoba has also been suggested (Bachu and Hitchon, 1996).

Given the meteoric origin of these surface waters, the high TDS content of the more saline surface waters also suggests the influence of the dissolution of evaporite beds, and not an evaporative influence. There was a strong linear correlation of Na/Cl (R^2=0.98) for the brackish to saline ponds of the study area, which is consistent with the dissolution of halite (Grasby and Betcher, 2002) (Figure 2.15). The Na/Cl slopes of both the freshwaters and brackish/saline ponds also present a distinctly different source of waters throughout the study area.

This study indicates that caution should be used when applying Gibb's conceptual model to continental regions with heterogeneous geology and complex local to regional groundwater flow interactions. Therefore, it may be presented that the increased proportion of sodium and chloride in ponds graphed on the ascending limb of the Gibbs model does not represent the evaporation-crystallization mechanism in a continental climate, but is likely a complex relationship involving the residence time of subsurface waters and the degree of mixing with shallow groundwaters and local surface flows. Similarly the descending limb should perhaps represent waters typical of continental precipitation (dilute water with proportionately low concentrations of sodium), which are dominated by calcium-bicarbonate, rather than sodium-chloride waters typical of coastal areas. This suggests that a modified envelope is required for continental waters in comparison to the envelope originally presented by Gibbs (1970).

2.4.3 Water Chemistry within the Saskatchewan River Delta

Understanding of local to regional connectivity of ponds and wetlands within the SRD is critical to fully assess and manage the integrity of wetland and river ecosystems. The majority of the ponds that did not conform to the Gibbs model were ponds with higher proportions of sodium and chloride associated with moderate measures of TDS, and was generally associated with the SRD. A number of the ponds were located near the outlet of the Saskatchewan River as it enters Cedar Lake (Figures 2.9 to 2.12). The majority of these ponds follows a major topographic low of the province and is located along a hydraulic divide between the intermediate-scale freshwater flow system from the east and the regional flow of saline waters from the Williston Basin as defined by Grasby and Betcher (2002). The majority of these ponds were also located within alluvial sediments or organics likely overlying coarse-grained sediments. These conditions are ideal for mixing of local up to, and including basin scale flow systems. Therefore, these waters may also be the result of different proportions of mixing between deep subsurface waters, shallow groundwater and local surface flows.

2.4.3.1 Surficial Geology

Within the SRD, surficial geology determines the type of surface and groundwater connection to the ponds. A portion of the ponds in the lower delta are driven by meteoric waters while the upper delta and ponds near the outlet into Cedar lake are influenced by a mixture of regional groundwater and seasonal flooding by the Saskatchewan River. In general, within the SRD there were two types of waters, a sodium-chloride type and calcium-bicarbonate type of water

(Figures 2.9 and 2.12). Findings by Bell et al. (2003) showed that measures of conductivity and the chemical characteristics of the Mackenzie River Delta did not vary to any large degree across two transects of the delta, suggesting that the majority of the pond-wetland complexes were connected either by surface water channels or by subsurface connections via alluvial sediments. Unlike the Mackenzie River Delta, the SRD displayed large variability and heterogeneity with respect to concentrations of TDS and chemical composition of surface waters. The higher TDS, sodium-chloride waters were typically all located within the alluvial sediments, and organics likely overlying coarse-grained porous material in both the upper and lower delta (Figures 2.9 and 2.12). As mentioned previously, these conditions are ideal for mixing of local up to, and including basin scale flow systems. The calcium-bicarbonate waters were all located on the glacial till within the Lower Delta, and further inspection of the surface water drainage network shows that these ponds may not even drain into the Saskatchewan River. This suggests that from a water chemistry and flowpath perspective, perhaps the boundary used to delineate the SRD should be reconsidered or revised. Specifically, the boundary of the northeast portion of the SRD could be limited to the alluvial sediments and ponds contributing waters to the Saskatchewan River that drain into Cedar Lake. With respect to water chemistry, this suggests that there should be separate management regions defined with different conceptual models based on different water sources.

2.4.3.2 Water Chemistry in Relation to the Main Channel

It was hypothesized that the distance between a pond and a main river channel would increase measures of TDS and both the proportion of sodium and chloride as a result of evapoconcentration. However, results from the SRD showed that TDS and the proportion of sodium and chloride were slightly reduced with increased distance between ponds and a main river channel (Figure 2.17). The ponds sampled that were the furthest from a main river channel were generally located in surficial geologic settings of glacial till and resulted in dilute ponds. This indicates the till unit promotes isolation and local meteoric inputs.

Connection to a main river channel had a larger influence on water chemistry than distance to a main channel. In general, ponds not connected to a river channel were more saline with higher proportions of sodium and chloride (Table 2.5, Figure 2.18). These ponds were typically surrounded by large wetlands and overlayed alluvial sediments, and support the hypothesis that these shallow ponds are maintained by larger regional groundwater flowpaths mixing with local meteoric waters, not seasonal flooding of the SRD annually. Further, these ponds are likely in a regional scale discharge area, which will result in systematic changes in the water's ionic facies, from bicarbonate through sulphate and then to chloride, along local to intermediate and regional flow systems (Tóth, 1999). Ponds overlying alluvial sediments and connected to a main river channel were typically less saline and had relatively lower proportions of sodium and chloride (Table 2.5, Figure 2.18). These waters are likely a mixing of regional flowpaths with river water, as chemistries were driven towards water chemistry of the Saskatchewan River. Therefore, the degree of mixing between regional flowpaths, local meteoric flows, and river water determines the resultant chemistry of these shallow ponds. With respect to the upper delta, the majority of the ponds located south of the Saskatchewan River appeared to be influenced by regional groundwater flowpaths to some degree, while ponds north of the Saskatchewan River were influenced by more local meteoric events. Ponds located within the glacial till settings are likely the result of more local flowpaths and local geology as waters were generally more dilute and dominated by calcium, magnesium and bicarbonate.

2.4.3.3 Lake Order

It was hypothesized that higher order lakes are typically located lower in the landscape and tend to be in closer contact with aquifers, while lakes located higher in the landscape tend to be precipitation-dominated lakes that recharge aquifers (Cheng and Anderson, 1994). As this method is based on connections between a lake and the surface drainage network, lake order as it relates to the SRD was not a good predictor of lake water chemistry (Figure 2.18). These results further support the hypothesis that these waters within the SRD are the result of regional groundwater flowpaths as the model based on the surface water drainage network is a poor predictor of water chemistry within the study area. However, with an increase of lake order there was a trend of the reduction of the variance with measures of TDS. This may imply that longer surface flows may act as a buffering system, similar to a connection to a main river channel, and drive water chemistries to a more meteoric signature.

2.5 Conclusion

Within a mid-continental climate and transitional region with heterogeneity of geology, a wide variety of water types were observed, literally expanding the empirical range presented initially by Gibbs (1970), all in one relatively small area. The Gibbs model was first used to identify the major processes driving chemistry of major lakes and rivers of the world, however when applied to relatively smaller ponds of the study area, approximately 15% of the ponds fell outside of the predetermined envelope (Gibbs, 1970). Thus, the characterization of the dominant processes influencing the chemistry of these surface waters may be inappropriate for the continental region of central Canada. This leads to important management implications when trying to specify management units, and especially when extrapolating results of BMP from other areas, perhaps with much less heterogeneity.

The majority of the variability in water chemistry appears, at a regional level, to be explained by variation in geologic processes as hypothesized by Gibbs (1970). However, there are types of waters not explained by these models, indicating other processes need to be considered. Some of the deviations from the original global model can be explained by continental scale differences in precipitation chemistry, but also complex groundwater interactions in geologic diverse regions will need to be considered.

Findings from this study show that in a continental climate with potential for complex groundwater interactions, surface waters with relatively high proportions of sodium and chloride and high measures of TDS are not the result of the evaporation-crystallization process, but the result of either regional or deep basin scale discharge of groundwater mixing with local meteoric waters (Chebotarev, 1955, Toth, 1999). Both the ascending and descending limb, as described by Gibbs are the result of climate influencing the likelihood to produce overland flow. The ascending limb of the model, as it relates to the mid-continental waters more accurately represents a complex relationship involving the residence time of subsurface waters and the degree of mixing with regional groundwater, shallow groundwater and local surface flows. In the boreal climate of Saskatchewan and Manitoba the descending limb may be more accurately delineated if it were to conform to a mid-continental chemical signature of precipitation, being dominated by a dilute calcium and sulphate type of water as opposed to dilute sodium-chloride type of water originally presented by Gibbs. Other ponds that did not fall within the empirical model were dilute ponds with low proportions of sodium, likely influenced by local geology and short flowpaths; and moderately saline waters with proportionately low concentrations of chloride, likely influenced by local to intermediate scale discharge.

Understanding of local to regional connectivity of ponds and wetlands within the SRD is critical to fully assess and manage the integrity of wetland and river ecosystems.

The SRD is geologically considered a flood plain, alluvial silts deposited throughout by retreating glacial meltwater together with periodic flooding of the Saskatchewan River have left behind a fertile landscape that attracts a variety of waterfowl and wildlife (DUC, 2006). In addition to these ecologically distinct characteristics, most of the SRD differs in relation to water chemistry with respect to the surrounding landscape. A combination of low topographic position, located within geological interfaces between sandstones and dolomites associated with large deep basin-scale discharge areas and alluvial sediments has led to proportionately different solute characteristics of surface waters. With respect to a water chemistry perspective and potentially a water quantity perspective, the existing boundary of the lower delta could be revised to reflect the surficial geology of the area. High TDS and proportionately dominant sodium and chloride waters indicate that the application of management strategies to either control water quality or quantity would be at a regional to Williston Basin scale in comparison to the remaining landscape of the study area. Also, the implication that pond permanence and water quantity of the SRD may not be greatly dependent on local precipitation and annual flooding is also relevant to management practices. However, water quality within the SRD is dependent on local precipitation and seasonal flooding. Without seasonal flooding or dilution, some of the ponds associated with the SRD may be driven to more saline conditions which will alter vegetation and thus habitat for waterfowl. This results in a very complex region and further complicates management policy in a region experiencing widespread landuse and climate change.

Table 2.1. Canadian Climate Normals from 1971-2000 for key communities (see Figure 2.2) (Environment Canada, 2001). GE taken from Agriculture and Agri-Food Canada (1994). P=precipitation, GE=gross evaporation, P-GE = precipitation - gross evaporation.

Key Communities	**Lat.**	**Long.**	**January Daily Ave. (°C)**	**July Daily Ave. (°C)**	**Year Daily Ave. (°C)**	**Total P (mm)**	**GE* (mm)**	**P-GE (mm)**
Norway House (Man.)	53°57'N	97°51'W	-22.4	17.6	1.4	523	444	79
The Pas (Man.)	53°58'N	101°06'W	-20.6	17.7	0.1	442	487	-47
Hudson Bay (Sask.)	52°47'N	102°25'W	-18.5	17.4	1.3	413	~650	-237
Swan River (Man.)	52°03'N	101°13'W	-18.2	18.1	1.6	530	~650	-120

* - GE calculated using the empirical Meyer formula
~ - interpolated between gross evaporation contour lines

Table 2.2. Distribution of 210 ponds sampled and stratified by formation name and general rock type within the study area (Lauhn-Jensen, 1987, Fung, 1999, Grasby & Betcher 2002). Spatial distribution of bedrock types can be found in Figure 2.3.

General Rock Type	Unit Code and Time of Deposition	Formation Name	Rock Type
Dolomite, Limestone (N=66)	(lS) lower Silurian (N=62)	(SCL) Cedar Lake	Micrimitic, fossiliferous stromatolitic and bistromal dolomite and sandy argillaceous marker beds
	(uO) upper Ordovician (N=4)	(Osw) Stonewall	Dolomite, fine grained, sparsely fossiliferous
Shale, Dolomite, Limestone (N=23)	(mD) middle Devonian (N=17)	(DDB) Dawson Bay	Basal red shale, Bitumous dolomite and high calcium micrimitic limestone
	(uD) upper Devonian (N=6)	(DSR) Souris River	Basal red shale, Bitumous dolomite and high calcium micrimitic limestone
Shale (N=88)	(2uK) upper Cretaceous (N=80)	(KRM) Riding Mountain	Soft greenish bentonitic shale
	(1uK) upper Cretaceous (N=8)	(KFV) Favel (KVR) Vermillion River	Calcareous speckled shale, minor limestone, bentonitic and oil shale. Black carbonaceous shale
Sandstone (N=15)	(lK) lower Cretaceous (N=15)	(KSR) Swan River	Quartzose sandstone, in places glauconitoc shale and minor lignite
Intrusive Granite (N=18)	(WT) Neo Archean (N=18)	Neo Archean	Tonalite, mafic intrusive rocks

Table 2.3. Distribution of 210 ponds sampled within general rock type and surficial geologic units within the study area.

General Rock Type	Surficial Geology	# of Basins Sampled
Dolomite/Limestone N=66	Exposed Bedrock	10
	Coarse-grained Lacustrine	37
	Glacial Till	19
Shale/Dolomite N=23	Coarse-grained Lacustrine	6
	Glacial Till	9
	Fine-grained Lacustrine	8
Shale N=88	Coarse-grained Lacustrine	22
	Glacial Till	57
	Fine-grained Lacustrine	9
Sandstone N==15	Coarse-grained Lacustrine	12
	Fine-grained Lacustrine	3
Granite N=18	Coarse-grained Lacustrine	7
	Fine-grained Lacustrine	11

Table 2.4. Pearson Correlations of Nonmetric Multidimensional Scaling Ordination Axes. N=210.

Parameter Sampled (mg/L)	Axis 1	Axis 2
Chloride	0.933	-0.029
Sulphate	0.000	-0.857
Bicarbonate	-0.832	0.420
Carbonate	0.048	0.009
Sodium	0.930	-0.088
Potassium	0.042	-0.028
Calcium	-0.467	0.007
Magnesium	-0.158	0.068
Total Dissolved Solids	-0.028	0.054

Table 2.5. Mean, median, and range of TDS, and the proportion of Na and Cl relative to major ions sampled for ponds connected to a main river channel, ponds not connected to a main channel, and ponds/lakes within a till veneer setting.

Connection to River	**Mean/Median/ Min/Max**	**TDS (mg/L)**	**Na % of Total Cations Sampled**	**Cl % of Total Anions Sampled**
Not Connected n=26	Mean	743.4	41.1	54.8
	Median	389.3	40.3	53.7
	Min	192.3	9.1	2.1
	Max	3725.1	78.1	97.6
Connected n=9	Mean	250	29.9	24.7
	Median	261.7	32.2	19.0
	Min	72.8	5.9	0.7
	Max	399.1	40.1	49.3
Till veneer n=13	Mean	298.5	19.2	14.6
	Median	294.0	15.0	6.0
	Min	128.8	2.8	0.3
	Max	435.7	41.3	54.4

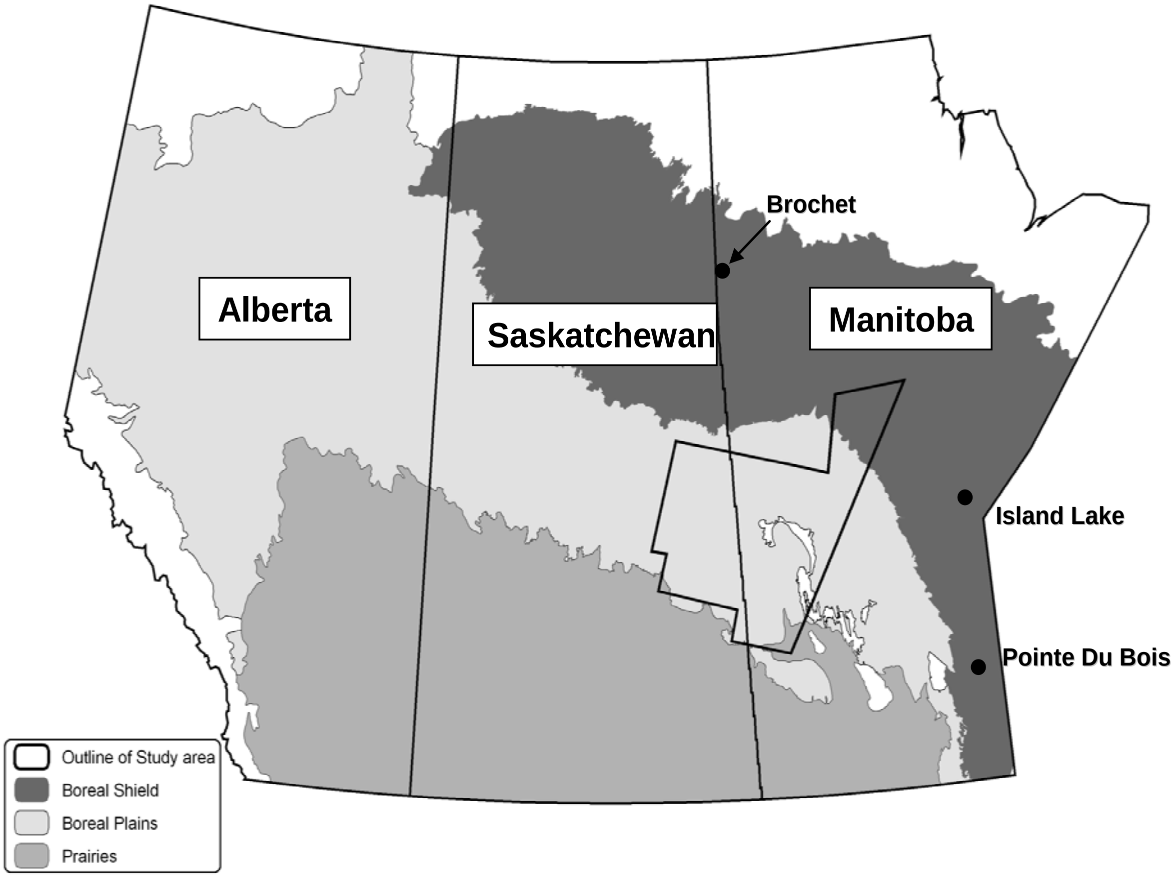

Figure 2.1. Location of the study area within the Boreal Plains and Boreal Shield. Canadian Ecozone boundaries represented by contrasting colors. The locations of precipitation chemistry used on Figures 2.6, 2.7 and 2.8 are also included.

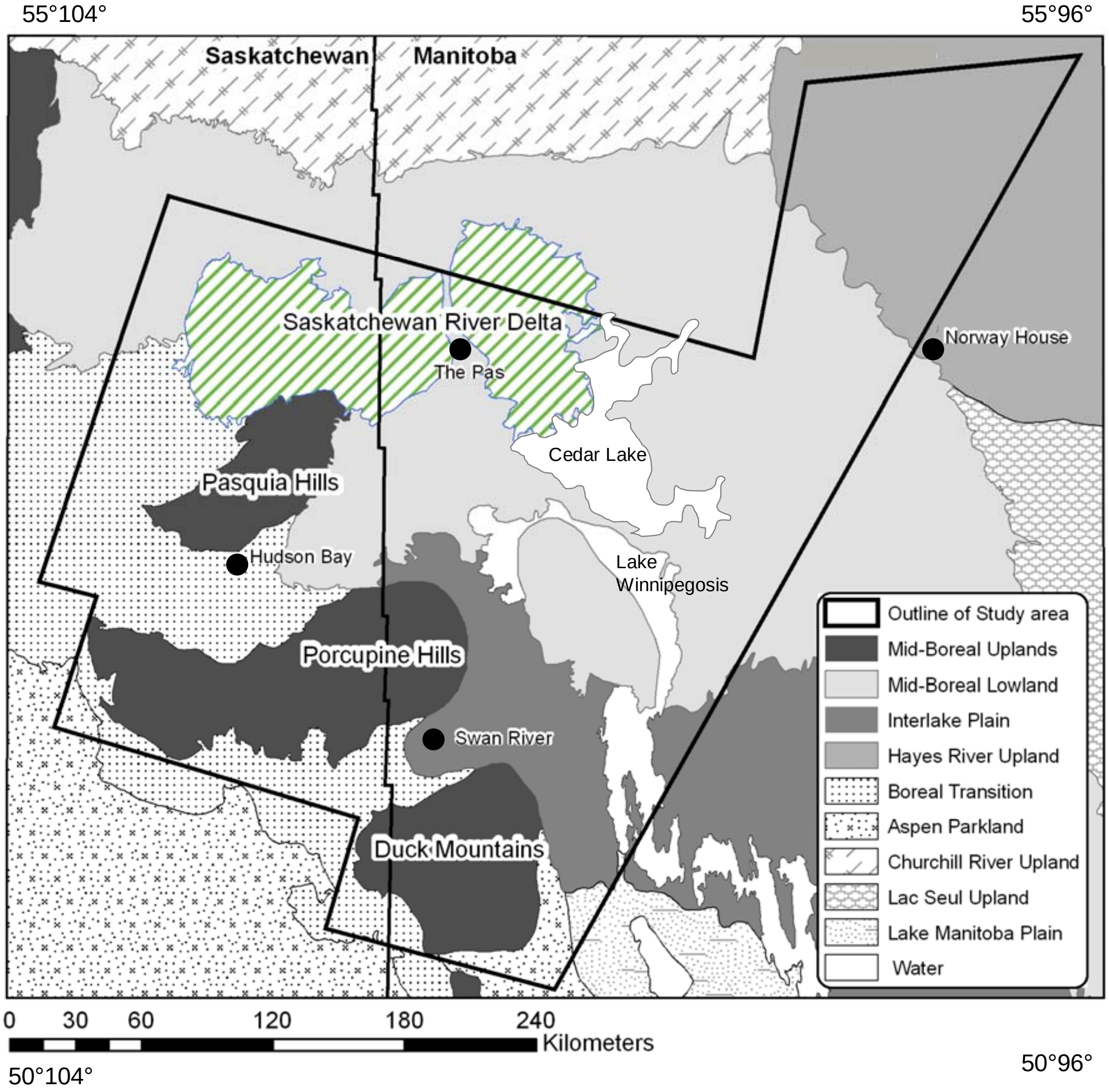

Figure 2.2. Spatial location of all ecoregions and key communities of the study area. Climate details in Table 2.1. Areas of ecological interest are also marked on the figure (Saskatchewan River Delta, Pasquia Hills, Porcupine Hills, Duck Mountains).

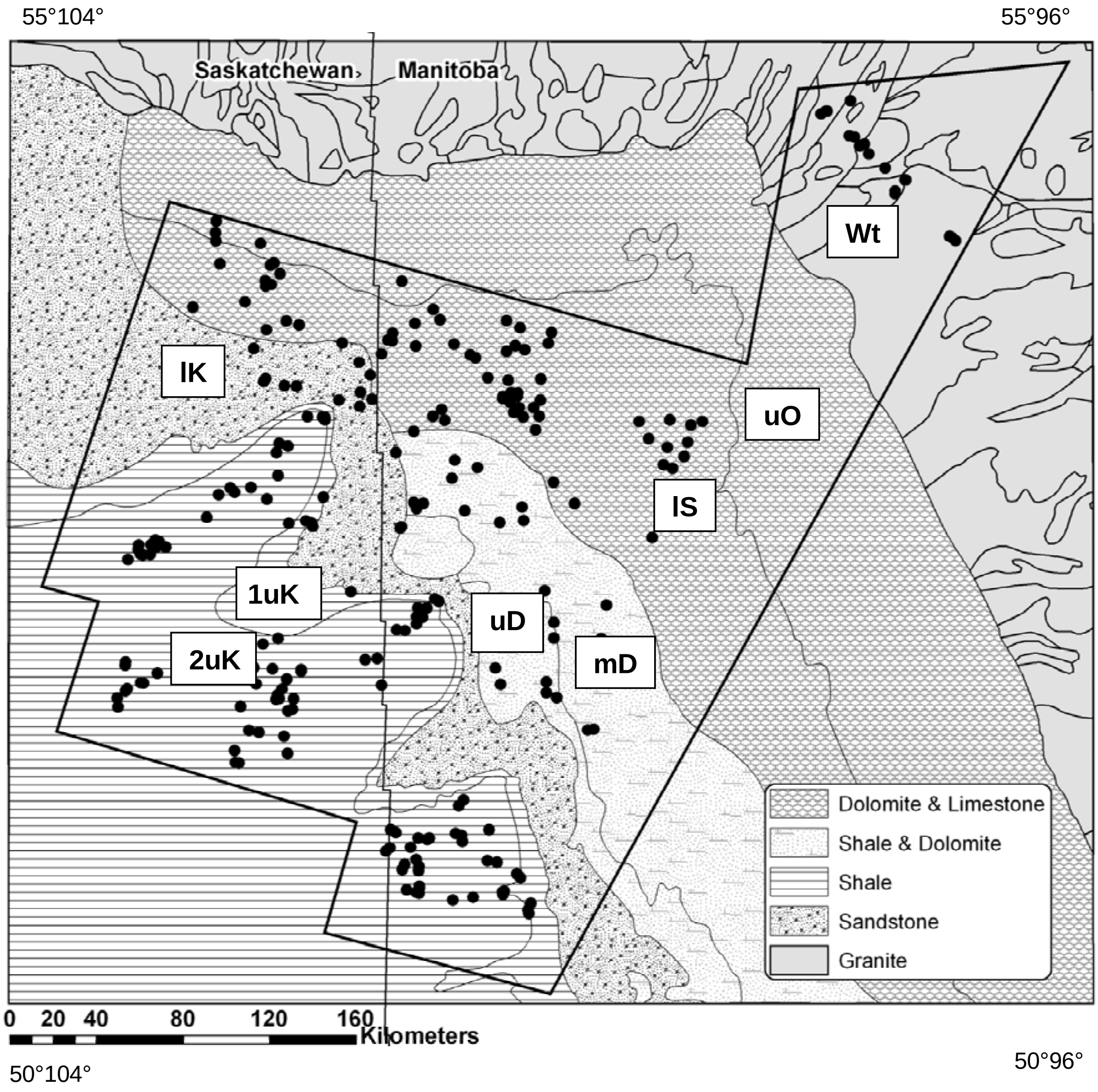

Figure 2.3. Near surface bedrock geology of the study area. Stratification of major geologic units is by major rock types. Bedrock unit codes (2uk, 1uk, lK, mD, uD, lS, and uO) and associated formation names and mineralogy are summarized in Table 2.2. Black dots represent location of ponds sampled. Map revised from Wheeler et al. (1997).

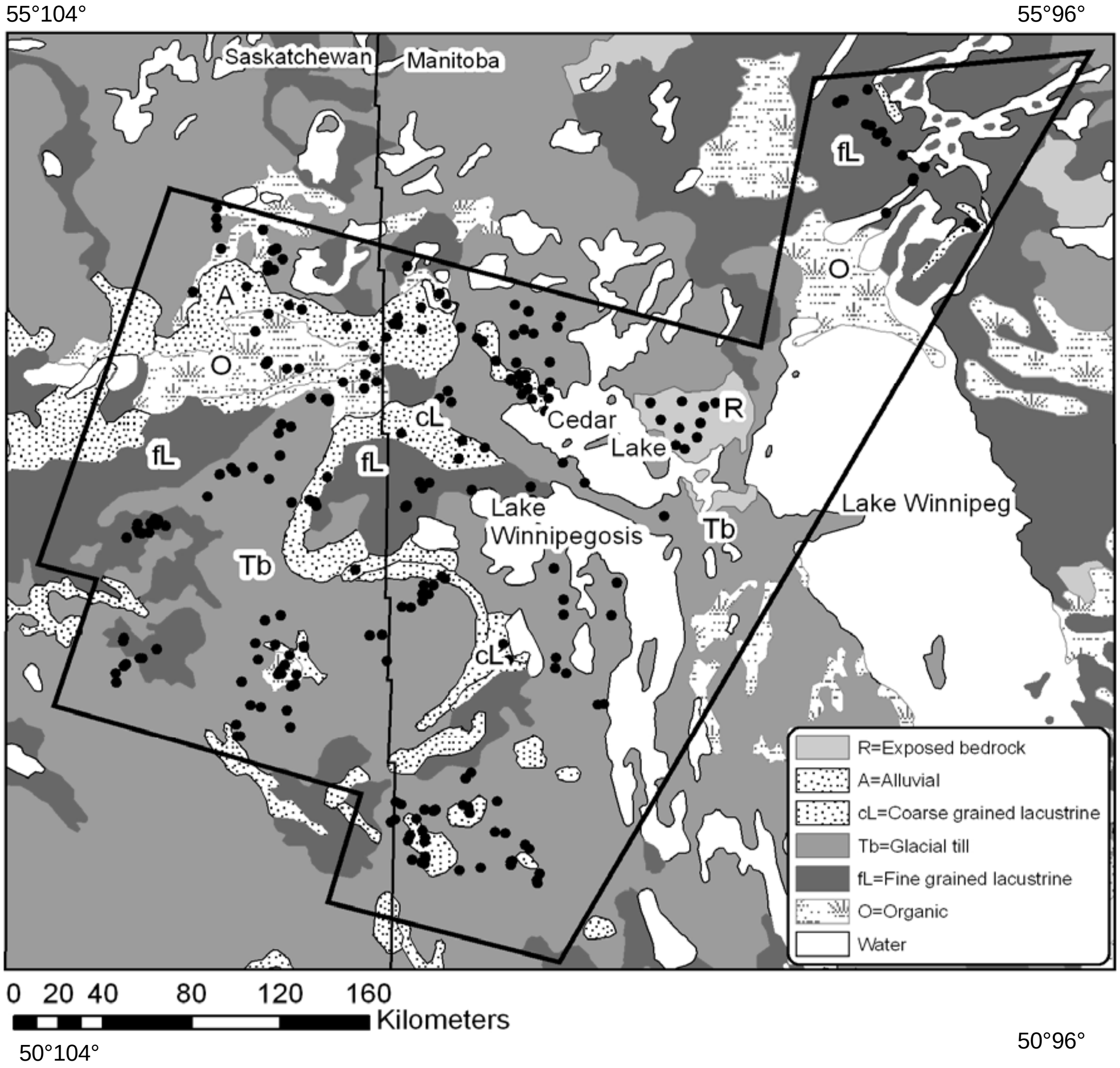

Figure 2.4. Quaternary geology of the study area. Black dots represent the spatial distribution of ponds sampled. Map revised from Fulton (1995).

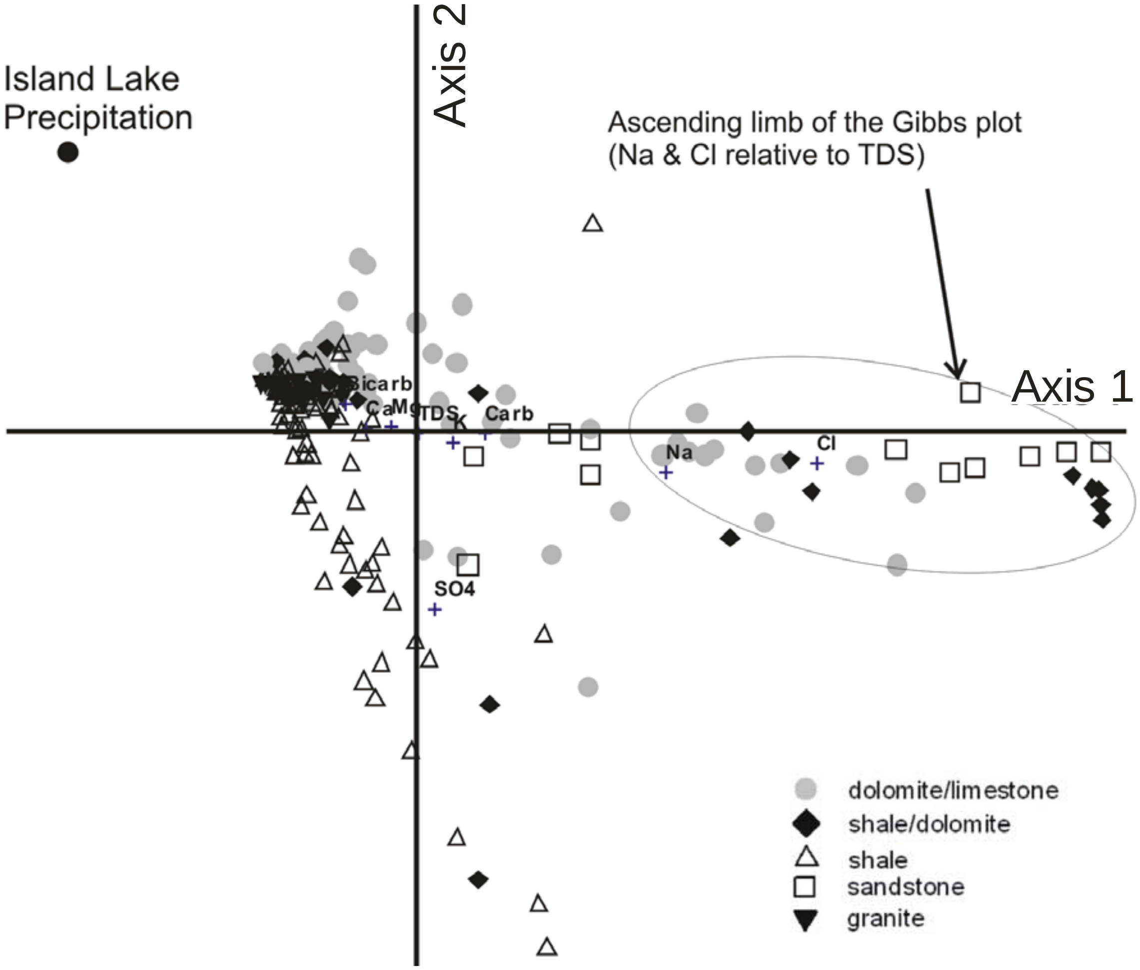

Figure 2.5. Ordination of major ion chemistry for 210 ponds within the study area. Ponds are stratified by underlying bedrock geology. Precipitation chemistry is from Island Lake, Manitoba located approximately 400 km east of The Pas, Manitoba (Krawchuck, 1998).

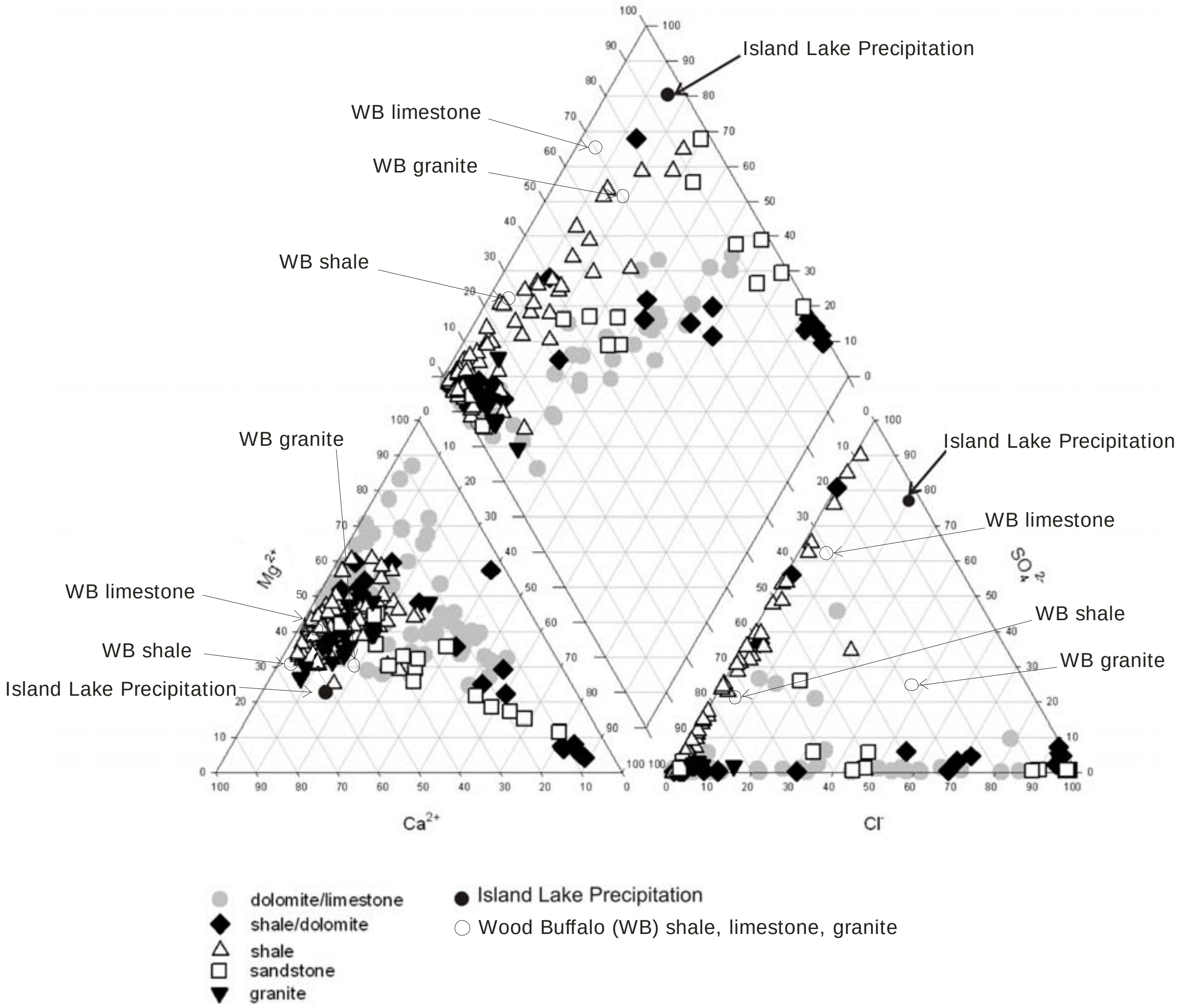

Figure 2.6. Piper plot of surface water chemistry within the study area. Ionic characteristics are further stratified by bedrock geology. Ionic composition of precipitation from Island Lake was similar to Brochet and Pointe Du Bois. Additional average surface water compositions relative to geology from Wood Buffalo, Alberta are reported from Moser et al. (1998).Classification diagram for cation and anion facies is included on Figure A.1 in Appendix A.

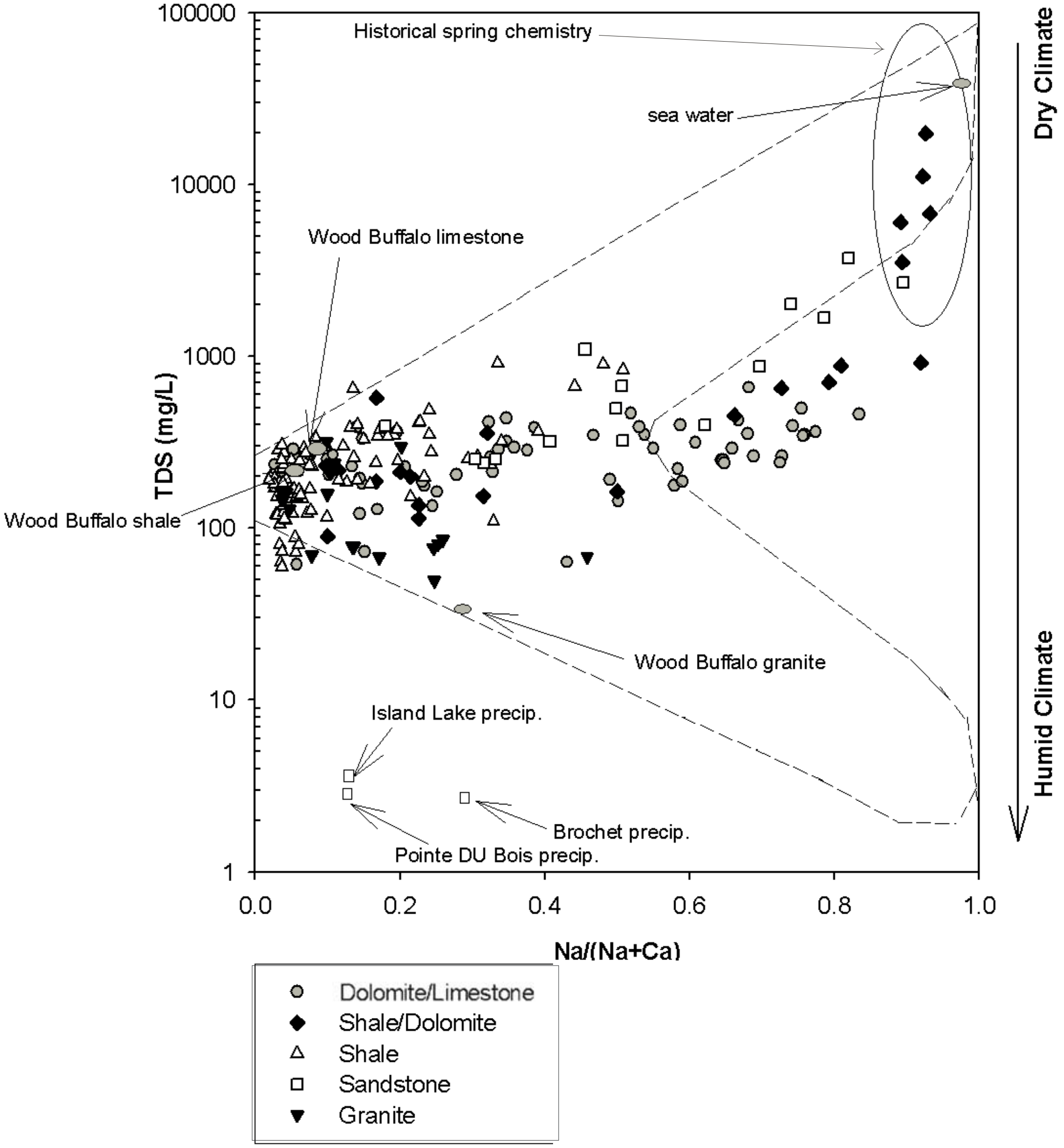

Figure 2.7. Variation of the weight ratio Na/(Na + Ca) as a function of TDS of ponds, and then stratified by major bedrock geological units of the study area. Dashed line represents empirical boundary of world waters as delineated by Gibbs (1970). Average compositions relative to TDS of surface water samples relative to geology from Wood Buffalo, Alberta are reported from Moser et al. (1998). Precipitation chemistry reported from Krawchuk (1998), Island Lake (53°51'N 94°44'W), Brochet (57°54'N 101° 33'W), and Pointe Du Bois (50°18'N, 95°35'W). Ellipse displays the approximate range of Na/(Na+Ca) as a function of the total dissolved salts of brackish to saline springs West of Lake Winnepegosis (Grasby and Betcher, 2002).

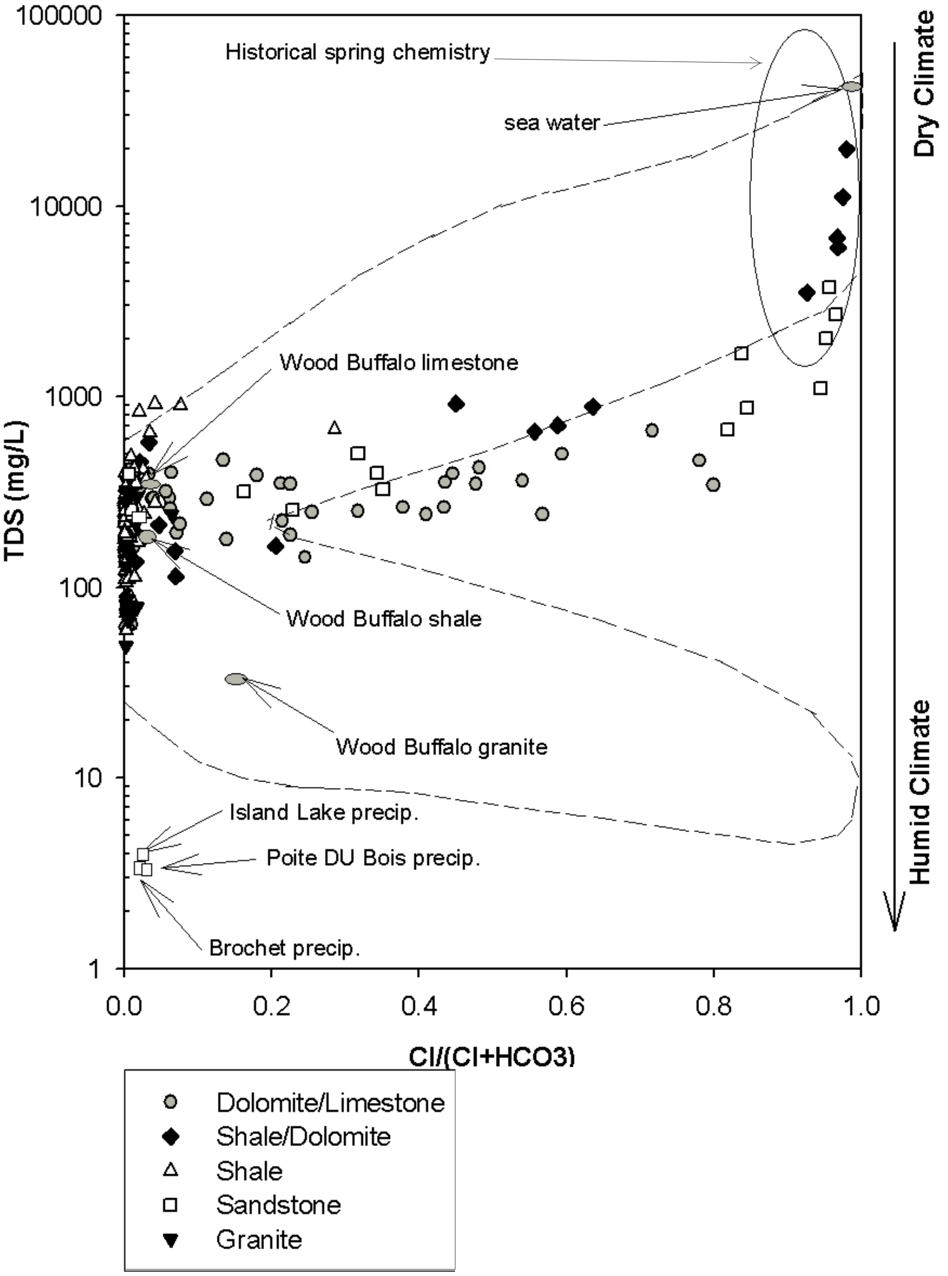

Figure 2.8. Variation of the weight ratio Cl/(Cl + HCO_3) as a function of TDS of ponds, then stratified by major bedrock units of the study area. Dashed line represents empirical boundary of world waters as delineated by Gibbs (1970). Average compositions relative to TDS of surface water samples relative to geology from Wood Buffalo, Alberta are reported from Moser et al. (1998). Precipitation chemistry reported from Krawchuk (1998), Island Lake (53°51'N 94°44'W), Brochet (57°54'N 101° 33'W), and Pointe Du Bois (50°18'N, 95°35'W). Ellipse displays the approximate range of Na/(Na+Ca) as a function of the total dissolved salts of brackish to saline springs West of Lake Winnepegosis (Grasby and Betcher, 2002).

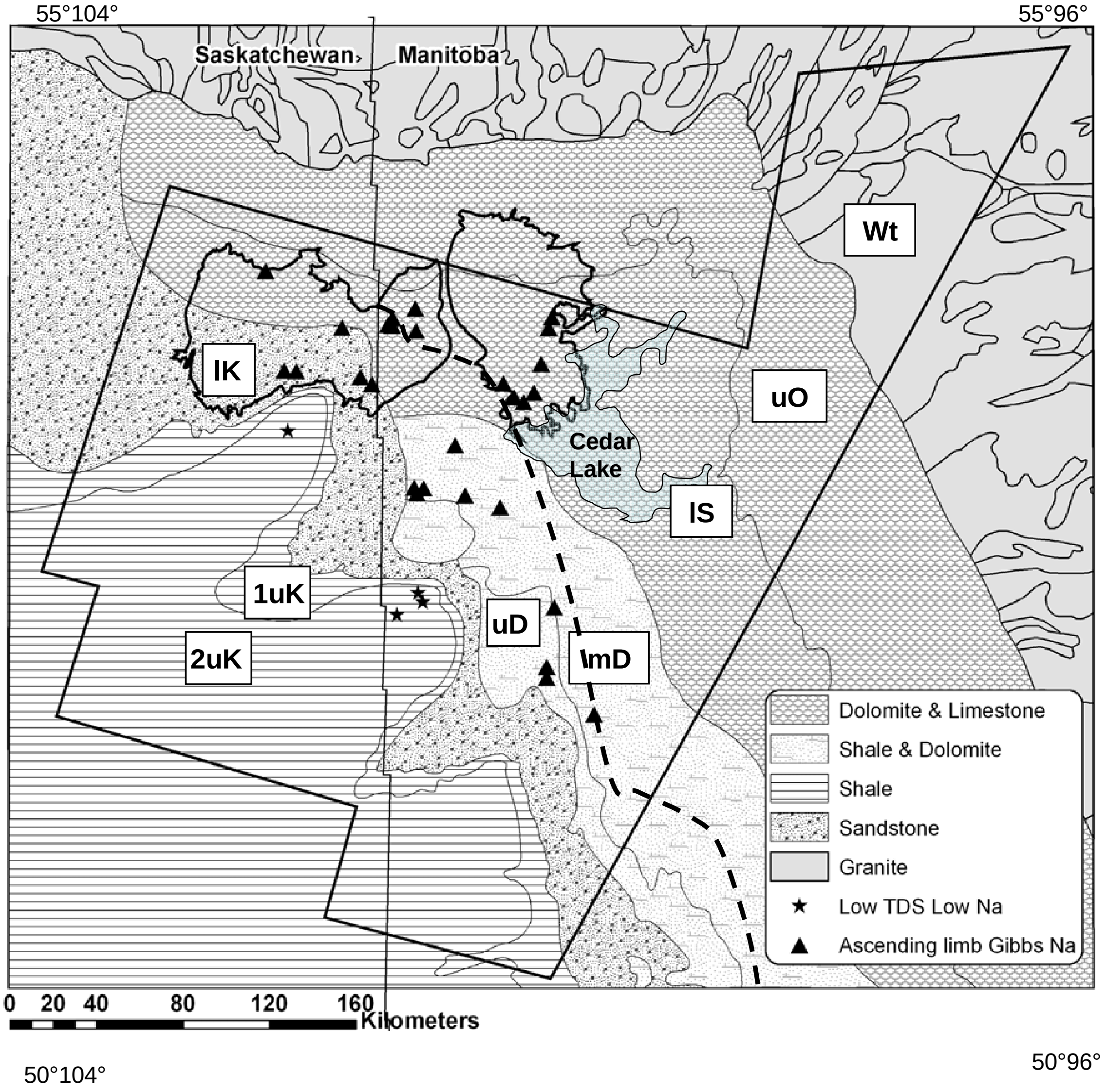

Figure 2.9. Spatial variation of pond TDS measurements relative to the ratio of Na/(Na + Ca) concentrations and stratified by bedrock geology. Includes location of waters that conform to the Gibbs model (ascending limb of Gibbs model) and waters that do not fall within the Gibbs model (dilute upland lakes). Dashed line is approximate location of the outcrop belt of the carbonate aquifer (Grasby and Betcher, 2002). Outline of SRD in northwest corner. Map revised from Wheeler et al. (1997).

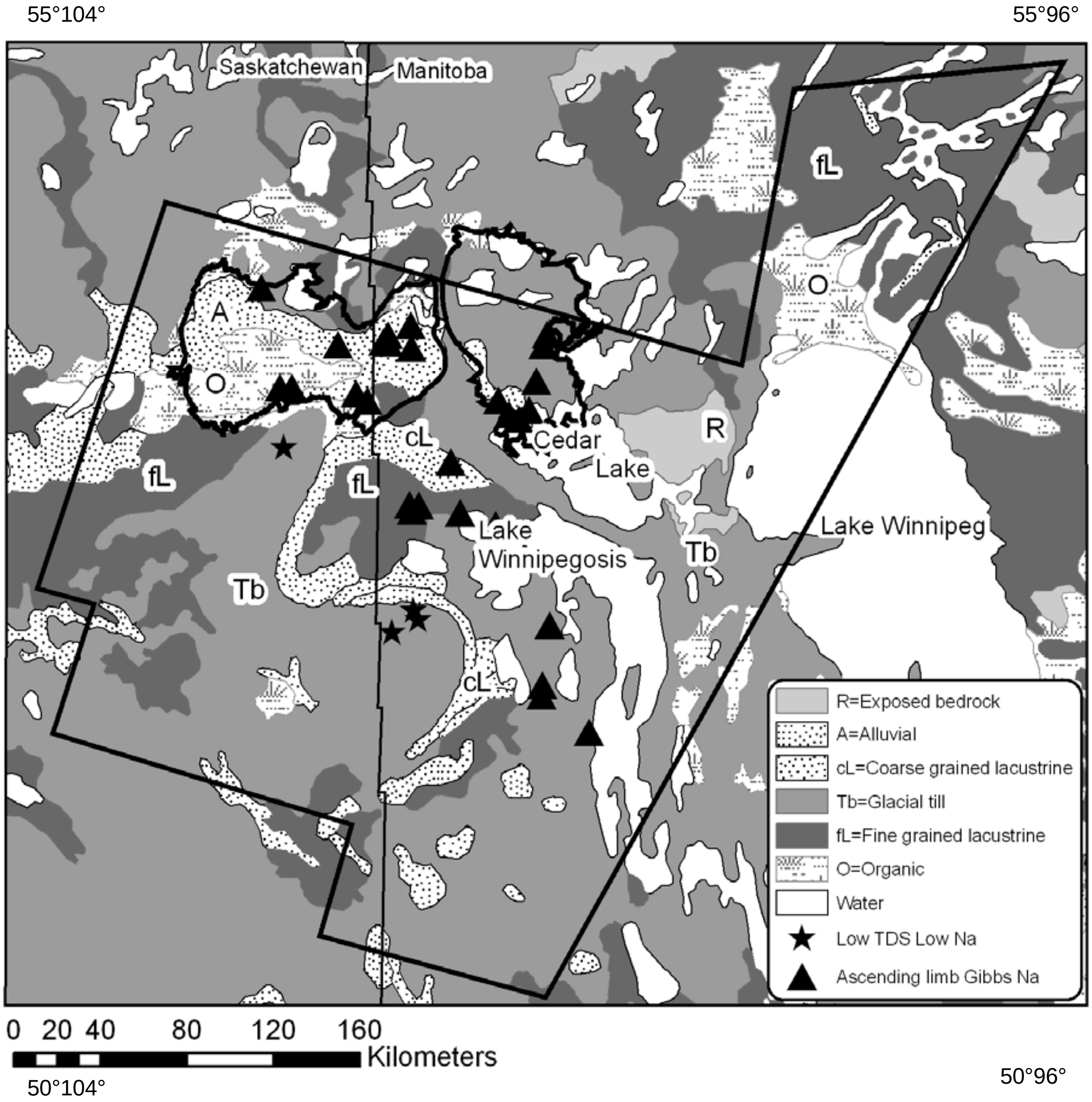

Figure 2.10. Spatial variation of pond TDS measurements relative to the ratio of Na/(Na + Ca) concentrations. Includes location of waters that conform to the Gibbs model (ascending limb of Gibbs model) and waters that do not fall within the Gibbs model (dilute upland lakes). The figure is further stratified by surficial geology. Outline of SRD in northwest corner. Map revised from Fulton (1995).

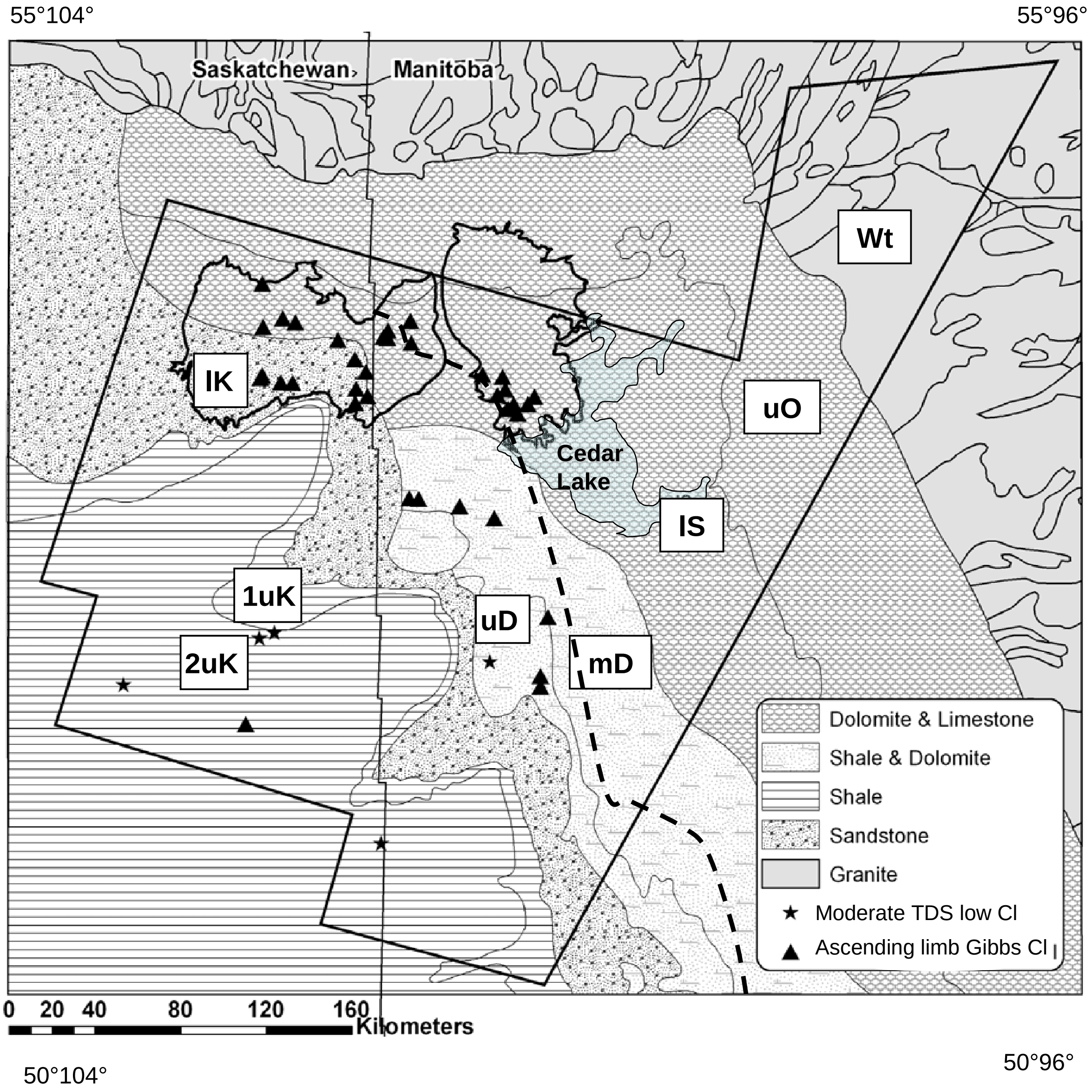

Figure 2.11. Spatial variation of pond TDS measurements relative to the ratio of Cl/(Cl + HCO_3) concentrations and bedrock geology. Includes location of waters that conform to the Gibbs model (ascending limb of Gibbs model) and waters that do not fall within the Gibbs model (lakes overlying the shale bedrock with high sulphate proportions). Dashed line is approximate location of the outcrop belt of the carbonate aquifer (Grasby and Betcher, 2002). Outline of SRD in northwest corner. Map revised from Wheeler et al. (1997).

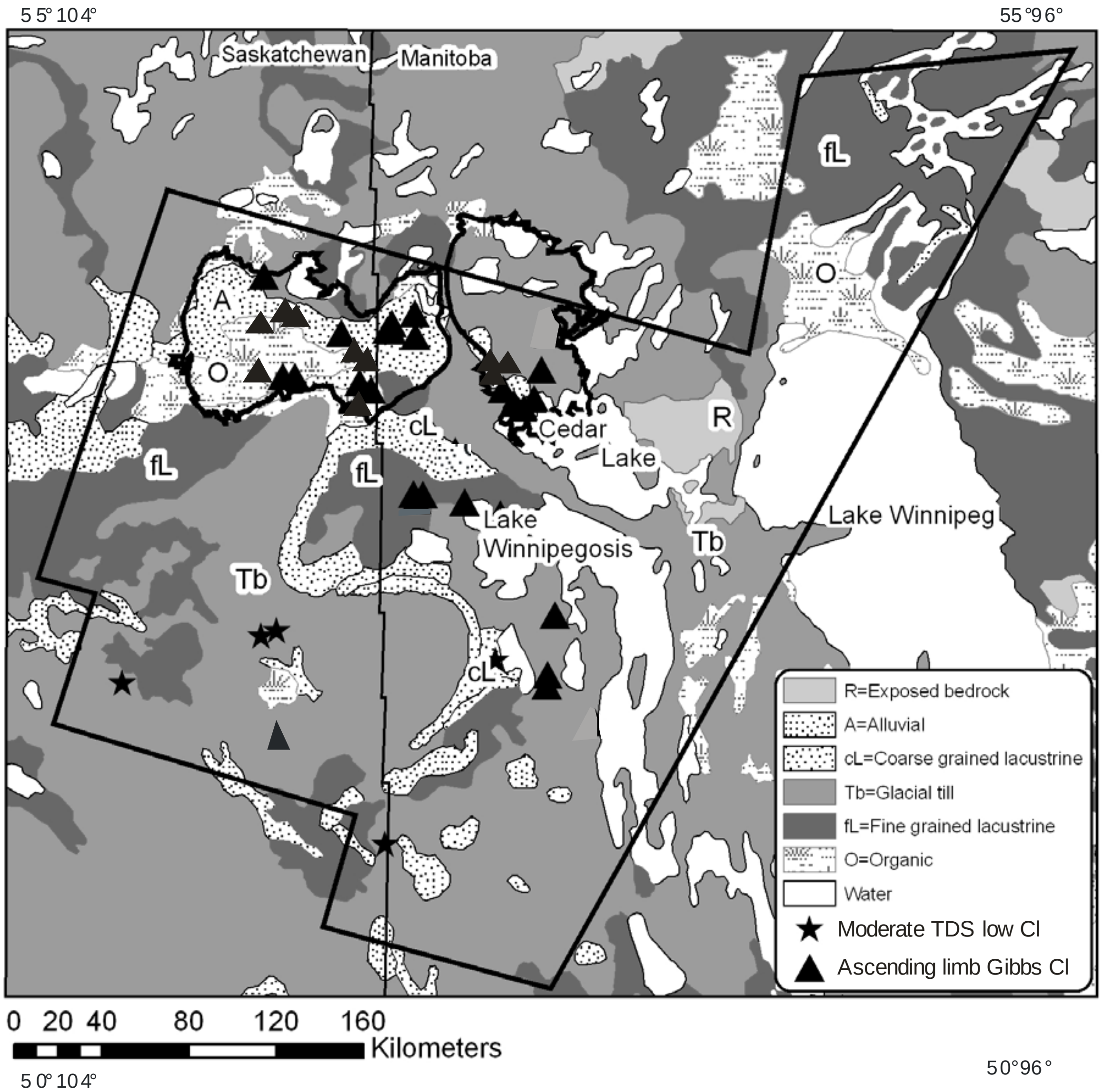

Figure 2.12. Spatial variation of pond TDS measurements relative to the ratio of Cl/(Cl + HCO_3) concentrations and surficial geology. Includes location of waters that conform to the Gibbs model (ascending limb of Gibbs model) and waters that do not fall within the Gibbs model (lakes overlying the shale bedrock with high sulphate proportions). Outline of SRD in northwest corner. Map revised from Fulton (1995).

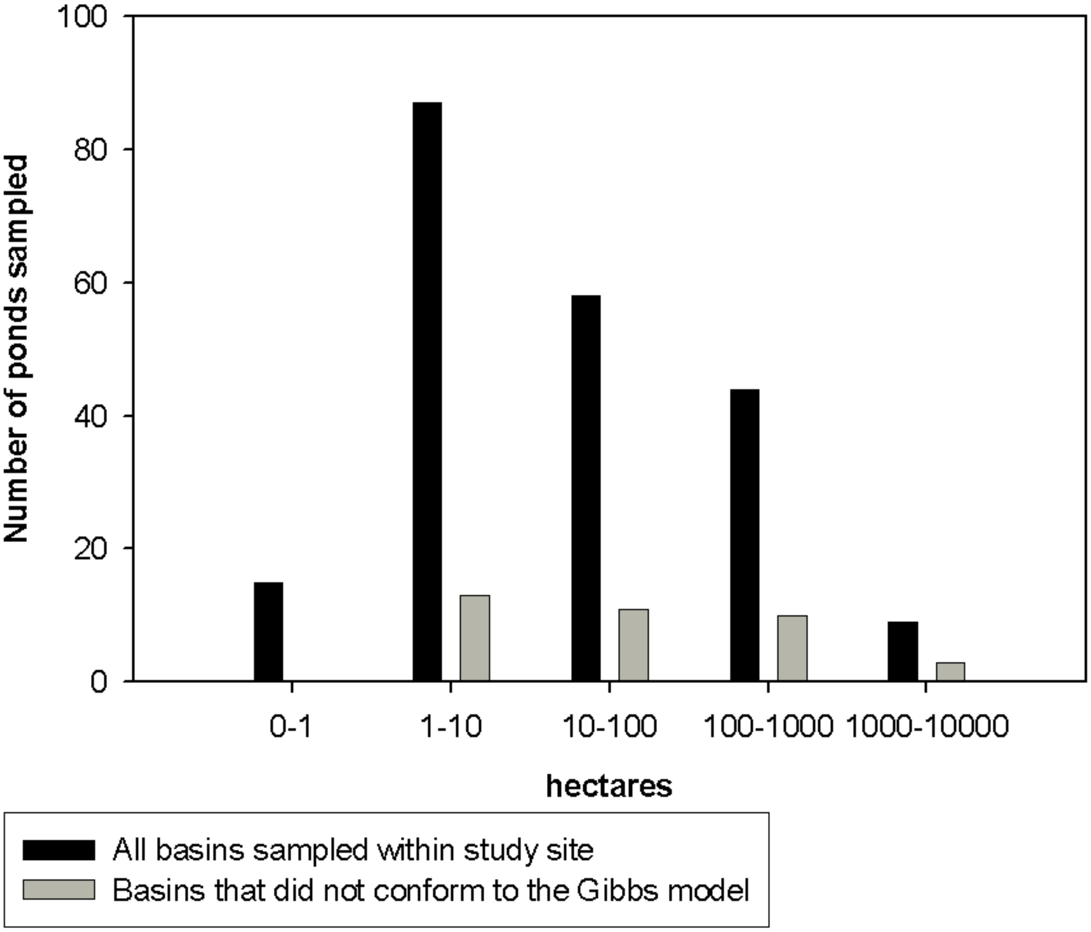

Figure 2.13. Histogram of ponds that fall within and outside the boundary of the Gibbs (1970) model within the study area. N = 210

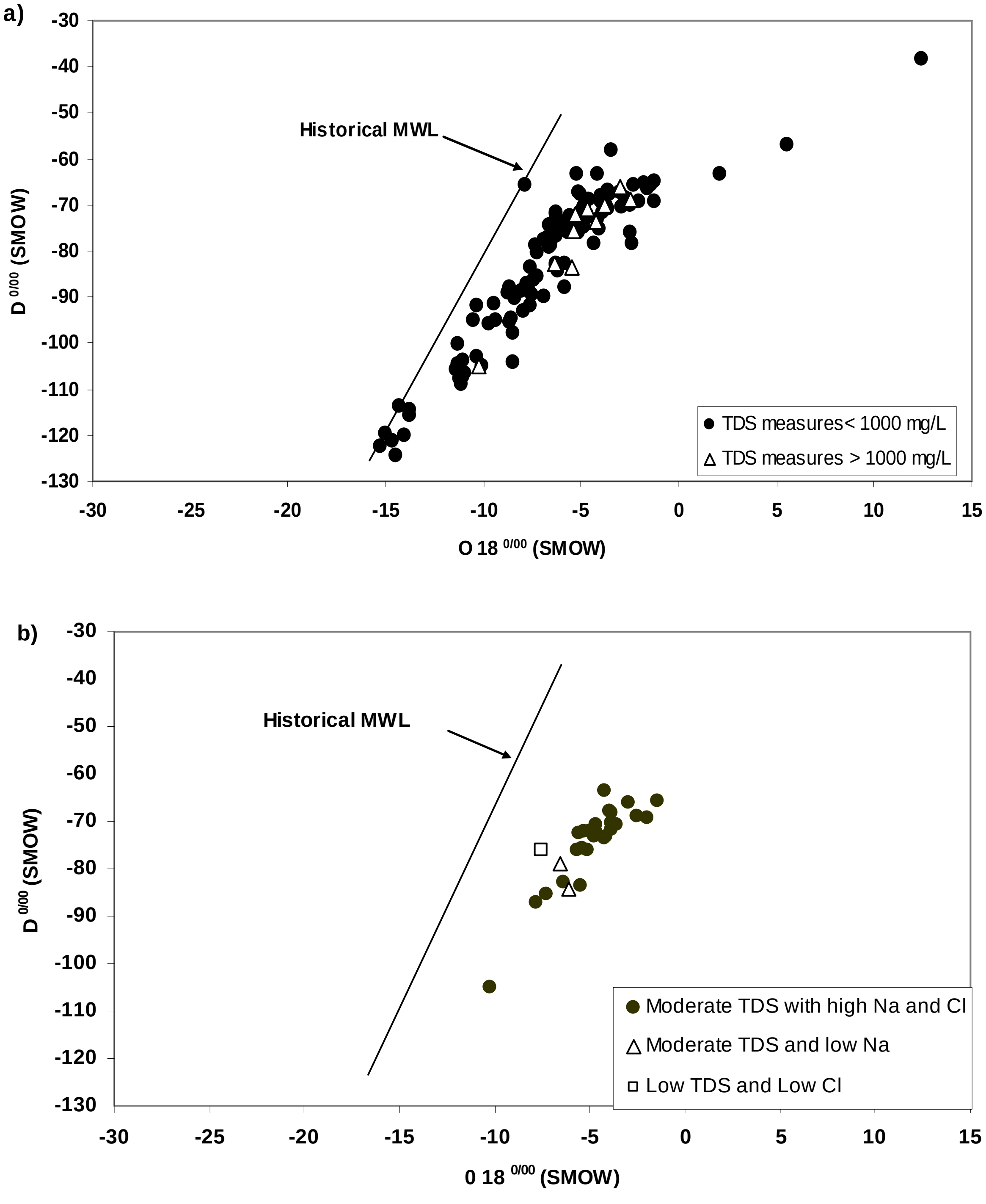

Figure 2.14. Spatial variation of oxygen 18 and deuterium in ponds relative to a) TDS concentrations > and < 1000 mg/L and b) 3 water types that fell outside the Gibbs (1970) model. Meteoric water line obtained from The Pas, Manitoba (IAEA/WMO, 2001)

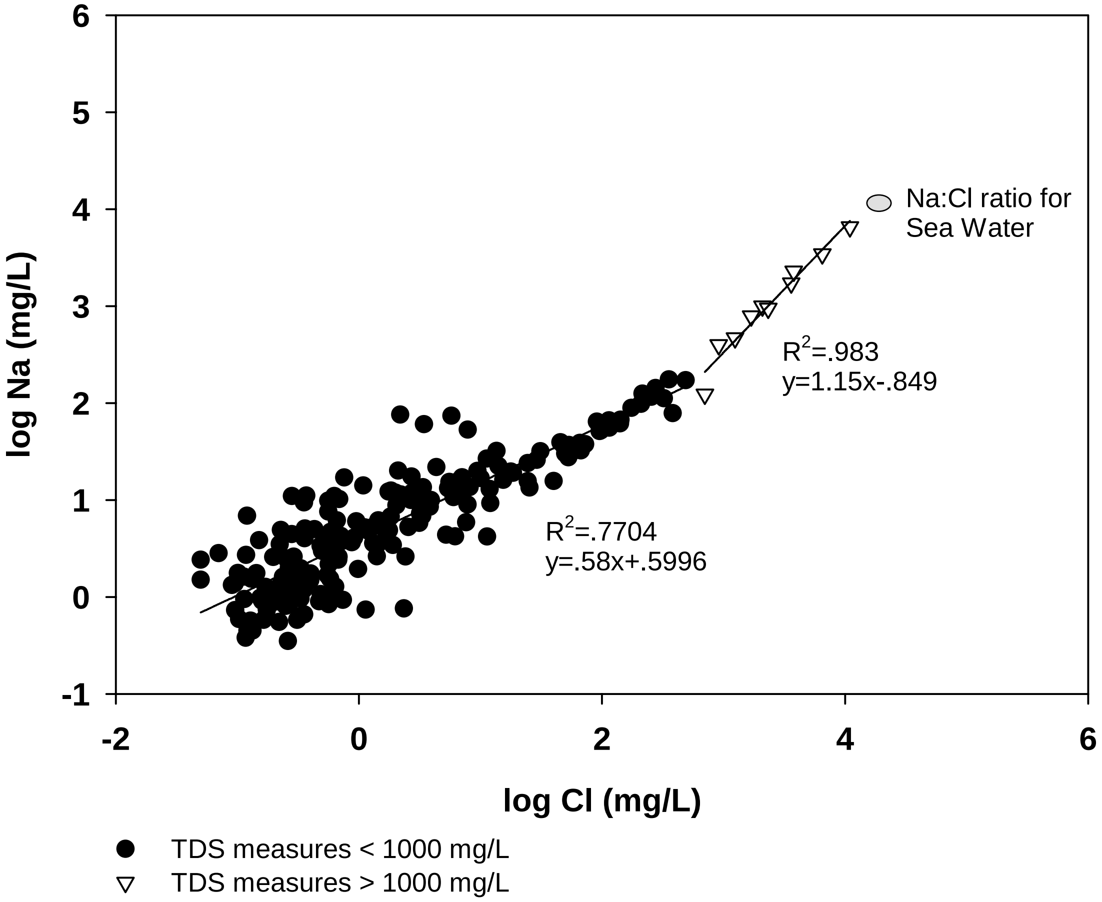

Figure 2.15. Plot of Cl vs. Na for ponds with TDS values > and < 1000 mg/L.

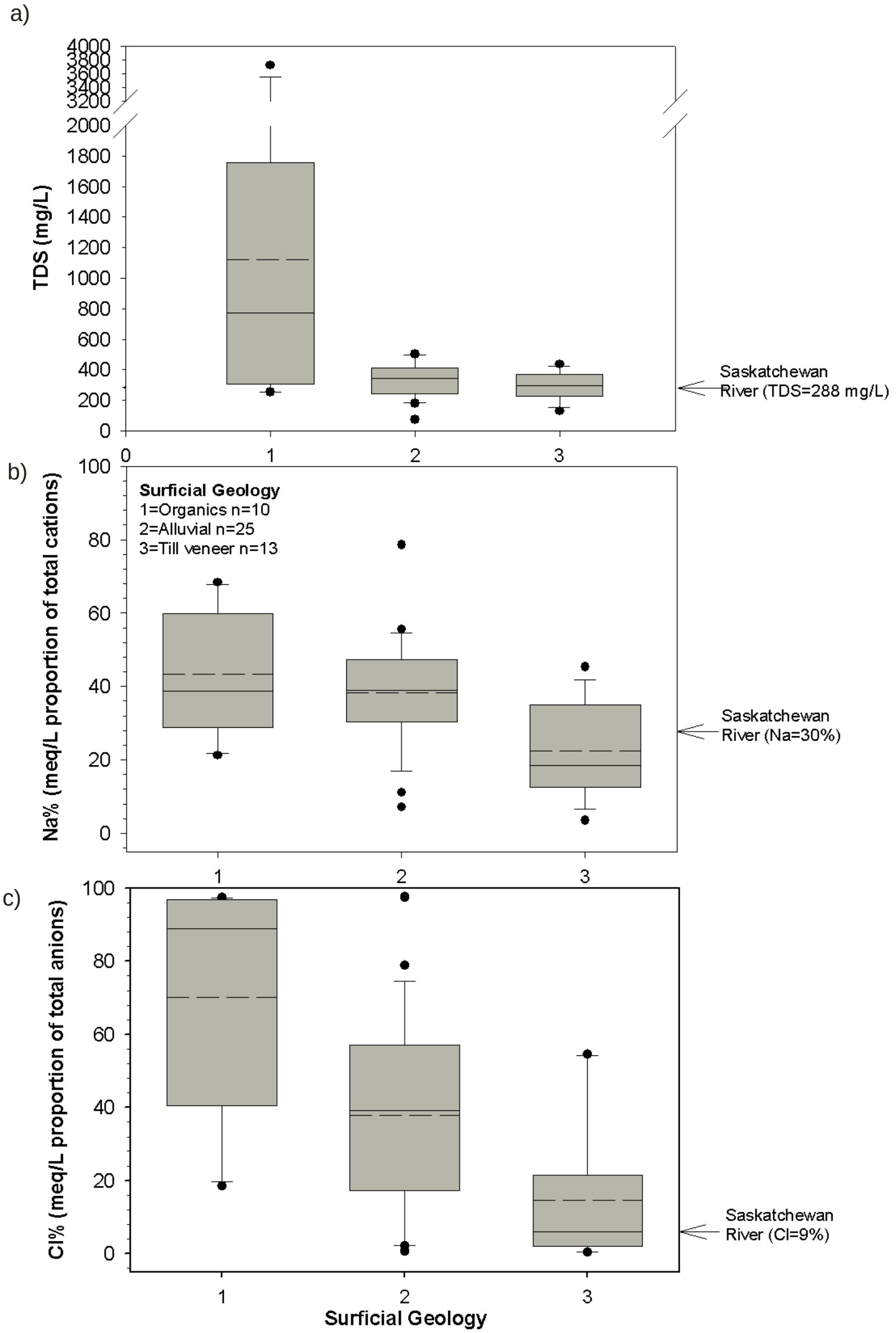

Figure 2.16. Box plots of a) TDS and the proportion of b) Na and c) Cl, with respect to the total anions or cations within the Saskatchewan River Delta (box = 50%, whisker = 40% and dots = 10%). X-axis represents surficial geologic units. Median = solid line, mean = dashed line.

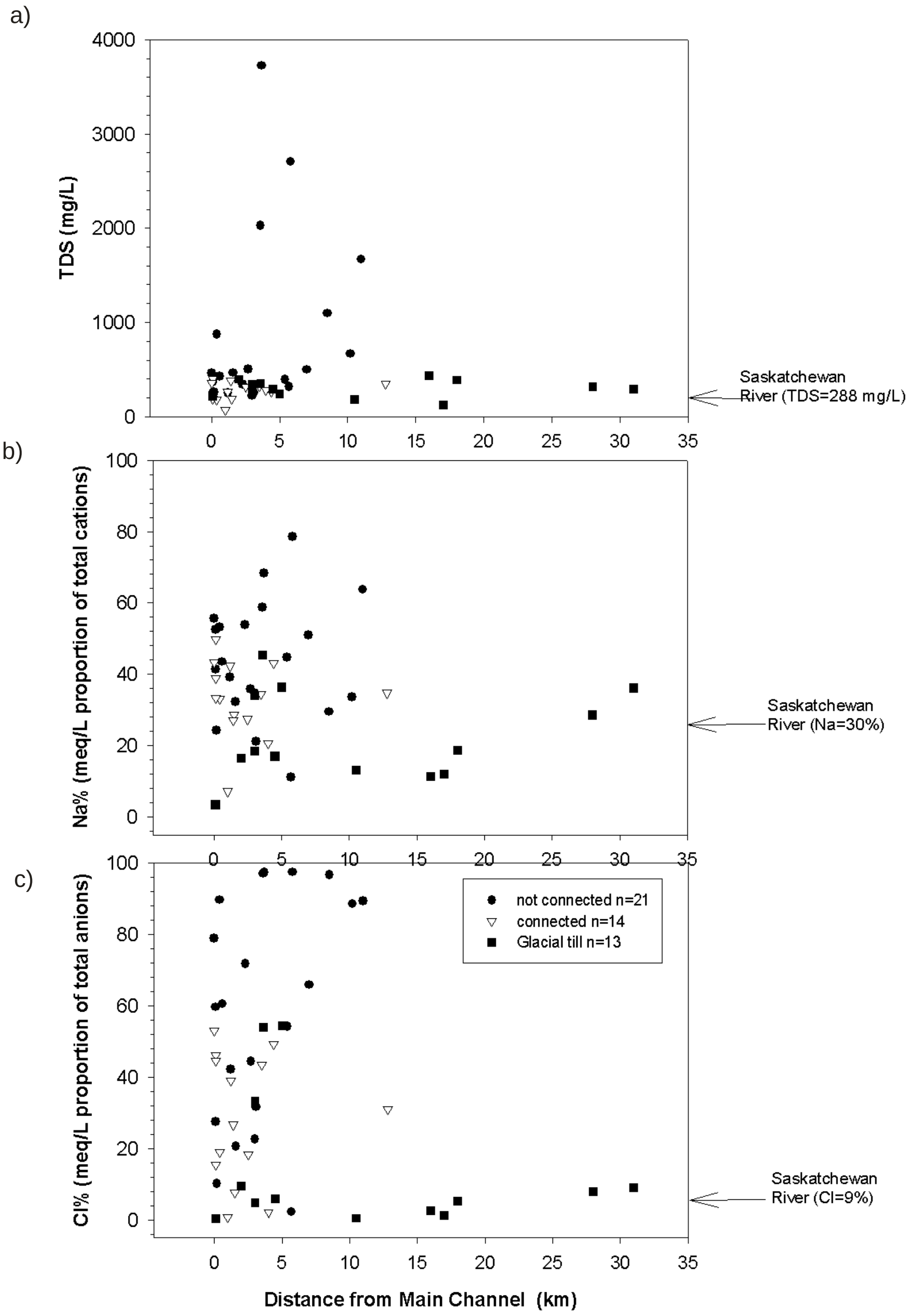

Figure 2.17. The relationship of distance from the main channel of the Saskatchewan River and a) TDS and the proportion of b) Na and c) Cl with respect to the major anions or cations sampled within the Saskatchewan River Delta.X-axis is the distance between the shallow ponds sampled and the closest main channel. Ponds are further stratified by their connection to a main channel (connected or not connected) and whether the pond is located on glacial till.

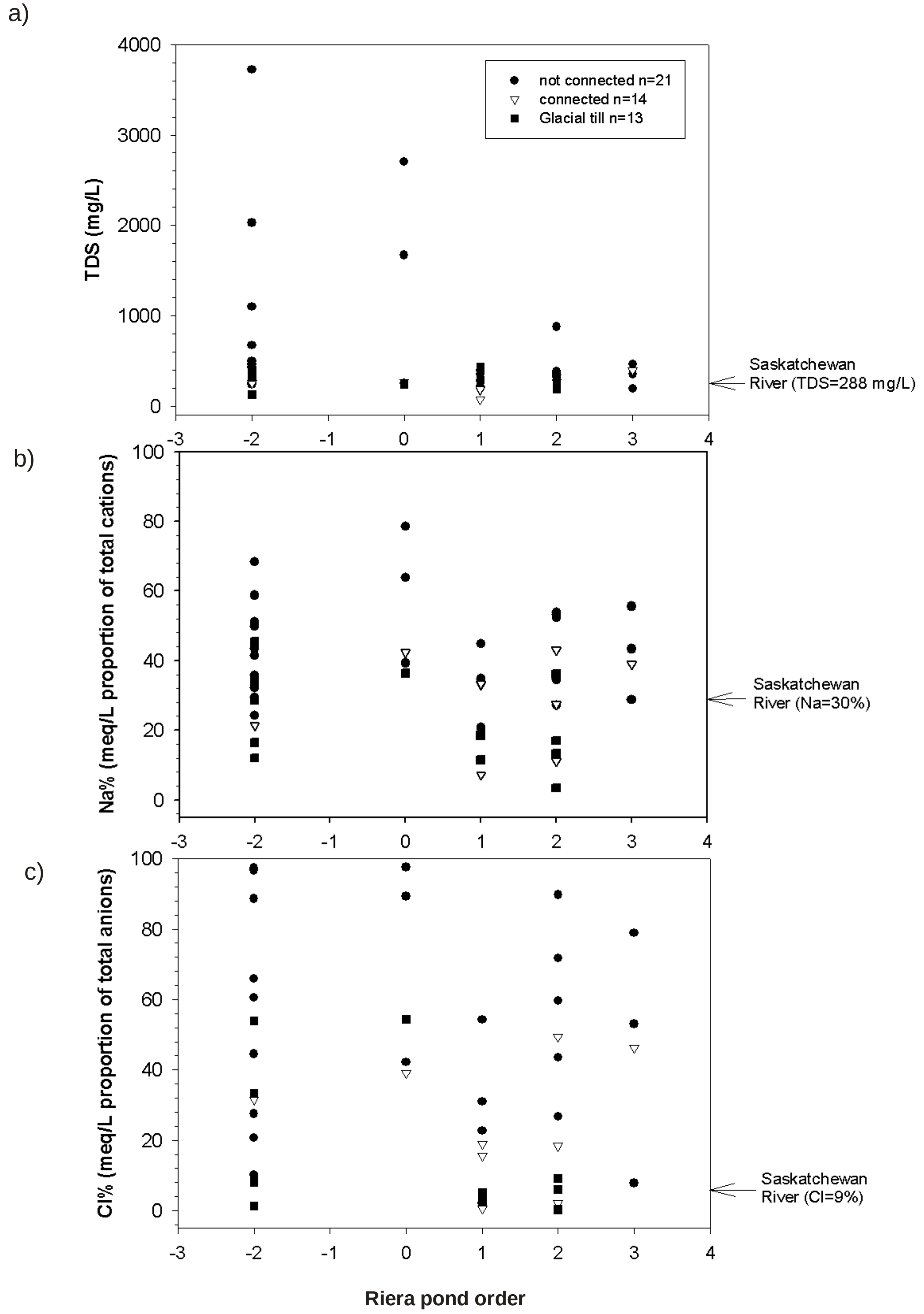

Figure 2.18. The relationship of Riera pond order and a) TDS and the proportion of a) Na and c) Cl with respect to the major anions or cations sampled within the Saskatchewan River Delta. X-axis is pond order as characterized by Riera et al. (2000). Ponds are further stratified by connection to a main channel or location within a till veneer geologic unit.

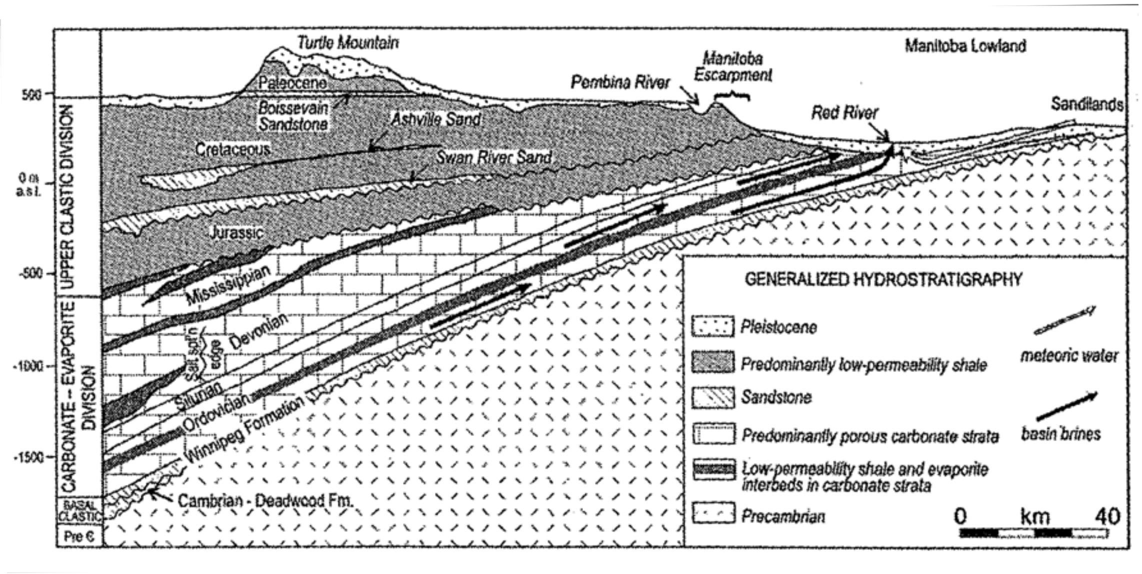

Figure 2.19. Hydrostratigraphic cross section of southern Manitoba (modified from Grasby and Betcher, 2002).

2.6 References

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Chapter 3

Landscape Controls of Nutrient and Ion Chemistry in Ponds of the Central Boreal Plain and Shield of Canada

3.1 Introduction

The Western Boreal Forest (WBF) is rapidly changing due to forestry, oil and gas exploration and extraction, agriculture, and climate change (AEP, 1998). A large portion of the Boreal Plains of Canada consists of wetland-pond complexes, which cover up to 50% of the landscape (Kuhry et al., 1993, Vitt et al., 1995). The response of Western Boreal ponds or lakes to future drier conditions, and potential water quality impacts as influenced by enhanced resource acquisition or development, cannot be effectively assessed without a better understanding of the natural variability of hydro-chemistry. Therefore, a baseline inventory is needed to assess the influence of anthropogenic or natural disturbances surrounding ponds or lakes. Hydrological controls will further influence water quality and are responsible for maintaining the ecological integrity of ponds or lakes at both the local and the regional scale and globally important for waterfowl.

Typically, the Boreal Plain (BP) and Boreal Shield (BS) of Saskatchewan and Manitoba experience a mid continental climate and is the transition between wet boreal and dry boreal and prairie regions. Precipitation (P) is generally equal to or less than potential evaporation (PE) within the BP (La Baugh et al., 1998). Variability of climate within the BP will consequently influence dominant flowpaths of water and consequently dominant mechanisms influencing surface water chemistry (Winter, 2001). The BP of Saskatchewan and Manitoba exhibits complex geology, and at a continental scale, changes in near surface bedrock are dramatic over short distances. The variability of geology can influence the concentration and composition of surface water chemistry via dissolution of parent material (Moser et al., 1998). Within the BP, deep heterogeneous glaciated deposits that result in complex groundwater interactions and further complicates surface water hydrology and thus chemistry (Devito et al., 2005a). As mentioned previously, wetlands-pond complexes cover up to 50% of the BP of Canada and have also been shown to influence surface water hydrology and surface water chemistry (Moser et al., 1998). A framework that considers the complete hydrologic system is needed to consider the movement and interaction between surface water and groundwater addressing the susceptibility of relatively pristine systems of the WBF.

3.1.1 Background Information

The Gibbs (1970) global model has gained widespread use as a practical tool to explain the variability of the world's surface water chemistry (Wetzel, 1983, Jorgensen and Vollenweider, 1989). Dominant processes influencing surface water chemistry have been explained by the interaction of climate and geology. Three major mechanisms have been identified by this empirical model and consist of the atmospheric precipitation process, the rock dominance process, and the evaporation-crystallization process. The Gibbs model was applied to ponds of the Boreal Plain and Shield in chapter 2. Variability of surface water chemistry within the major mechanisms identified, and specifically in surface waters that fall within the rock dominance mechanism is not addressed in the model. Therefore, further understanding of the hydrologic cycle is needed and thus the interaction of atmospheric precipitation, surface water and groundwater can be used to further explain water chemistry variability. The considerable variation of surface water composition and concentration of geologic dominated systems requires further resolution to effectively predict surface water chemistry and apply best management practices (BMP) in this region.

Currently, more research is needed on the processes controlling either the hydrologic function or the spatial variability of nutrient and solute chemistry of wetland-ponds in the WBF (Buttle et al., 2000). The location, movement, and chemical characteristics of water are fundamental to many water-resource related issues, therefore a conceptual framework for designing data networks, syntheses, and research is needed based on the hydrologic system (Winter, 2001). Understanding the natural spatial variability of water chemistry in relatively pristine ponds and lakes is required for effective interpretation of the effect of disturbance within any hydrogeological setting. Estimates of probable background chemistry can be useful in assessing the relative susceptibility of wetland-ponds to eutrophication or siltation following disturbance, which can result from increased decomposition of dead woody material, compaction, or increased yields of runoff (Nip, 1991).

Water chemistry of lakes and wetlands is the result of an interaction of a number of environmental variables, although frequently one or two of these variables dominate (Sorrano et al, 1999). Lakes and wetlands in a region can share similar traits at a regional scale such as origin, climate, and catchment geology; and at the local scale lake morphometry, foodwebs, geomorphic setting, and hydrology (Sorrano et al., 1999). Lakes and wetlands may share these traits but can vary in their physical, chemical, and biological characteristics, and understanding these varying characteristics has been an ongoing challenge for regional limnologists. The influence of geology and vegetation on the physical and chemical properties of 35 lakes in Wood Buffalo National Park of northern Alberta and the Northwest Territories, Canada was described by Moser et al. (1998). Their results showed that the physical and chemical properties of lakes were influenced more by geology rather than vegetation.

Winter (2001) stated that the hydrological function of landscapes can be conceptualized in terms of land-surface slope, hydraulic properties of the soils geologic material, and its climatic setting. To address the need for a framework that considers the complete hydrologic system, it is necessary to consider the movement of surface water, groundwater, and the interactions between the two. The application of the hydrologic landscape concept was used in a qualitative way to compare the chemistry of lakes in the context of ground water flow systems for four small research watersheds (Winter et al., 2001). It was implied that the different sources of water to the wetlands would require different techniques to protect their water supply and water quality.

The need for a broad scale classification of a hydrologic response unit was also discussed and presented by Devito et al. (2005a). This framework consisted of a hierarchy of factors nested within each other to characterize the relative importance of different scales and types of hydrologic interactions ranging from local to regional interactions. The order in which these factors influence hydrologic flowpaths were presented as climate, bedrock geology, surficial geology, soil type and depth and lastly topography It was argued that a broad scale classification of catchments was required to generalize dominant hydrologic processes before relying on topographic hydrologic boundaries that have become common practice and can be easily defined by land managers. A hierarchical classification could be used to generalize the dominant controls of water cycling, and to develop a conceptual framework to determine the dominant component of the hydrologic cycle, and to determine the scale of interaction that should be considered. The interaction of ponds and lakes with their surrounding environment influences the spatial variability in surface water chemistry, as well as susceptibility to climate change and land use (Devito et al. 2000).

This project addresses natural processes and their influence on surface water quality of shallow open water wetlands or ponds, potholes and lakes, hereafter referred to as ponds. To predict the susceptibility of ponds to climate change and land use, dominant controls of background chemical composition and concentration, as well as nutrient status need to be predicted. Thus, when setting up management areas, it is questioned if specific controls or a combination of controls can be applied to manage surface water chemistry.

3.1.2 Factors Influencing Hydrologic Flowpaths

The hierarchy of factors that influence hydrologic flowpaths that will be tested consists of climate, bedrock geology, surficial geology wetland connection and landscape position. How these factors influence flowpath and thus chemistry is discussed below.

3.1.2.1 Climate

P and evapotranspiration (ET) ultimately determine the source of water for the hydrologic cycle which will play a large role in surface water chemistry. Climate sets the constraints, that determine the role of soil storage, vegetation water demand on soil moisture regimes, and the dominant direction of flow (vertical vs. lateral) as the amount of excess water for groundwater recharge and/or hillslope runoff (Devito et al., 2005a). The spatial distribution of wetlands indicates that climatic parameters are dominant factors that influence the development and differentiation of wetland types (Vitt et al., 1995).

Long term averages of evaporation and precipitation can be used to help explain spatial differences in aridity at a large scale, soil deficits that control vegetation growth and thus recharge and runoff (Labaugh et al., 1998). Thus, in humid environments the potential to generate overland flow (OLF) is increased in comparison to arid environments where ET exceeds P and recharge and discharge of groundwater plays a larger role in water cycling. In summary, P and ET can affect the distribution, timing, and magnitude of surface runoff and groundwater recharge throughout a region. Long term changes in climate and land-uses can significantly interact and alter the upland - wetland - pond hydrologic linkages. Thus, the impact of climate cycles on wetland and water table dynamics and maintenance needs to be placed in hydrogeologic context to generalize findings on natural variation and impacts of anthropogenic disturbance on hydrologic function and water chemistry and its relation to productivity and diversity of wetland types.

Within the study area, precipitation and gross evaporation range from a surplus in the northeast to a deficit in the southwest. This implies that there may be more lateral flow versus vertical flow, respectively. As a result, with respect to controlling nutrient and solute chemistry of ponds of the study area, the relative role of the underlying bedrock will influence surface water ion composition and concentration (Gibbs, 1970, Wetzel, 1983).

3.1.2.2 Bedrock Geology

Bedrock geology can influence surface water chemistry by mineral weathering and or by influencing scale of flow.

Geochemical interactions between rocks and water will differ between different types of rock mineralogy. The hydrochemistry of surface waters globally have been explained by reference to their underlying bedrock geology by numerous researchers, however these studies were typically conducted in more simple geologic environments (Banens 1987, Johnson et al., 1997, Moser et al., 1998). Waters, which originate from rocks containing one or more chemically resistant minerals, such as felsic igneous rocks, tend to have lower total ion content and lower concentrations of phosphorus than waters from chemically soluble minerals such as limestone (Kalff, 2002). Waters associated with limestone or dolomites are typically ion rich and dominated by the release of calcium, magnesium, and bicarbonate (Kalff, 2002). Sedimentary rocks, which predominately cover the Western Boreal Plain generally result in waters with high total ion contents and result from sedimentary rocks deposited in marine environments. The cementing material and adsorbed ions in these rocks also tend to be highly soluble (Brownlow, 1996). Shales are more complex than limestones or dolomites and contain minerals such as illite and quartz, which are relatively unreactive and contribute little to runoff chemistry. Waters draining shales also often contain higher concentrations of chloride and sodium, which are thought to originate from seawater trapped in the shale at the time of deposition and sulphate which is commonly associated with oxidation of pyrite in shales.

Bedrock lithology, depth, and heterogeneity can be used to describe the regional groundwater flow system, which can determine the location and extent of groundwater recharge and discharge zones and the relative dominance of local-scale vs. regional-scale flows on surface water chemistry (Tóth, 1999, Freeze and Witherspoon, 1967). On a coarse scale, different rock types can result in different configurations, flow-lengths and flow-paths of surface water and groundwaters (Winter, 2001). Typical environmental effects and conditions resulting from the action of groundwater moving through different flow systems (local, intermediate and regional) will result in systematic changes in the groundwater ion facies from bicarbonate through sulphate to chloride (Chebotarev, 1955). The location of ponds within the discharge areas of these flow systems will influence surface water chemistries. The geological setting can determine if groundwater will follow topography and if groundwater flow coincides with topographic divides (Winter and LaBaugh, 2003).

The bedrock geology of the study area is typically complex and includes a multitude of bedrock types as you move from the sedimentary deposits of the

Boreal Plain to the Precambrian intrusive rocks of the Shield. Thus, in predicting the variability and assessing potential impacts of landuse and climate change, understanding the role of flowpath and flowlength or direct mineral weathering of the bedrock which influences surface water chemistry is needed in complex geologic landscapes.

3.1.2.3 Surficial Geology

Sources of chemistry for ponds of the glaciated BP and BS may originate from precipitation, or from local, intermediate, and regional groundwater flow systems as influenced by the topography, depth and type of surficial material, and permeability of the underlying bedrock (Tóth, 1970, Tóth, 1999). The porosity and permeability of the subsurface environment generally control flowpath and the behavior of surface flow and groundwater systems. Hydrologic-linkages and function of wetlands are influenced by topographic location as well as the surficial geology (substrate types) and differences in water transmission properties of the substrates (Devito et al., 1996, LaBaugh et al., 1998, Seigel, 1986). Thus, hydraulic conductivity of more permeable substrates such as glaciofluvial and outwash areas can be assumed to be higher than substrates of lower permeabilities such as fine-grained lacustrine clays. Infiltration capacity, the maximum rate at which the soil surface can absorb falling rain (or meltwater) also decreases asymptotically over time as the upper part of the soil profile becomes progressively saturated from the surface down (Burt and Haycock, 1996).

Within the study area, surficial geology ranges from fine-grained lacustrine sediments which will favor overland flow and relatively shorter flowpaths and local flow systems to coarse-grained lacustrine sediments which will favor subsurface flow, relatively longer flowpaths and intermediate to regional flow systems. Ponds overlying fine-grained sediments should result in calcium bicarbonate water with relatively lower measures of solutes and the ponds overlying coarse-grained sediments will result in potentially sulphate to chloride type waters and increased solute concentrations via the natural evolution of groundwaters (Chebotarev, 1955, Tóth, 1999). However, the interaction between surficial geology and flow may not be able to be transferred to the concept of flow and chemistry across landforms. Flow over fine-grained sediments may favor overland flow, however the hydrologic residence times of soil and water over periods of little precipitation can result in increased solutes and ion exchange over short distances (Bache et al., 1984). Conversely, coarse-grained sediments favor subsurface flowpaths, but mineral weathering of quartz sand is low, thus limiting ion exchange to groundwater (Bache et al., 1984). Determining whether local or intermediate/regional flowpaths influence pond chemistry or nutrients over the influence of geologic weathering are important in predicting spatial variability in pond chemistry and establishing management areas.

3.1.2.4 Pond Position

The hydrologic position of a lake within the regional flow regime can determine the relative importance of groundwater and precipitation to a lake (Kratz et al., 1997, Devito et al., 2000). Lakes higher in the landscape receive a greater proportion of their water from precipitation, while the role of groundwater is increased with lakes located lower in the landscape. As discussed previously, the ion facies of waters change with different flow system scales (Tóth, 1999). Landscape position will also affect how surface waters will react to drought (Webster et al., 2000). Chemical response to drought appears to be affected by two opposing mechanisms (Kratz et al., 1997). Drought leads to increased water retention times and evapoconcentration, which can cause base cations in lakes and ponds to increase in concentration (Schindler et al., 1990). However drought can also cause diminished groundwater supply of these cations to a lake, which if prolonged over a long enough period would cause a decrease in cation concentrations (Webster et al., 2000). Ponds located lower in the landscape will result in relatively higher concentrations of solutes from increased groundwater contributions and longer flowpaths, lower concentrations of nutrients as a result of high rates of nutrient retention and dilution from increased groundwater inputs (Rechkow and Chapra, 1983 and Williams, 1985).

3.1.2.5 Wetland Connectivity

In a sub-humid climate, runoff generation is primarily from near surface flow from peatland areas connected to ponds (Devito et al., 2005a and b). In drier regions many upland areas result in a lower water table and increased storage which produces little runoff, while peatland areas maintain a high water table by reducing actual evapotranspiration (AET) and are effective in generating runoff (Devito et al., 2005b, Redding and Devito, 2008). Gibson et al. (2002) found that runoff to lakes in wetland-dominated catchments were found to be significantly higher than runoff to upland-dominated lakes, with generally higher contributions from catchments with low bog/fen ratios.

Peat consists of two distinct layers, the upper acrotelm, which consists of the upper horizon of roots and decomposing plant material, and the lower catotelm, composed of dense peat which is anoxic for most of the year. The relatively higher conductivity of the upper horizon enables the ability for rapid near surface runoff (Evans et al., 1999). The catotelm characteristically has a lower specific yield, which allows the peat to hold onto thin layers of water, which can allow a greater response of the watertable to storm events and generate near surface flow. Root systems are also characteristically shallower in peatlands compared to mineral soils, which minimizes transpiration losses and maintains watertable levels near the acrotelm layer in drier conditions.

Prepas et al. (2001) showed that total nitrogen, total phosphorus and dissolved organic carbon (DOC) were positively correlated with wetland cover in their associated watershed. Macrae et al., (2005 and 2006) also showed that surface water and soil water flowing through organic soils showed increased concentrations of nitrogen and phosphorus in comparison to groundwater which flowed through mineral soils. Thus with increased wetland area connected to the pond, there is an expected increase of near surface hydrologic flushing of nutrients to the pond (Devito et al., 2000).

Within the study area, wetlands range from small isolated swamps and marshes connected to ponds to large fen complexes surrounding the ponds. The sub humid climate of the study area makes it hard to exceed storage of forested uplands, thus, peatlands and ephemeral draws are the primary source of runoff (Devito et al., 2005a, Redding and Devito, 2008). This connection of marshes, swamps and peatlands may provide a measure of effective runoff generating areas and result in flushing of peat and non-peat forming wetlands which are primary sources of nutrients (Ferone and Devito, 2004, Macrae et al., 2005, Macrae et al., 2006). Conversely, Sass et al. (2008) found lower chlorophyll a and assumed lower phosphorus concentrations in ponds with large areas of wetland connected and attributed this to dilution by large surface flows. Determining the relative role of wetlands and their connection to ponds vs geologic weathering or influence on flowpath and surficial geology and flowpath is important for management applications across this landscape.

In chapter 2, it was discussed that within the context of the Gibbs model and the general climate of the study area, ponds of the Central Boreal Plain and Shield should be influenced by their underlying geology (Gibbs, 1970). A number of ponds showed high concentrations of solutes and were proportionately dominated by sodium and chloride ions. Rather than being controlled by the evaporative mechanism as described by Gibbs (1970), these chemically distinct ponds were hypothesized to be the result of Williston Basin scale groundwater mixing with local meteoric water. Chapter 2 placed surface water chemistry in context of continental scale groundwater and lithology. In this chapter the local to intermediate scale controls of surface water chemistry typical of the Boreal Plains and the ponds reported as under geologic control within the Gibbs model are addressed. After removing the ponds under the influence of Williston Basin scale flowsystems, there were a total of 147 ponds remaining in the data set.

3.1.3 Objectives and Hypotheses

The objectives of this research are:

1) to acquire a baseline inventory of the natural variability of relatively pristine surface water chemistry of a study region bordering the Canadian Boreal Plain and Shield.

2) to test whether surface water chemistry can be related to hydrological controls of scale and flowpath, and to determine which scale and which

landscape unit best predicts surface water chemistry of the Canadian Boreal Plain and Shield.

Specific objectives and hypotheses are as follows:

3.1.3.1 Climate

1) To examine the influence of climate on the spatial distribution of nutrient and solute chemistry of ponds within the study area.

It is hypothesized that across the study area there is a range from excess soil moisture to a deficit which influences evapoconcentration and results in an increase in solutes and reduced proportion of sodium and chloride is predicted across the range of excess soil moisture to a deficit (Gibbs, 1970). Alternatively, the deficit in the region is not large and the influence or variability of geology will control pond chemistry.

3.1.3.2 Bedrock Geology

2) To examine where and at what scale bedrock geology provides the best prediction of nutrient and ion chemistry of ponds within the study area.

It is predicted that pond chemical characteristics will reflect the major chemical composition and weathering rates of the underlying bedrock minerals (Brownlow, 1996). Specifically, within the study area, waters draining a dolomite/limestone-dominated landscape will have greater proportions of magnesium and bicarbonate, relatively higher solute concentrations and generally higher concentrations of nutrients. Waters overlying shales which commonly contain pyrite will result in higher proportions of sulphate. Waters in a granitic geologic setting will be dominated by calcium and bicarbonate, lower solute concentrations and lower nutrients as a result of lower weathering rates associated with insoluble granitic rocks. Alternatively, bedrock type, and specifically permeability, will influence flowpath and flowlength which will influence solute composition and concentration and nutrient chemistry of ponds.

In general the natural evolution of water from local, intermediate and regional flow systems is from bicarbonate, sulphate and chloride type waters, respectively (Chebotarev, 1955). Ponds overlying low permeability granite will result in lateral movement of water and local flow systems (Devito et al., 2005a). This will result in pond surface water ion composition similar to meteoric waters, low concentrations of solutes and potentially higher concentrations of nutrients as the organic layer of soils can be major contributors of nutrients to ponds. Ponds overlying permeable sedimentary bedrock will result in more vertical movement of water and result in intermediate to regional flow systems. This will result in pond surface water chemistry ion composition similar to intermediate and regional flow systems, high concentrations and lower concentrations of nutrients as groundwater is typically nutrient poor and will dilute nutrients as a result of increased groundwater contributions (Williams, 1985).

3.1.3.3 Surficial Geology

3) To examine the relative role of surficial geology in predicting nutrient and ion chemistry of ponds within the study area.

It is predicted that the texture of surficial deposits will influence the extent, ephemeral nature and type of flowpath connecting slopes to ponds, and will influence surface water chemistry composition and nutrient concentrations (Devito et al., 2005a). Ponds overlying a fine-grained geological environment will have more potential to generate OLF or lateral flow and will generally be characterized by local flow systems dominated by calcium bicarbonate and low solute concentrations. This will result in greater nutrient transport from organic and mineral layers to the ponds from adjacent uplands (Wetzel, 1983). Ponds overlying a coarse-grained geological environment will have more potential to be groundwater fed with ion compositions similar to groundwater, higher solute concentrations and nutrient poor (Williams, 1985). These waters may also reflect intermediate to regional groundwater flow characteristics with higher proportions of sulphate and chloride (Tóth, 1999). Alternatively, when the climatic environment permits, the residence time of waters connecting uplands to ponds can be increased in fine-grained material and result in an increase in ion exchange as a result of longer residence times and thus, increased soil-water interactions. Ion exchange can also be reduced in coarse-grained material when residence times are reduced between groundwater and insoluble quartz sands (Bache et al., 1984).

3.1.3.4 Pond Position

4) To determine the role of pond position (pond order) in determining nutrient and ion chemistry of ponds within the study area.

It is predicted that ponds located higher in the landscape will be situated in recharge areas and display characteristics of local flow systems. Pond chemistry in local flow systems will be dilute, ion composition will reflect precipitation or be a calcium-bicarbonate type water and nutrient poor. Ponds located lower in the landscape will be located in groundwater discharge areas and display characteristics of intermediate to regional flow systems. Pond chemistry in intermediate to regional flow systems will show an increase in solutes and ion composition will reflect groundwater. Alternatively, ponds located in recharge areas may be isolated and experience evaporative influence. This will result in an increase in solute concentration and nutrients and no difference in chemical parameters will be detected between different landscape positions.

3.1.3.5 Wetland Connectivity

5) To examine the relative influence of wetland connectivity in determining nutrient and ion chemistry of ponds within the study area.

It is predicted that an increase of connected wetland area will result in an increase of OLF and quick flow generation during precipitation events due to increased moisture and relatively high water table. Wetlands (peat forming and non-peat forming), due to moisture and redox are often major sources of organic nutrients such as phosphorus, nitrogen and DOC (Prepas et al., 2001, Macrae et al., 2005, Macrae et al., 2006). With increased wetland area, pond chemistry will result in greater nutrient loading from wetlands, ion composition similar to precipitation and lower solute concentrations. Alternatively, the increase of wetland complexes connected to ponds will increase surface runoff inputs and dilute nutrient and solute concentrations by flushing surface controlled systems. Ponds connected to very large wetlands will be groundwater fed and result in ion composition reflecting groundwater, a higher concentration of solutes and nutrient poor (Williams, 1985).

3.2 Methods

3.2.1 Study Area

This research was conducted in cooperation with the Western Boreal Division of Ducks Unlimited Canada (DUC). The study area is one of a number of areas within the WBF where DUC has conducted waterbird inventories and water chemistry surveys, to be used to evaluate the use of wetlands by waterfowl and other wetland-dependent waterbirds (Bell et al., 2003, 2005). The study area encompasses a 97,500 km^2 area of the Boreal Plains and Shield ecozone extending from 96^{o}50'W, 54^{o}58'N and 103^{o}50'W 52^{o}01'N, respectively, and was discussed in detail in chapter 2.

3.2.1.1 Ecoregions and Climate

Within the Boreal Plain ecozone there are a number of notable features within the study area and were discussed in chapter 2. General climate data for communities within the study area were also discussed in chapter 2.

3.2.1.2 Bedrock Geology and Rock Type

Near surface bedrock geology of the study area consists of eight formations based on genesis. As geology may influence surface water chemistry composition and concentration, bedrock units were grouped based on similar mineralogical rock types and similar weathering rates. The distribution of the reduced data set (147 ponds) relative to bedrock geology is shown on Figure 3.1. Near surface bedrock type, formation name and age were discussed in detail in chapter 2.

3.2.1.3 Surficial Geology, Vegetation and Land Use

The study area is composed of a mosaic of glacial deposits typical of the Western Boreal Plain. These glacial deposits vary in particle size from region to region and are presented on Figure 3.4 and were discussed in detail in chapter 2. General vegetation and land use within the study area were also discussed in chapter 2.

3.2.2 Sampling Design

Two-hundred and ten ponds were sub-sampled for water chemistry from a total of six-hundred and eighteen DUC waterbird survey ponds. The DUC waterbird survey ponds were randomly sampled within ecodistricts. The ponds sampled for water chemistry on the Boreal Shield were not a subset of the DUC waterbird survey ponds and were selected based on accessibility on foot.

To address the question of the influence of geology, ponds were selected from the DUC waterbird survey ponds to incorporate all bedrock geologic types observed in the area. The final distribution of ponds sampled within bedrock and surficial geologic units is summarized in Table 3.1. The number of ponds sampled largely represents the % area covered by each geologic unit. There are five dominant bedrock units identified within the study area (Figure 3.1). To address interaction of surficial geology and bedrock geology, the study area was further stratified by a total of four different surficial deposits (Figure 3.2). Of the five bedrock types present in the study area, approximately ten ponds were selected from each surficial geological unit. Surficial geologic units were not all present within each of the bedrock units and in some cases there were not ten ponds to be sampled within surficial geologic units. Ponds overlying organic deposits were assigned to the nearest surficial deposit. Wetland connectivity and pond order were determined for each pond after water chemistry sampling had occurred.

3.2.2.1 Removal of Ponds from Data Set.

As described in chapter 2, the interaction of continental scale groundwater flow with local meteoric flows influenced a number of ponds within the SRD and west and southwest of Lake Winnipegosis (Figures 3.3 and 3.4). The chemistry and potential hydrogeology of ponds that fell within the ascending limb of the Gibbs (1970) model and ponds that fell outside of the Gibbs model have been discussed in chapter 2. The ponds from the SRD and ascending limb were removed and from herein, a subset of 147 ponds was used. The final distribution and summary of average chemistries of the 147 pond subset is summarized in (Table 3.1).

3.2.3 Water Chemistry

3.2.3.1 Water Chemistry Sampling

A one litre grab sample of water was collected from the middle of the open water by helicopter in July/August of 2003 or approximately two meters from shore by hand for the Boreal Shield sites as described in chapter 2. All water samples were collected from approximately 20 to 30 centimeters below the water surface.

Initial preparation of water samples was conducted the day of sampling (within 8 hours). Perishable parameters with time sensitive hold times (soluble reactive phosphorus, ammonium and nitrate) were filtered through a Millipore membrane filter (pore size-0.45um) within 8 hours of sampling and frozen until analysis. The pH and conductivity of the pond water was measured within 8 hours of sampling using a Fischer Scientific Accumet 925 pH meter and an Oakton Con 300 conductivity meter, respectively. Water samples were packed in ice filled coolers and shipped to the University of Alberta Limnology lab and received within 72 hours. A subset of pond water samples were shipped to the University of Calgary Isotope Science Laboratory for deuterium/hydrogen isotope analysis.

3.2.3.2 Water Chemistry Analysis

A full suite of dissolved anions (negatively charged) and cations (positively charged) were analyzed to allow for a complete ion charge balance, and general measure of water quality for each pond as described in chapter 2. In addition, water samples for DOC were filtered using a Millipore membrane filter (pore size-0.45um) and processed using methods described by Greenberg et al. (1992), on an Ionics Model 1505 Programmable Carbon Analyzer. Samples for total dissolved nitrogen (TDN) were filtered in the lab using a Gelman glass fiber filter (pore size =1.0um) and processed using methods described by Stainton et al (1977). Analysis was performed on a Technicon^{TM} Autoanalyzer^{TM} II. Samples for total dissolved phosphorus (TDP) were filtered in the lab using a Gelman glass fiber filter (pore size =1.0um) and processed using methods described by Prepas and Rigler (1982). The instrument used for analysis was a Cary 50 UV/Visible

Spectrophotometer, Varian Australia Pty Ltd, Mulgrave, Victoria 3170 Australia. TDS concentrations were calculated by summing the major anions and cations.

The deuterium/hydrogen isotope analysis of water was determined by chromium reduction as described in chapter 2, using methods of Freidman (1953), Coleman et al. (1982), Gehre et al. (1996), Nelson and Dettman (2001) and Donnelly et al. (2001).

The O^{18}/O^{16} ratio of natural waters is determined using the common CO_2-H_2O equilibration technique in which millimole quantities of CO_2 are equilibrated with water samples under constant temperatures. Subsequently, the CO_2 is cryogenically purified and analyzed mass spectrometrically for its O^{18}/O^{16} ratio. Note that this technique measures the isotopic activity of O^{18} and not the actual O^{18} concentration. For dilute waters, differences between isotopic activity and concentration are negligible. For saline waters and brines (TDS > 1000 mg/L), longer equilibration times were needed based on work by Epstein and Mayeda (1953), Sofer (1972), O'Neil et al. (1975) and Horita et al. (1993).

For this study, water samples with an ionic charge balance ratio of less than 10% were utilized. All ions were converted to milli-equivalents and the difference between the sum of cations and sum of anions was divided by the total sum of anions and cations. A total of four basins were removed from this analysis as their ionic charge balances ranged from 15% to 27%.

3.2.4 Wetland Connectivity and Pond Order

Both wetland connectivity to the pond and pond order were assigned after the sampling of the ponds was conducted in the summer of 2003 and 2004.

For the purpose of this chapter, a wetland is defined as a bog, fen, marsh or swamp. Wetland connectivity was characterized using a combination of both air photos and NTS 1:50,000 topographic maps. All streams and wetlands that were connected via surface flow, whether permanent or temporary at a 1:50,000-map scale, and were up gradient of the pond of focus were considered connected. Wetland connectivity was measured up to the outflow of the pond of focus, or encircled the pond of focus if the basin was isolated. Elevation changes on 1:50,000-map scale NTS maps were also used to assign divides in the flow of wetlands. If there was no elevation gradient and there were no signs of flow direction on the airphoto, wetland connectivity was divided between the open water of the pond of focus and the nearest open body of water, weather it was standing water or moving water. Air photos were scanned and imported into Arc Map Version 9.1. Air photos were then georeferenced using 1:50,000 NTS digital maps. Wetlands were then digitized to quantify both the area of the wetland and the open water area of the pond.

Pond order was defined as the position of a lake in the groundwater flow system similar to that presented by Soranno et al. (1999) and Riera et al. (2000). In this case a wetland flow connected to the pond was given the same value as a stream on a topographic map. Pond order was defined as a metric to analyze the effect of landscape position on the chemical parameters tested and are summarized as follows:

- -2 = was assigned to ponds that were hydrologically unconnected to the drainage network by surface water or wetlands;
- -1 = ponds that were hydrologically isolated from the surface drainage network, but had a wetland that was = < 2 times the diameter of the basin of study;
- 0 = ponds with no inlets but an outlet are termed headwater lakes, and tend to be spring fed. An outlet of a permanent stream or wetland was considered an outlet; and
- 1 = A pond drained by a 1st order stream or wetland would be assigned an order of 1. Subsequent pond order was determined using the method presented by Horton (1965).

3.2.5 Statistical Analyses

3.2.5.1 Ranking of Categorical Variables and Grouping of Ordinal Predictor Variables

Bedrock geology was ranked on a weathering gradient or permeability from high to low. With increased permeability, there is more potential for vertical movement of groundwater and increased mineral weathering and with decreased permeability there is more potential for overland flow and a decrease in mineral weathering. The dolomite/limestone is the most permeable and soluble rock type followed by the mixture of shale/dolomite, shale, and finally granite.

Surficial geology was scaled from high permeability which promotes groundwater to low permeability which promotes overland flow. Within the study area, the exposed bedrock (dolomite bedrock) is the most permeable, then coarse-grained glaciofluvial sediments, then a till setting composed of a mix of clay, silt and sand, and lastly fine-grained lacustrine sediments composed primarily of clay.

Wetland area connected to the ponds was originally presented as a continuous variable and was later grouped into categorical data. The four categories consisted of wetland areas of 0-0.1 km^2, 0.1-1 km^2, 1-10 km^2 and >= 10 $km^2$and were also ranked from low to high on their potential to produce OLF.

Pond order was originally presented as four categories. These categories consisted of negative order ponds (-2, -1), zero order ponds, 1st order ponds and ponds with an order >=2. These categories were also ranked on their landscape position of high to low.

3.2.5.2 Statistical Analysis Conducted on 147 Pond Data Set

To quantify the strength of the relationship between each variable tested and the four landscape factors (bedrock geology, surficial geology, wetland connectivity, pond order), box and whisker plots were used to give a visual representation of the distribution properties of a sample based on non-parametric measures of central tendency, dispersion, and skewness. These plots give information about the number of cases in each category within the factor tested and their statistical distribution as well as the presence, strength, and shape of the relationship between factor and variable.

Differences within factors were tested using one-way analysis of variance (ANOVA), with the categories of the factor used. If an ANOVA suggested that the categories within the factor tested differed significantly, a Bonferroni multiple means comparison was used to test the difference among categories. Linear regression analysis was not used because the environmental factors tested were not continuous, but ordinal data. The three ponds located within the sandstone geologic unit (KSR) were not applied to the ANOVA analysis or tests of orthogonality due to small sample size. P-values from the ANOVA's were discussed and presented as $p =< 0.001$ (very significant), $p > .0010 =< 0.010$ (strongly significant), $p > 0.010 <= 0.050$ (significant) and $p > 0.050 <= 0.100$ (marginally significant).

Tests of orthogonality were also conducted by running least squares means regression. This was used to determine the strongest relationship (linear, quadratic, or cubic) between variables and landscape factors tested.

3.2.5.2.1 Major Assumptions Applied When Using the One-Way ANOVA

Major assumptions are assumed when using an ANOVA and are summarized as follows. A one way ANOVA assumes that the population of scores within any factor of study is normally distributed and that the variance is the same for all the factors addressed and that each score is sampled randomly and independently from a normally distributed population.

The assumption of normality was checked by visual assessment of plotted residuals.

Outliers were identified by Systat for Windows© Version 11 (Systat) and removed one at a time until the p-value was not influenced. A Kruskal Walis one-way non-parametric analysis of variance was then run on the data and compared to the p-value of the ANOVA. The Kruskal Wallis analysis does not assume a normally distributed data set, therefore if the p-value was relatively close to the ANOVA the data were determined to be normally distributed. If the Kruskal Walis analysis did not confirm the results of the ANOVA, a log transformation of the data was performed and the ANOVA was run again.

ANOVA analysis was performed using Systat.

The following transformations or removal of data points were conducted on the data set prior to running the ANOVA analyses. Assessment of the data showed that the $SO_4/(SO_4+HCO_3)$ ratio data did not fit a normal distribution, therefore the data were transformed logarithmically before an ANOVA was run. A normal distribution of TDS was assumed, however there were a total of five extreme outliers identified by Systat Version 11. These outliers were removed from the ANOVA analysis and with respect to bedrock geology as a normal distribution is assumed; four outliers were in the shale and one in the shale/dolomite. Within surficial geology, there were two outliers in the coarse-grained lacustrine deposits and three in the glacial till. Within connected wetland area there was one outlier in the 0.1-1 km^2 area, three in the 1-10 km^2 area and one in the >=10 km^2 area of connected wetlands. Within pond order, there were three outliers in the negative order group, one in the 1st order and one in the >=2 order. Assessment of the TDP data indicated that the data needed to be transformed and a logarithmic transformation was applied to the data. Following the logarithmic transformation, there was an extreme outlier identified by Systat Version 11 and was removed from the ANOVA analysis. This shallow pond occurred in the shale/dolomite bedrock, the coarse-grained lacustrine surficial unit, was connected to >=10 km^2 area of connected wetlands, and was assigned a >=2 pond order. There were a total of two extreme outliers identified by Systat Version 11 with respect to TDN. These ponds were both located within the shale geologic unit, one in the glacial till and one in the fine-grained lacustrine surficial geologic units, both ponds were connected to 1-10 km^2 connected wetland areas and both ponds were assigned a negative pond order.

3.2.5.3 Nonmetric Multidimensional Scaling (NMS)

NMS is an ordination method suited to data that are non-normal or are on arbitrary, discontinuous, or otherwise undefined scales. This method can be used both as an ordination technique and as a method for assessing the dimensionality of a data set (McCune and Grace, 2002). NMS is an iterative search for a ranking and placement of n entities on k dimensions (axes) that minimizes the stress of the k-dimensional configuration.

Main advantages of NMS are as follows. NMS avoids the assumption of linear relationships among variables. Its use of ranked distances tends to linearize the relationship between distances measured in species space and distances in environmental space. This relieves the zero truncation problems, a common problem with heterogeneous community data sets. NMS also allows the use of any distance measure or relativization.

For this analysis PC-ORD version 4 was used to run the ordination. There were no data transformations performed on the data, however a general relativization was used on the data before the NMS ordination was run. The Sorenson (Bray Curtis) distance measure was used for the ordination. The starting configuration was produced with a random number generator. Comparing the final stress values among the best solutions assessed dimensionality of the data set and followed the methods described by McCune and Grace (2002).

NMS was conducted on the 147 subset of ponds and methods are similar to that described in chapter 2.

3.3 Results and Discussion

Mean chemistry of ponds based on geology and surficial geology are summarized in Table 3.1. Chemistry of ponds within the SRD and the ascending limb (within and outside the envelope) of the Gibbs (1970) model have much higher TDS and Na/Cl composition than adjacent ponds in similar geology and reflect the groundwater discharge from the Williston basin scale flow system. From herein, controls of chemistry of the ponds excluding ponds influenced by Williston basin groundwater discharge and ponds within the SRD are analyzed and discussed. The surface water composition and concentration of these ponds fall under the geologic control as defined by Gibbs (1970).

3.3.1 Ion Composition

The proportion of major ions can be used to determine the source of water and reflected by bedrock geology (Brownlow, 1996, Kalff, 2002) are presented on Figure 3.5. Variability of ion composition was generally related to bedrock geology. In general, ponds overlying the dolomite/limestone were a magnesium-bicarbonate type water, ponds overlying the shale/dolomite were a magnesium-bicarbonate type water. Ponds overlying the shale ranged from a calcium-magnesium-bicarbonate type water to a calcium-magnesium-sulphate type water, ponds overlying the sandstone were a calcium-bicarbonate type water, and ponds overlying the granite were a calcium-bicarbonate type water.

The ionic composition of precipitation obtained from Island Lake, Manitoba is generally a calcium-sulphate type water. This contrast of ion chemistry between the precipitation sample from Island Lake and the ponds indicates that most of the ponds are dominated by geology as described by Gibbs (1970). Only a few (< 5%) of the ponds showed similar ion composition to precipitation and were located in the shale bedrock. However the ponds with higher proportions of sulphate, similar to precipitation, were generally associated with higher TDS concentrations (400 to 1000 mg/L) which does not imply precipitation dominance.

The continental climate is moderate, and there is no observable trend in chemistry from the wetter northeast shield area to the drier southwest region. At this scale climate variability is not great enough to effect regional changes in chemistry. In this study area geology varies more widely and as expected from the Gibbs (1970) model, will potentially have the greatest influence on surface water chemistry.

An NMS ordination of all major ions was run on the 147 pond data set and is shown on Figure 3.6. A Pearson correlation is shown on Table 3.2 and indicates that in general, carbonates are correlated with axis 1 and all other ions are correlated with Axis 2. Ponds overlying the dolomite/limestone bedrock were characterized by higher concentrations of carbonates which reflect the underlying geology and Axis 1. Ponds overlying the limestone/dolomite bedrock showed variability in chemistry. The majority of the waters showed higher concentrations of ions implying more groundwater interactions. Only a few ponds trend toward a precipitation signature which implies hydraulic isolation or low weathering rates. Ponds overlying the shale showed two groups. The first group was characterized by higher concentrations of sulphate which would imply increased groundwater interactions or increased weathering of the bedrock. The second group was characterized by lower concentrations of ions and trended towards a precipitation signature, which would imply some isolation and in the regional uplands of the study area. The ponds overlying the granite bedrock were characterized by low concentrations of all ions and trended towards the precipitation signature and imply isolation or low weathering rates of the bedrock. Ponds located on all bedrock types pulled towards precipitation; however no waters showed the same signature of precipitation which would indicate some local controls or isolation.

3.3.1.1 Major Cations

Further analysis of cations and the relative controls of bedrock geology with local controls of surficial geology, pond order and wetland connectivity were also assessed. The relative proportion of major cation chemistry of ponds within the study area consisted of calcium-magnesium and magnesium-calcium types of water (Figure 3.5). The relative proportion of sodium and potassium rarely exceeded 20% of the major cations sampled (Figure 3.5).

To test the relationship between major cation chemistry and landscape factors, a ratio of Ca/(Ca +Mg) was used for the ANOVA analysis. Complete ANOVA tables are in Included in Appendix A. An increase in the Ca/(Ca+Mg) ratio indicates an increase of the relative proportion of calcium in the ponds. A range of regional and local scale interactions may influence the cation composition.

The Ca/(Ca +Mg) ratio varied very significantly with bedrock geology ($p = 0.000$, $r^2 = 0.427$) and surficial geology ($p = 0.000$, $r^2 = 0.261$), and was strongly significant with wetland connectivity ($p =0 .002$, $r^2 = 0.093$) (Table 3.3 and Figure 3.7). There was a very significant positive linear trend with the increase of the Ca/(Ca +Mg) ratio in ponds across bedrock with varying weathering rates or reduced permeability (Table 3.4, Figure 3.7a). Higher proportions of magnesium in ponds overlying the dolomite/limestone geology have been observed to increase via mineral dissolution of dolomite/limestone in groundwater, which results in a lower Ca/(Ca +Mg) ratio (Kalff, 2002). Shorter flowpaths and increased OLF to ponds overlying the granite bedrock resulted in a higher Ca/(Ca +Mg) ratio and thus, reflects a precipitation signature. All trends were significant between surficial geology and the Ca/(Ca +Mg) ratio. There was also a very significant quadratic relationship between the Ca/(Ca +Mg) ratio and wetland connectivity (Table 3.4, Figure 3.7d). This indicates that surface waters are trending towards a precipitation signature with increasing wetland connectivity. However, when wetland connectivity exceeded 10 km^2 the Ca/(Ca +Mg) ratio decreased and reflected larger contributions of groundwater. This may be due to the fact that large fen complexes in a sub humid climate are typically groundwater fed (Mitch and Gosselink, 1993).

Analyses of interactions between variables are shown on Figure 3.8. Bedrock geology tends to override cation composition, as the Ca/(Ca +Mg) ratio differs between bedrock types (Figure 3.8a). If surficial geology has control, the Ca/(Ca +Mg) ratio would be expected to decrease with longer flowpath. The results show that the ponds sampled within the exposed bedrock were all sampled on the dolomite/limestone, thus the low Ca/(Ca +Mg) ratio reflects dissolution of magnesium rich dolomite bedrock rather than influence on flowpath via surficial geology (Figure 3.8a). Trends in the Ca/(Ca +Mg) ratio were not consistent among bedrock types with the decrease in texture of surficial geology and thus the potential for subsurface flow (Figure 3.8a). The dominance of dolomite bedrock in ponds connected to large wetlands appears to influence cation composition (Figure 3.8b). Large wetlands override in regions of permeable bedrock (dolomite/limestone) and the potential for groundwater flow.

Banens (1987) and Johnson et al. (1997) showed findings that suggested that the ionic proportions of surface water chemistry were related to the rock mineralogy of the underlying bedrock. However, these studies were conducted in simple geologic settings with little or no till deposits and have generally not been applied to more complex geological settings of the Boreal Plains of Canada. As hypothesized, there were lower proportions of calcium and larger proportions of magnesium associated with ponds overlying the dolomite/limestone, as the most common source of magnesium in natural waters is mineral weathering of dolomite (Hounslow, 1995). This indicates that even though the glacial till in the study area ranges from a couple of metres in the till veneer settings up to approximately three-hundred meters in the Duck Mountains, the cation composition of ponds within the study area are derived or influenced by their underlying bedrock geology. Relatively higher proportions of calcium were associated with ponds overlying the granite setting, which are likely the result of relatively shorter or shallower flowpaths over top of hard insoluble granite. These shorter flowpaths are the result of shallow or absent till deposits overlying impermeable granite, which can result in more lateral flows of water which reflect the ionic characteristics of precipitation (Winter, 2001). Findings presented by Moser et al., (1998) indicated that geology was the major driver of physical and chemical variables in Wood Buffalo Park. Moser et al. (1998) indicated that the proportion of calcium increased from lakes overlying granite, limestone and then shale. Whereas, within the study area, the proportion of calcium increased in ponds overlying the dolomite/limestone, shale and then granite. These results may differ as the cation composition of precipitation may differ between study areas. Waters overlying the shield sites in Wood Buffalo National Park indicate greater proportions of sodium and potassium which may imply the source water composition is different and short flowpaths dominate or direct mineral weathering of granite with no glacial till releases more sodium.

These results suggest that mineral weathering of the underlying geology is the major driver of cation composition of ponds of the study area. To a lesser extent, the permeability of bedrock as it influences scale of flow may also influences the relative proportion of calcium in ponds within the study area.

3.3.1.2 Major Anions

The relative proportion of major anion chemistry of ponds within the study area ranged from bicarbonate to sulphate water types (Figure 3.5). Approximately 85% of the ponds sampled within the study area were bicarbonate type water, while the remaining 15% ranged from bicarbonate-sulphate and sulphate waters (Figure 3.5). Chloride composition of all these ponds was low. Therefore, to test the relationship between pond anion chemistry and the landscape factors tested a ratio of $SO_4/(SO_4+HCO_3)$ was used. An increase in the $SO_4/(SO_4+HCO_3)$ ratio indicates an increase of the relative proportion of sulphate in the water.

The $SO_4/(SO_4+HCO_3)$ ratio varied very significantly with bedrock geology ($p = 0.000$, $r^2 = 0.390$) and varied significantly with surficial geology ($p = 0.031$, $r^2 = 0.061$) (Table 3.3 and Figure 3.9). A very significant quadratic relationship between the $SO_4/(SO_4+HCO_3)$ ratio and bedrock geology indicates that the $SO_4/(SO_4+HCO_3)$ ratio was not related to the reduced weathering rate of the bedrock (Table 3.4, Figure 3.9a). Rather, the higher $SO_4/(SO_4+HCO_3)$ ratio was correlated with ponds overlying the shale/dolomite or shale bedrock. A significant cubic relationship between surficial geology and the $SO_4/(SO_4+HCO_3)$ ratio, indicates elevated proportions of sulphate in ponds overlying coarse-grained lacustrine and fine-grained lacustrine sediments (Table 3.4, Figure 3.9b). There was no significant correlation between the $SO_4/(SO_4+HCO_3)$ ratio and wetland connectivity or pond order. Analyses of interactions between bedrock geology and surficial geology show that the higher $SO_4/(SO_4+HCO_3)$ ratios are related to either the shale or the shale/dolomite geology underlying the ponds (Figure 3.10).

The results discussed above are likely not the result of scale of flow as influenced by different bedrock types, but mineral weathering of the underlying bedrock. In general, the $SO_4/(SO_4+HCO_3)$ ratio increased in ponds overlying the shale and shale/dolomite bedrock. These results agree with findings by Meybeck et.al (1989), who found that on average waters draining from shale bedrock had higher proportions of sulphate in comparison to carbonate rocks. Cole (1994) discussed that pyrite and gypsum contain sulfur and are common in sulfide ore deposits and reduced rocks like coal and some shales. Furthermore, Moyle's (1956) study of the regional limnology of Minnesota also clearly showed that Cretaceous seas resulted in elevated sulphate concentrations in lakes. These findings may likely be true for the Cretaceous and Devonian shales underlying the glacial deposits of the study area.

Similar to cation composition, the results suggest that mineral weathering of the bedrock is the major driver of anion composition of ponds of the study area.

3.3.2 Weathering Parameters

3.3.2.1 pH

pH differed very significantly with bedrock geology ($p = 0.000$, $r^2 = 0.124$), surficial geology ($p = 0.001$, $r^2 = 0.112$) and wetland connectivity ($p = 0.000$, $r^2 = 0.137$) (Table 3.3 and Figure 3.11). There was a very significant negative linear trend between pH and the reduced weathering rate or reduced permeability of the underlying bedrock (Table 3.4, Figure 3.11a). The highest pH values were in ponds overlying the dolomite/limestone and the lowest pH values were associated with ponds overlying the granite bedrock. The data also showed a very significant negative linear trend between pH and the reduced texture of surficial geology (Table 3.4, Figure 3.11b). The highest pH values were associated with ponds overlying the exposed limestone/dolomite bedrock, while the lowest pH values were associated with ponds overlying the fine-grained lacustrine sediments. There was also a very significant quadratic relationship between pH and wetland connectivity (Table 3.4, Figure 3.11d). As wetland connectivity increased, there was a decrease in pH which may reflect an increase in a precipitation signature. However, in ponds connected to large wetland complexes the pH increased which may reflect an increase in groundwater. There was no significant relationship between pond order and pH.

Analyses of interactions between variables and how they influence pH is shown on Figure 3.12. Although pH differed between bedrock types, pH generally decreased from exposed bedrock to fine-grained sediments with the exception of ponds overlying the shale (Figure 3.12a). The ponds overlying the exposed bedrock were as previously mentioned located on the dolomite/limestone geologic unit and drove the significant p-value for the ANOVA. The Bonferroni test supports this as significant differences between groups were between ponds overlying the exposed bedrock and the glacial till or fine-grained lacustrine sediments (Figure 3.11b). Also, the lowest pH values were within ponds overlying fine-grained lacustrine sediments overlying the granite bedrock. A quadratic trend in pH was also consistent with the potential for wetlands to produce OLF within different bedrock units; however the lower pH values for ponds connected to a 1-10 km^2 area of wetlands was potentially driven by ponds overlying the granite bedrock (Figure 3.12b).

It was found that bedrock geology was the best predictor of pH within the study area. Similar to findings by Moser et al. (1998) higher measures of pH were associated with soft sedimentary carbonate rocks and lowered in the presence of hard igneous rocks, and is likely attributed to the mineral weathering of the soils and rocks of the surrounding catchments. The decrease in pH may also be attributed to scale of flow, as flow overlying permeable bedrock is characterized by intermediate to regional flow systems which can result in more vertical flow (Devito et al., 2005a). These relatively larger flow systems will result in a higher pH from groundwater. Flow overlying impermeable bedrock is characterized by intermediate to local flow systems and lateral flow through surficial substrates dominates (Devito et al., 2005a). This will result in lower pH values that reflect the low pH of local precipitation.

Surficial geology was also significant in explaining pH, however these results are spurious and likely reflect the influence of the underlying geology as the exposed bedrock was overlying the dolomite/limestone bedrock and the lowest pH values were associated with the fine-grained sediments overlying the hard granite bedrock.

Wetland connectivity was also found to express significant differences in pH between groups. This can be explained by the relative contribution of precipitation to the overall water budget of the ponds of the study area. As hypothesized, ponds connected to larger wetlands showed a relative decrease in pH and are driven towards the normal range of precipitation (pH of approximately 5-6.7) as described by Brownlow (1996). This implies that the general flowpath of waters influencing ponds connected to 1-10 km^2 of wetlands were driven by relatively shorter surface flows and by increased OLF. Ponds connected to large wetland complexes are likely fed by groundwater and result in higher values of pH as the proportion of bicarbonate and carbonate increases with water rock interactions (Tóth, 1999). The majority of the ponds connected to large wetlands (>=10 km^2 area) were typically large fen complexes, which are typically fed by a combination of groundwater and surface water sources, which result in longer hydrological flowpaths (Mitch and Gosselink, 1993).

In summary, bedrock geology and to a lesser extent wetland connectivity are good estimators of pH. This indicates there is some complexity between the controls of regional bedrock geology and wetland connection across the study area.

3.3.2.2 TDS

TDS concentrations varied strongly with bedrock geology ($p = 0.002$, $r^2 = 0.101$) and were significant with both surficial geology ($p = 0.018$, $r^2 = 0.072$) and wetland connectivity ($p = 0.044$, $r^2 = 0.058$) (Table 3.3 and Figure 3.13). There was a strong significant negative linear trend between TDS and the reduced weathering rate or permeability of the underlying bedrock geology (Table 3.4, Figure 3.13a). TDS concentrations varied the most between ponds overlying the granite and all other bedrock types. There was also a strong negative linear and quadratic relationship with the reduced texture of surficial geology and TDS (Table 3.4, Figure 3.13b).

Analyses of interactions between variables and how they influence TDS are shown on Figure 3.14. These results support the results discussed earlier that bedrock geology, specifically the granite bedrock influences TDS concentrations via reduced weathering rates or by increasing OLF into the ponds. Within bedrock units, there is a general decrease in TDS concentrations with reduced grain size of surficial geology with the exception of ponds overlying the shale bedrock (Figure 3.14a). Visually the data appear to follow a linear trend. This indicates more flow which results in dilution of the solutes in the pond or more OLF which does not contain appreciable amounts of solutes as a result of less ion exchange with shorter residence times between soil and water (Williams, 1985). These results may be spurious as the largest difference was between ponds overlying the exposed bedrock of the dolomite/limestone and the remaining surficial geologic units. Across shale and granite bedrock, TDS concentrations generally decreased with wetland area connected to the ponds and increased with ponds connected to large wetlands (Figure 3.14b).

Isotopes oxygen 18 relative to deuterium with TDS concentrations are plotted on Figure 3.15. By using methods presented by Krabbenhoft et al., (1994), the majority of the ponds generally appear to indicate some level of evaporative influence as they are skewed away from the meteoric water line (MWL) derived from The Pas, Manitoba. In general, evaporative processes are influencing the higher TDS concentrations (300-900 mg/L) and the higher TDS concentrations may be the result of some evapoconcentration as observed in isolated ponds in Minnesota (Webster et al., 2000). The ponds that plot closest to the MWL are generally dilute waters and likely reflect a precipitation signature. However, ponds with TDS measures between 100 to 300 mg/L appear to indicate a complex interaction between atmospheric precipitation, groundwater and evaporative influences to the ponds of the study area.

Bedrock geology explained the most variance in regards to TDS concentrations. It was hypothesized that easily weathered carbonate rocks would result in higher measures of TDS. The TDS of ponds would decrease as the catchment rock stability or hardness increased from soft sedimentary carbonate rocks to hard igneous rocks. The more dilute waters were associated with ponds overlying the granite bedrock, which coincides with findings by Meybeck et al. (1989) and Moser et al (1998), while the highest measures of TDS were located in ponds overlying the shale geologic unit and the sedimentary carbonate rocks. The observed salinity and component ions in fresh waters are usually determined by reactions that take place in the soils and rocks of the catchments surrounding the ponds of the study area. The higher measures of TDS may also be associated with more complex groundwater flow systems associated with the permeable carbonate rocks and lower TDS concentrations associated with harder impermeable granitic bedrock (Tóth, 1999).

Similar to pH, surficial geology was found to be significant in explaining TDS concentrations, however these results may be spurious as the higher concentrations of TDS were associated with the exposed dolomite/limestone bedrock which drove the significance of the ANOVA. However there was still a general decrease in TDS concentrations with reduced grain size of surficial geology. This indicates increased OLF or rapid flow generation over fine-grained material with relatively high antecedent soil moisture to dilute surface waters (Mulholland et al., 1990). The exception was ponds located in fine-grained lacustrine sediments over shale bedrock. These are relatively isolated, and some evapoconcentration may be occurring, or dissociation with clay rich sediments (Webster et al., 2000)

Wetland connection was also found to be significant in explaining TDS concentrations of ponds. TDS concentrations decreased with increased connected wetland area which indicates increased saturated overland flow as peatlands and riparian wetlands are considered key runoff generating areas (Devito et al., 2005a). Higher concentrations of TDS were associated with ponds connected to large fen complexes (>=10 km^2) and were likely groundwater fed. There is no trend observed between pond order and TDS which likely reflects poor drainage and lack of a catchment to delineate TDS concentration.

In summary, bedrock geology and to a lesser extent surficial geology and wetland connectivity are good estimators of TDS. This indicates some complexity between the controls of regional scale bedrock geology, local surficial geology and wetland connectivity across the study area.

3.3.3 Nutrients

3.3.3.1 DOC

DOC concentrations varied very significantly when stratified by surficial geology ($p = 0.000$, $r^2 = 0.120$) and were marginally significant when stratified by wetland connectivity ($p = 0.068$, $r^2 = 0.050$) (Table 3.3 and Figure 3.16). A very significant positive linear trend between DOC and texture of surficial geology was observed (Table 3.4, Figure 3.16b). There was also a marginally significant positive linear trend between DOC concentrations and wetland connectivity (Table 3.4, Figure 3.16d).

Analyses of interactions between variables and how they influence DOC is shown on Figure 3.17. In general, DOC concentrations in the ponds increase with wetland connectivity within the fine-grained and coarse-grained sediments, except there is little change from moderate to large connectivity of wetlands to ponds on the exposed dolomite/limestone bedrock. DOC concentrations of ponds connected to large wetlands decreased with ponds overlying the glacial till and exposed bedrock which suggests increased groundwater interactions or dilution.

Isotopes of oxygen 18 and deuterium with DOC concentrations are plotted on Figure 3.18. In general, evaporative processes are influencing the higher DOC concentrations (40-110 mg/L) and appear to be the result of evapoconcentration or isolation (Webster et al., 2000). The ponds with dilute to moderate concentrations of DOC (0-40 mg/L) range from plotting near the MWL and skew away from the MWL. The plot of TDS and DOC is a relatively poor relationship ($r^2 = 0.0258$) (Figure 3.19). The lower concentrations of DOC may result from a complex interaction between surface peatland connections and the subsurface geologic connection between the ponds.

Within the study area, surficial geology was the most significant factor in assessing differences in DOC concentrations. The ponds in the poorly drained fine-grained sediments resulted in surface waters with the highest concentrations of DOC. As stated by Winter (2001) the porosity and permeability of the subsurface environment generally control the behavior of surface flows and groundwater systems. Higher antecedent moisture levels maintained by fine-grained materials permit infiltration capacities to be reduced as the upper part of the soil profile becomes saturated more rapidly (Burt and Haycock, 1996). In streams and most lakes, much of the detrital organic carbon, mostly dissolved, is of terrestrial origin from direct leaching from living vegetation or from soluble compounds carried in runoff from dead plant material in various stages of decomposition (Wetzel, 1983). Therefore, catchments dominated by fine-grained surficial material promote both development of peat and near surface and overland flow resulting in large sources of DOC to ponds. Local scale factors of surficial geology and to a lesser extent wetland connectivity were significant in explaining DOC concentrations of ponds across the study area.

3.3.3.2 TDP

TDP varied very significantly with surficial geology ($p = 0.001$, $r^2 = 0.106$), pond order ($p = 0.002$, $r^2 = 0.104$) and wetland connectivity ($p = 0.001$, $r^2 = 0.109$) and (Table 3.3, Figure 3.20). A strongly significant quadratic relationship between surficial geology and TDP indicates concentrations decreased in ponds overlying the exposed bedrock, coarse-grained sediments and glacial till surficial geology and increased in ponds overlying the fine-grained sediments (Table 3.4, Figure 3.20b). Opposite to that observed with the weathering products and indicators of groundwater sources, a very significant quadratic relationship exists between TDP and wetland connectivity (Table 3.4, Figure 3.20d,). This indicates that TDP concentrations increased with wetland connectivity and decreased dramatically with large wetlands connected to ponds. A strongly significant negative linear trend between pond order and TDP was also shown (Table 3.4, Figure 3.20c).

Analyses of interactions between variables and how they influence TDP are shown on Figures 3.21 and 3.22. Excluding shale/dolomite bedrock, there is a general increase in TDP with decrease in particle size (and potential for OLF)

(Figure 3.21). The quadratic relationship results from high TDP concentrations in the dolomite/limestone exposed bedrock and higher TDP concentrations in ponds on fine-grained sediments. The high TDP concentrations in ponds overlying the exposed dolomite/limestone bedrock may result from increased weathering and geochemical weathering of the source rock (Wetzel, 1983). Ponds overlying the coarse-grained sediments, glacial till and fine-grained sediments showed an increase in TDP concentrations with wetland area connected to the ponds and a decrease in TDP concentrations with connection to large wetlands (Figure 3.22a). With the exception of ponds overlying the coarse-grained lacustrine sediments, there was generally a decreasing trend in TDP with pond order (Figure 3.22b).

Isotopes of oxygen 18 relative to deuterium indicate that higher TDP concentrations (20-160 μg/L) are associated with higher oxygen 18 values which indicate evapoconcentration or isolation (Figure 3.23). The ponds with more dilute concentrations of TDP (0-20 μg/L) show lower oxygen 18 values and range from plotting near the MWL and skew away from the MWL. These relatively lower concentrations of TDP may result from the complex interaction between nutrient poor precipitation or the adsorption of phosphorus to sediments in groundwater.

Surficial geology, wetland connectivity, and pond order influenced phosphorus concentrations across the study area. Phosphorus was not correlated to bedrock via mineral weathering or flowpath. This indicates the TDP concentrations are related to more intermediate to local scales of flow. Surficial geology was found to be significant and implies that with finer-grained sediments and lower hydraulic conductivity, there is an increasing trend in TDP concentrations. Higher antecedent moisture levels maintained by fine-grained materials reduce infiltration rates and the upper part of the soil profile becomes saturated more rapidly (Burt and Haycock, 1996). This permits biologically available nutrients from the shallow organic and mineral layers to be released, and can be a source of phosphorus to ponds (Huang and Schoenau, 1996 and Evans et al., 2000). Therefore,with fine-grained material there is an increase of near surface flow through organic materials which increases phosphorus inputs to ponds.

Wetland connection, as it relates to predicting TDP concentrations was found to be significant. With increasing wetland connection, surface flow pathways dominate with quick flow generation which can occur during precipitation events (Devito et al., 2005a). As mentioned previously, peatlands and riparian wetlands can be major sources of phosphorus to lakes (Macrae et al., 2005 and Devito et al., 2000). However, when large wetlands are adjacent to ponds, TDP concentrations decreased within the study area. The reduced phosphorus concentrations are attributed to either nutrient poor groundwater associated with large wetlands or nutrient concentrations in ponds are diluted with increased flow (Mitch and Gosselink, 1993, Williams, 1985).

Pond order was also significant in explaining the variance of TDP. TDP concentrations generally decreased with increasing pond order. In contrast, Soranno et al. (1999) showed increasing concentrations of phosphorus with lake order, with the exception of lake chains where groundwater flow was the dominant hydrologic flowpath between lakes. Soranno et al. (1999) expected reactive variables such as phosphorus and nitrogen to decrease with increasing lake number due to the high retention of nutrients (removal by deposition into sediments) that is known to occur in lakes. Biological dynamics may also reduce the occurrence of landscape patterning of nutrient concentrations with landscape position (Rechkow and Chapra, 1983). Dilution and nutrient poor groundwater of higher order ponds can also result in the lower concentrations of nutrients (Williams, 1985).

In summary, local scale factors of surficial geology, wetland connectivity and pond order were good estimators of TDP in ponds across the study area.

3.3.3.3 TDN

TDN concentrations varied significantly when stratified by bedrock geology ($p = 0.043$, $r^2 = 0.057$) and was marginally significant when stratified by surficial geology ($p = 0.068$, $r^2 = 0.050$) (Table 3.3 and Figure 3.24). TDN showed a significant quadratic relationship with the reduced weathering rate or reduced permeability of bedrock geology (Table 3.4, Figure 3.24a). TDN concentrations increased in ponds overlying the dolomite/limestone, shale/dolomite and shale bedrock and than decreased in ponds overlying the granite bedrock. TDN concentrations showed a significant positive linear relationship with the decreasing texture of surficial geology (Table 3.4, Figure 3.24b).

To show possible interaction or a confounding relationship between bedrock geology and surficial geology or connected wetland area, further analysis of TDN concentrations in ponds is shown on Figure 3.25. In general, TDN concentrations increased with finer-grained texture of surficial geology, with the exception of ponds overlying the shale/dolomite (Figure 3.25a). Similar to TDP, TDN concentrations followed the same trend at a local scale. With increasing connected wetland area, there was an increase in TDN concentrations (Figure 3.25b). When ponds were connected to large wetlands there was a decrease in TDN concentrations and was likely the result of nutrient poor groundwater through mineral soil or increased flow which led to dilution (Macrae et al., 2006, Williams, 1985).

Isotopes of oxygen 18 and deuterium with TDN concentrations are plotted on Figure 3.26. In general, evaporative processes are influencing the higher TDN concentrations (1500-6500 μg/L) and appear to be the result of evapoconcentration or isolation. The ponds with more dilute concentrations of TDN (0-1500 μg/L) range from plotting near the MWL and skew away from the MWL. These lower concentrations of TDN may be influenced by a combination of precipitation or nutrient poor groundwater.

Unlike TDP, the best predictor of TDN was found to be bedrock geology, with nitrogen concentrations in ponds relatively lower in basins overlying the granite geologic unit and highest in ponds overlying the shale geology. Inputs of nitrogen by groundwater can be a major part of the annual nitrogen loading in many lakes, especially regions rich in limestone, as some limestones have been found to be major sources (Wetzel, 1983). Studies have also shown that precipitation can be a major source of nitrogen to oligotrophic lakes in mountainous regions of granitic bedrock as it is not easily weathered (Likens and Bormann 1972). However, lakes and their drainage basins from atmospheric sources have generally been considered to be minor in comparison with that from direct terrestrial runoff (Wetzel, 1983).

The variability of nitrogen concentrations were not significant when compared to surficial geology, connected wetland area and pond order, but trends were similar to TDP and can be attributed to scale of flow and hydrological flowpath. Therefore as previously discussed, near surface flows as influenced by surficial geology would appear to be influencing TDN concentrations with the exception of basins located in coarse-grained lacustrine sediments overlying the shale/dolomite geologic unit which may be a potential source.

Wetland connectivity and TDN concentrations of ponds was not found to be significant. However, similar to TDP concentrations, with increasing wetland connectivity, surface OLF pathways dominate with quick flow generation through surface organic layers which can be sources of nitrogen to these ponds (Macrae et al., 2006). As discussed previously, reduced nitrogen concentrations associated with large wetlands are attributed to either nutrient poor groundwater associated with large wetlands or surface waters diluted with increased OLF and quick flow generation (Devito et al., 2000, Devito et al. 2005a).

Pond order was not significant in explaining the variance of TDN, however TDN concentrations generally decrease with pond order. As discussed previously, reactive variables such as phosphorus and nitrogen tend to decrease with increasing lake number due to the high retention of nutrients that is known to occur in lakes (Rechkow and Chapra, 1983).

3.3.3.4 Nutrients Summary

Plots of TDP vs. DOC, TDN vs. DOC and TDP and TDN are presented on Figures 3.27, 3.28 and 3.29; and the plots show r^2 coefficients of 0.2812, 0.6123 and 0.5502, respectively. These results imply that TDN is highly correlated to DOC and the potential source of TDN may be associated with flow through peatlands or soil organics, while the source of phosphorus is soil organics, with some noise. The good relationship between TDN and TDP indicate similar processes are influencing nutrient chemistry. Differences between TDP, TDN and DOC may be attributed to in lake processes which remove colored organic compounds by a combination of photodegradation and photobleaching (Curtis and Schindler, 1997).

With the exception of TDN, there is no trend between bedrock geology and the nutrient parameters tested. Surficial geology and wetland connectivity were significant in explaining DOC and TDP, as the potential to increase OLF through organic and mineral layers of the soil can be a major source on nutrients to ponds or lakes (Huang and Schoenau, 1996 and Evans et al., 2000). The local factor of pond order was also significant with TDP, and concentrations generally decreased with increasing order. With increasing order it is hypothesized that there was an increase in nutrient poor groundwater as nutrients are often adsorbed or buffered (Rechkow and Chapra, 1983).

3.4 Conclusion

The main objective of this chapter was to test whether surface water chemistry can be related to hydrological processes, and to determine which scale and which landscape unit best predicts surface water chemistry of the Canadian Boreal Plain and transition to the Shield.

The climatic gradient across the study area was minimal (gross evaporation generally exceeded precipitation). Thus, the influence of climate on flowpath and flowlength and its influence on nutrient and solute chemistry of ponds were not directly evaluated. Of the ponds tested in chapter 3, TDS ranged from 49 to 914 mg/L and composition included calcium-bicarbonate, magnesium-bicarbonate and calcium-magnesium-sulphate type waters. There was no increase in solutes or the relative proportion of sodium and chloride across the range of excess soil moisture to soil moisture deficit of the study area. This indicates that solute proportion, and to some degree concentration was largely influenced by local processes interacting with geology and not the evaporation-crystallization process. Evapoconcentration may influence or increase solute concentration, but not enough to affect the precipitation of calcium bicarbonate from these waters.

At a regional scale, bedrock geology was the best estimator of major ion composition, weathering parameters (TDS and pH) and to a lesser extent TDN. Bedrock geology influenced the relative proportion of ions, pH and TDS by one of two mechanisms. The first mechanism is by direct mineral weathering of the bedrock; and the second mechanism is by the permeability of the bedrock as it influences flowpath and flowlength. Ponds overlying granite bedrock were characterized by lower concentrations of solutes, ionic composition similar to local precipitation and lower measures of pH and TDS. These results can be associated with more surface dominated flowpaths as influenced by the permeability of the bedrock or reduced weathering rates. Ponds overlying more permeable sedimentary bedrock were characterized by higher measures of pH and TDS, and ionic composition of the waters reflected more groundwater dominated flowpaths or mineral weathering of the bedrock.

At a more local scale, the texture of surficial deposits influenced the nature and type of flowpath connecting slopes to ponds of the study area. Ponds overlying a fine-grained surficial geologic environment appeared to have more potential to generate overland flow as concentrations of TDP, TDN and DOC increased and to a lesser extent, TDS concentrations decreased. The increased concentrations of nutrients resulted from the increased potential for overland flow through organic layers of catchments as they can be major sources of nutrients (Macrae et al, 2005 and Macrae et al., 2006). TDS concentrations were generally lower in ponds overlying the fine-grained lacustrine sediments. This implies shorter flowpaths which results in reduced hydrologic residence time of water with soil, which reduces ion exchange (Bache et al., 1984). Ponds overlying coarse-grained lacustrine sediments appeared to reflect more groundwater contributions and were likely located in intermediate to regional flowpaths as concentrations of TDP, TDN and DOC were respectively lower and TDS concentrations were relatively higher. The lower concentrations of TDP and DOC were the result of nutrient poor groundwater to the ponds or dilution via increased groundwater (Williams, 1985).

At a local scale, with an increase in wetland connectivity, there is potentially an increase in overland flow and quick flow generation during precipitation events. This resulted in a general increase in TDP, TDN and DOC concentrations and a decrease in pH and TDS concentrations across similar bedrock and surficial geologic settings. The increase of nutrients is likely the result of overland flow through nutrient rich organic layers or wetlands within the catchments (Macrae et al., 2005 and Macrae et al., 2006). While the reduced pH and TDS concentrations is likely the result of increased OLF and reduced ion exchange. Large wetland complexes connected to the ponds resulted in reduced TDP and TDN concentrations and increased pH and TDS concentrations and indicates increased nutrient poor groundwater contributions or dilution from increased flow into the pond (Williams, 1985). DOC concentrations were largely related to surficial geology and there was some relationship with connected wetland area. The lack of a strong relationship indicates complex interaction between wetland connectivity and the subsurface geologic connection to the ponds of the study.

Landscape position (pond order) was a relatively poor measure to characterize nutrient and solute chemistry of the study area. A decrease in TDP concentrations with increasing pond order was the only significant trend observed at a local scale. There was a decreasing trend in pH and TDN with increasing pond order, but they were not significant. Ponds located lower in the landscape did not show increased solute concentrations from increased groundwater contributions, but there were lower concentrations of nutrients. This was likely the result of nutrient retention (removal by deposition into sediments) or dilution from increased groundwater (Rechkow and Chapra, 1983 and Williams, 1985).

Understanding the dominant hydrological processes and their influence on major ion composition, concentration and nutrient chemistry will allow managers to assess the susceptibility of aquatic systems to landuse and climate change. Dominant controls of surface water chemistry varied across the study area. In general, bedrock geology was the major control of chemical composition, TDS and pH, and had little to no control on nutrients status of the ponds, with the exception of TDN. Thus to manage salinity and composition of waters, a generalization across bedrock types would suffice. In general, a shift to more local scale factors of surficial geology and wetland connectivity were significant in explaining the variability of nutrients across the study area. Thus, to manage the nutrient status of ponds and their susceptibility to landuse and climate change, surficial geology and wetland connectivity should be applied.

Table 3.1. Distribution and average chemistry of ponds sampled between geologic units of the study area. Ponds noted with * were removed from the analysis for chapter 3 (located within the SRD or fell within the ascending limb of the Gibbs model) as they were previously discussed in detail in chapter 2.

Bedrock Geology	km^2	Surficial Geology	km^2	Basins Sampled	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	CO_3 (mg/L)	pH	TDS (mg/L)	TDP (µg/L)	TDN (µg/L)	DOC (mg/L)
Dolomite/ Limestone N = 66	20,133	Coarse-grained Lacustrine	2,724	1	28.3	16.4	3.2	1.2	0.5	1.1	140.7	12.4	8.9	203.8	7.8	793.6	39.4
				24*	22.8*	20.1*	39.2*	7.1*	64.6*	9.1*	122.3*	18.5*	8.9*	303.5*	14.1*	1285.9*	25.2*
		Exposed Bedrock	1,687	10	20.6	38.7	2.7	1.8	1.3	0.8	212.7	27.6	8.6	303.7	13.3	920.3	16.5
		Glacial Till	11,696	27	19.7	20.9	8.3	2.8	4.6	1.2	154.4	8.65	8.2	218.8	8.29	1201.1	32.1
				4*	22.2*	19.4*	29.6*	5.8*	55.8*	0.8*	115.5*	19.7*	8.75*	267.7*	11.1*	1424.8*	31*
		Fine-grained Lacustrine	1,317	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Shale/ Dolomite N = 23	8,239	Coarse-grained Lacustrine	1,173	5	34.6	24.7	11.3	3.6	9.1	66.6	148.1	4.4	8.3	301.4	41	1581.9	37.5
				1*	30.8*	28.5*	60.4*	3.4*	3.4*	164.9*	159.3*	3.29*	8.5	454.1*	10.7*	1466.6*	49.3*
		Glacial Till	5,832	6	22.9	13.9	3.5	1.3	2.1	0.2	129.3	5.7	8	175.6	9.2	948.6	23.1
				4*	54.3*	49.8*	546.6*	20.3*	928.1*	74.0*	174.8*	37.1*	8.4*	1883.8*	14.3*	2347.6*	47.2*
		Fine-grained Lacustrine	1,192	2	17.4	12.4	6.7	0.5	4.8	0.2	105.5	0.2	8	145.1	11.9	1250.9	44.1
				5*	238.3*	106.1*	2565.3*	72.3*	4685.4*	374.6*	178.2*	4.1*	8*	8224.1*	24.6*	3323.3*	64.5*
Shale N = 88	30,463	Coarse-grained Lacustrine	2,287	22	35.5	20.2	8.1	3.1	1.3	49.5	154.5	3.7	8	275.8	12.8	1186.5	26.3
				2*	29.6*	15.8*	3.0*	2.4*	0.7*	19.4*	144.9*	0*	7.9*	215.7*	5.6*	1001*	20.9*
		Glacial Till	21,953	44	30.6	17	6.6	2.9	0.9	43.7	129.1	2.6	7.9	232.9	10.6	1136	25.1
				11*	31.8*	13.0*	6.7*	1.6*	7.9*	16.6*	136.2*	1.2*	7.8*	214.9	21.0*	1093.0*	21.0*
		Fine-grained Lacustrine	5,856	9	41.1	24.3	9.3	7.3	2.7	65.8	162.5	8	8.1	321	23.1	2614.7	53.9
Sandstone N = 15	13,841	Coarse-grained Lacustrine	4,642	12*	88.7*	45.8*	263.1*	8.1*	675.7*	7*	122.7*	3.9*	8.2*	1214.9*	9*	1094*	23*
		Glacial Till	3,668	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Fine-grained Lacustrine	2,658	3	35.3	21.3	11.8	1.8	2	2.9	218.7	1.9	8.1	295.8	13.3	1233.5	38.7
Granite N = 18	7,977	Coarse-grained Lacustrine	291	7	22.2	6.5	1.6	1.4	0.5	0.2	97.7	0.7	8	130.8	7.6	614.9	16.2
		Exposed bedrock	17	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Glacial Till	73	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Fine-grained Lacustrine	678	11	20.5	10.4	4	1	1.6	0.2	109.3	1.8	7.3	148.7	11.9	939.2	30.5

Table 3.2. Pearson Correlations of Non-metric Multidimensional Scaling Ordination Axes. N=147.

Parameter Sampled (mg/L)	**Axis 1**	**Axis 2**
Chloride	0.002	0.291
Sulphate	0.001	0.335
Sodium	0.020	0.469
Potassium	0.025	0.416
Calcium	0.004	0.643
Magnesium	0.228	0.643
Bicarbonate	0.244	0.358
Carbonate	0.493	0.217

Table 3.3. One-way ANOVA for the ratio of Ca/(Ca + Mg), $SO_4/(SO_4 + HCO_3)$, pH, TDS, DOC, TDP and TDN in ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained lacustrine, glacial till, and fine-grained lacustrine), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of connected wetland area (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >=10 km^2). * = very significant, ** = strongly significant, *** = significant, **** = marginally significant.

	F-stat	**r^2**	**P-value (ANOVA)**
Ca/(Ca+Mg)			
Bedrock Geology	34.736	***0.427***	0.000*
Surficial Geology	16.486	***0.261***	0.000*
Pond Order	0.735	0.016	0.533
Connected Wetland Area	5.018	***0.093***	0.002**
SO_4/SO_4+HCO_3			
Bedrock Geology	29.822	***0.390***	0.000*
Surficial Geology	3.033	***0.061***	0.031***
Pond Order	1.662	0.034	0.178
Connected Wetland Area	1.326	0.028	0.258
pH			
Bedrock Geology	0.358	***0.124***	0.000*
Surficial Geology	5.862	***0.112***	0.001*
Pond Order	0.722	0.015	0.540
Connected Wetland Area	7.247	***0.137***	0.000*
TDS			
Bedrock Geology	5.058	***0.101***	0.002**
Surficial Geology	3.466	***0.072***	0.018**
Pond Order	0.486	0.011	0.693
Connected Wetland Area	2.779	***0.058***	0.044***
DOC			
Bedrock Geology	0.910	0.012	0.438
Surficial Geology	6.295	***0.120***	0.000*
Pond Order	0.683	0.015	0.564
Connected Wetland Area	2.431	0.050	0.068****
TDP			
Bedrock Geology	0.714	0.015	0.545
Surficial Geology	5.494	***0.106***	0.001*
Pond Order	5.372	***0.104***	0.002**
Connected Wetland Area	5.666	***0.109***	0.001*
TDN			
Bedrock Geology	2.782	***0.057***	0.043***
Surficial Geology	2.431	0.050	0.068****
Pond Order	0.734	0.016	0.533
Connected Wetland Area	0.665	0.014	0.575

Table 3.4. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of Ca/(Ca + Mg), SO4/(SO4 + HCO3), pH, TDS, DOC, TDP and TDN across bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high). Linear regression was conducted on the associated trends described. * = very significant, ** = strongly significant, *** = significant, **** = marginally significant.

	Contrasts			**Least squares regression**		
	linear	**quadratic**	**cubic**	**linear**	**quadratic**	**cubic**
	(p-value)	**(p-value)**	**(p-value)**	**r^2**	**r^2**	**r^2**
Ca/(Ca+Mg)						
Bedrock Geology	**_0.000*_**	0.238	0.839	**_0.421_**	0.120	0.016
Surficial Geology	**_0.000*_**	**_0.000*_**	**_0.000*_**	**_0.049_**	**_0.046_**	**_0.036_**
Pond Order	**_0.008**_**	0.142	0.293	**_0.014_**	0.001	0.000
Connected Wetland Area	**_0.025***_**	**_0.001*_**	0.081	**_0.035_**	**_0.078_**	0.006
SO_4/SO_4+HCO_3						
Bedrock Geology	0.783	**_0.000*_**	**_0.034***_**	0.111	**_0.293_**	**_0.178_**
Surficial Geology	0.098	0.150	**_0.012***_**	0.001	0.001	**_0.031_**
Pond Order	0.289	0.708	0.954	0.010	0.001	0.001
Connected Wetland Area	0.187	0.266	0.278	0.016	0.012	0.011
pH						
Bedrock Geology	**_0.000*_**	0.443	0.541	**_0.115_**	0.005	0.000
Surficial Geology	**_0.000*_**	0.472	**_0.091****_**	**_0.094_**	0.001	0.000
Pond Order	**_0.051****_**	0.438	0.511	0.014	0.001	0.000
Connected Wetland Area	**_0.046***_**	**_0.000*_**	**_0.004**_**	**_0.028_**	**_0.107_**	**_0.057_**
TDS						
Bedrock Geology	**_0.003**_**	0.433	**_0.061****_**	**_0.045_**	0.003	0.038
Surficial Geology	**_0.016***_**	**_0.014***_**	0.685	**_0.028_**	**_0.029_**	0.007
Pond Order	0.787	0.683	0.232	0	0.001	0.007
Connected Wetland Area	0.847	**_0.024***_**	0.729	0	**_0.037_**	0.016
DOC						
Bedrock Geology	0.190	0.253	0.318	0.008	0.000	0.004
Surficial Geology	**_0.000*_**	0.732	**_0.065****_**	**_0.098_**	0.005	0.001
Pond Order	0.187	0.840	0.599	0.013	0.000	0.000
Connected Wetland Area	**_0.067****_**	0.491	0.168	0.024	0.003	0.014
TDP						
Bedrock Geology	0.835	0.165	0.499	0.005	0.015	0.000
Surficial Geology	0.694	**_0.010***_**	**_0.091****_**	0.001	**_0.073_**	0.039
Pond Order	**_0.010***_**	0.862	0.372	**_0.061_**	0.000	0.023
Connected Wetland Area	**_0.041***_**	**_0.001*_**	**_0.010***_**	**_0.029_**	**_0.069_**	**_0.045_**
TDN						
Bedrock Geology	**_0.071****_**	**_0.023***_**	0.520	0.004	**_0.032_**	0.014
Surficial Geology	**_0.023***_**	0.525	0.194	**_0.032_**	0.012	0.004
Pond Order	0.370	0.219	0.657	0.004	0.002	0.000
Connected Wetland Area	0.677	0.112	0.482	0.001	0.018	0.004

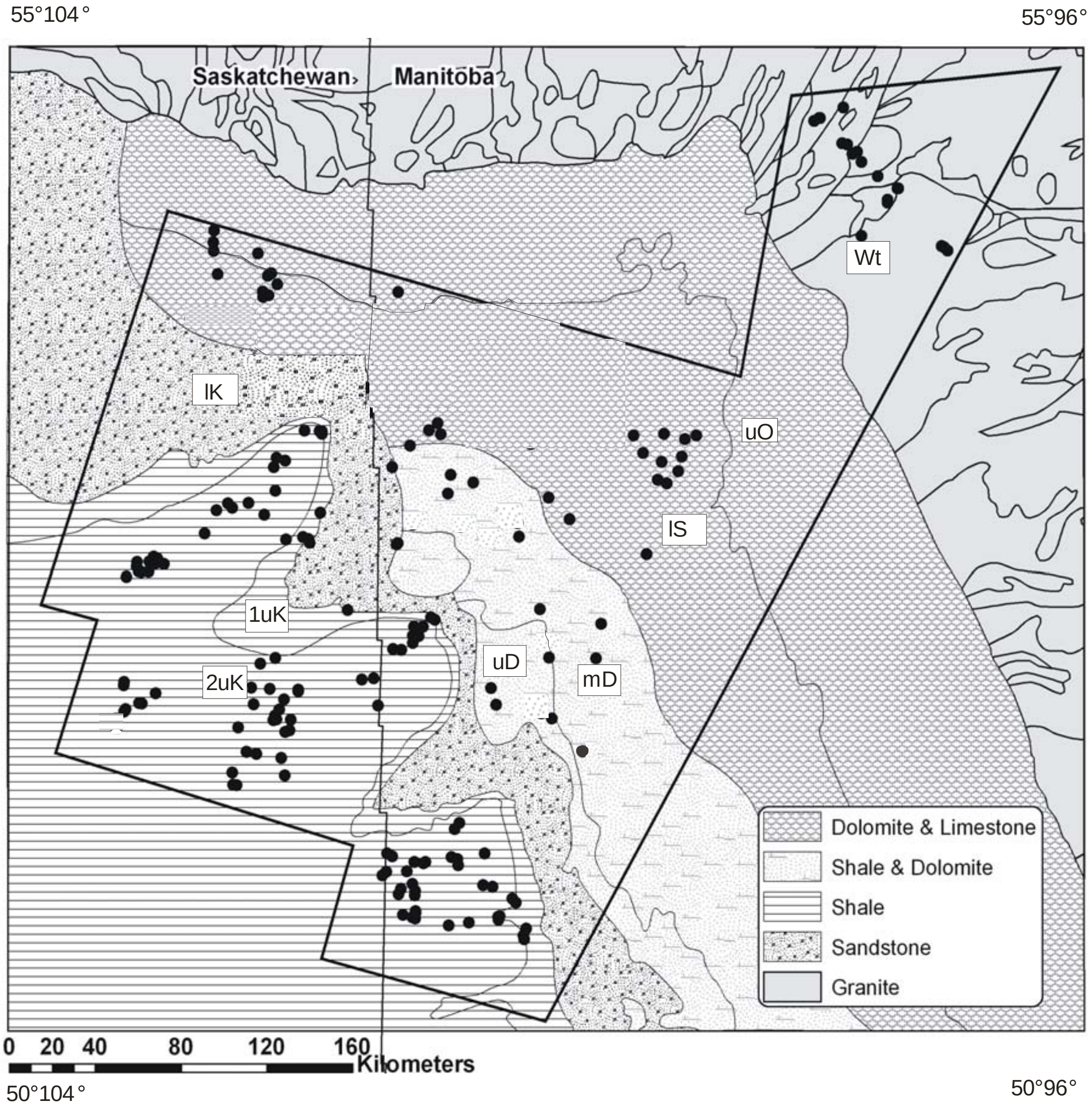


Figure 3.1. Near surface bedrock geology of the study area. Stratification of major geologic units is by major rock types. Bedrock codes (2uk, 1uk, lK, mD, uD, lS, and uO) and associated formation names and mineralogy are summarized in Table 3.2. Black dots represent location of 147 ponds sampled. Map revised from Wheeler et al. (1997).

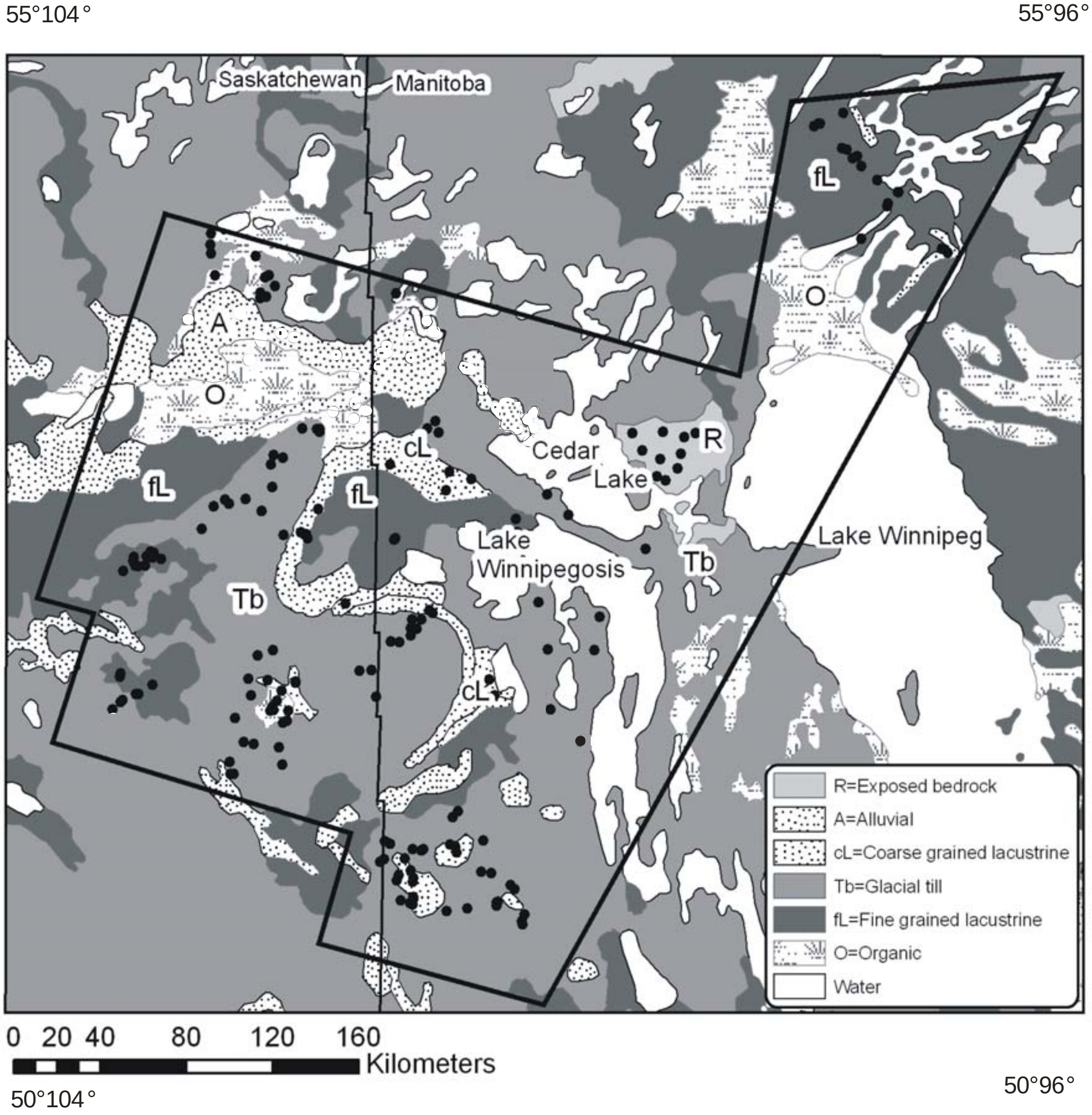


Figure 3.2. Quaternary geology of the study area. Black dots represent the spatial distribution of 147 ponds sampled. Map revised from Fulton (1995).

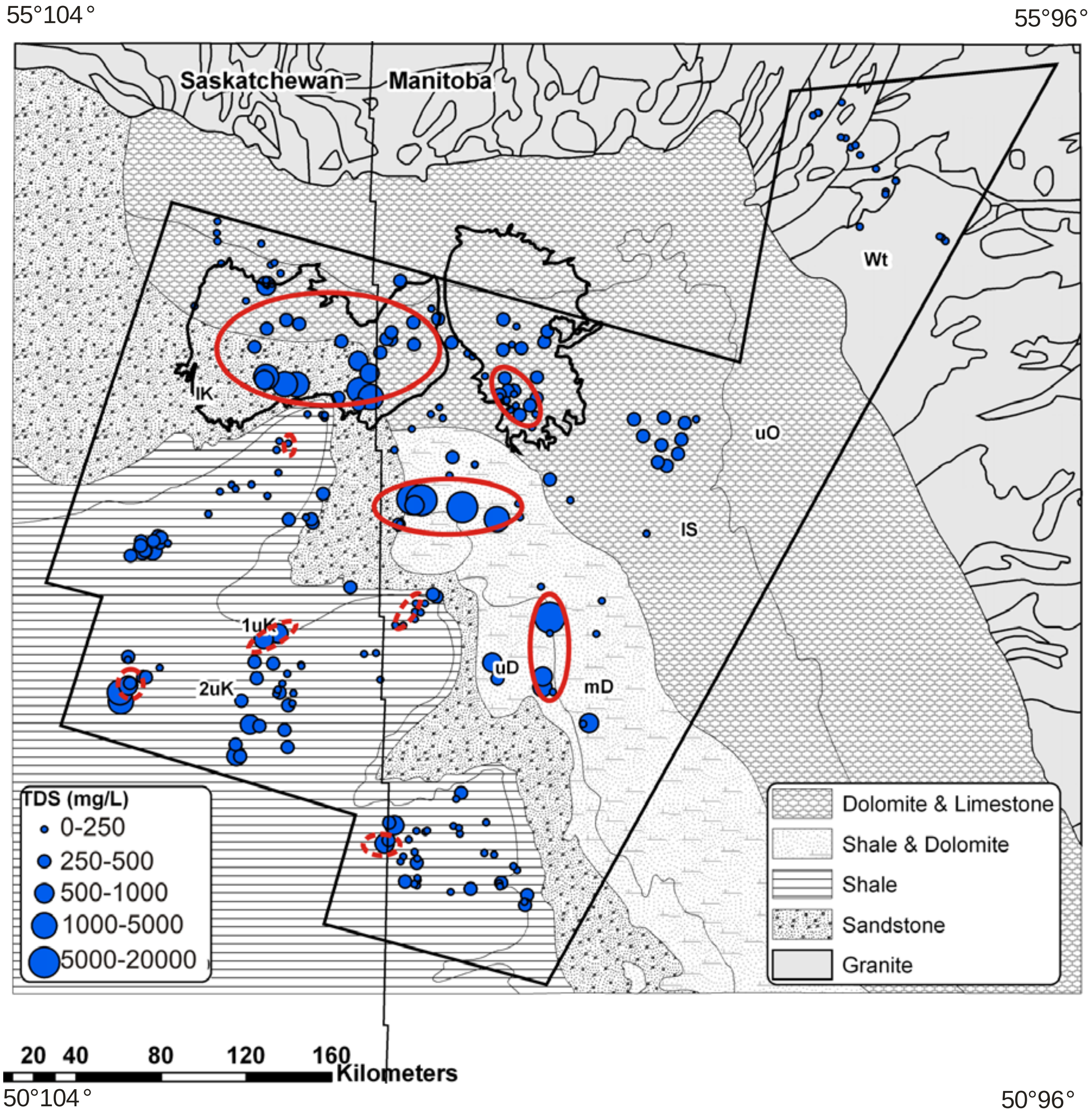


Figure 3.3. Location of ponds with chemically distinct characteristics within the study area stratified by bedrock geology. Black line within study area represents SRD. Solid red line represents ponds that fell within the ascending limb of the Gibbs model (ponds/lakes within and outside the envelope were removed for chapter 3 analysis). Red dotted line represents ponds that fell outside of the Gibbs model. Map revised from Wheeler et al. (1997).

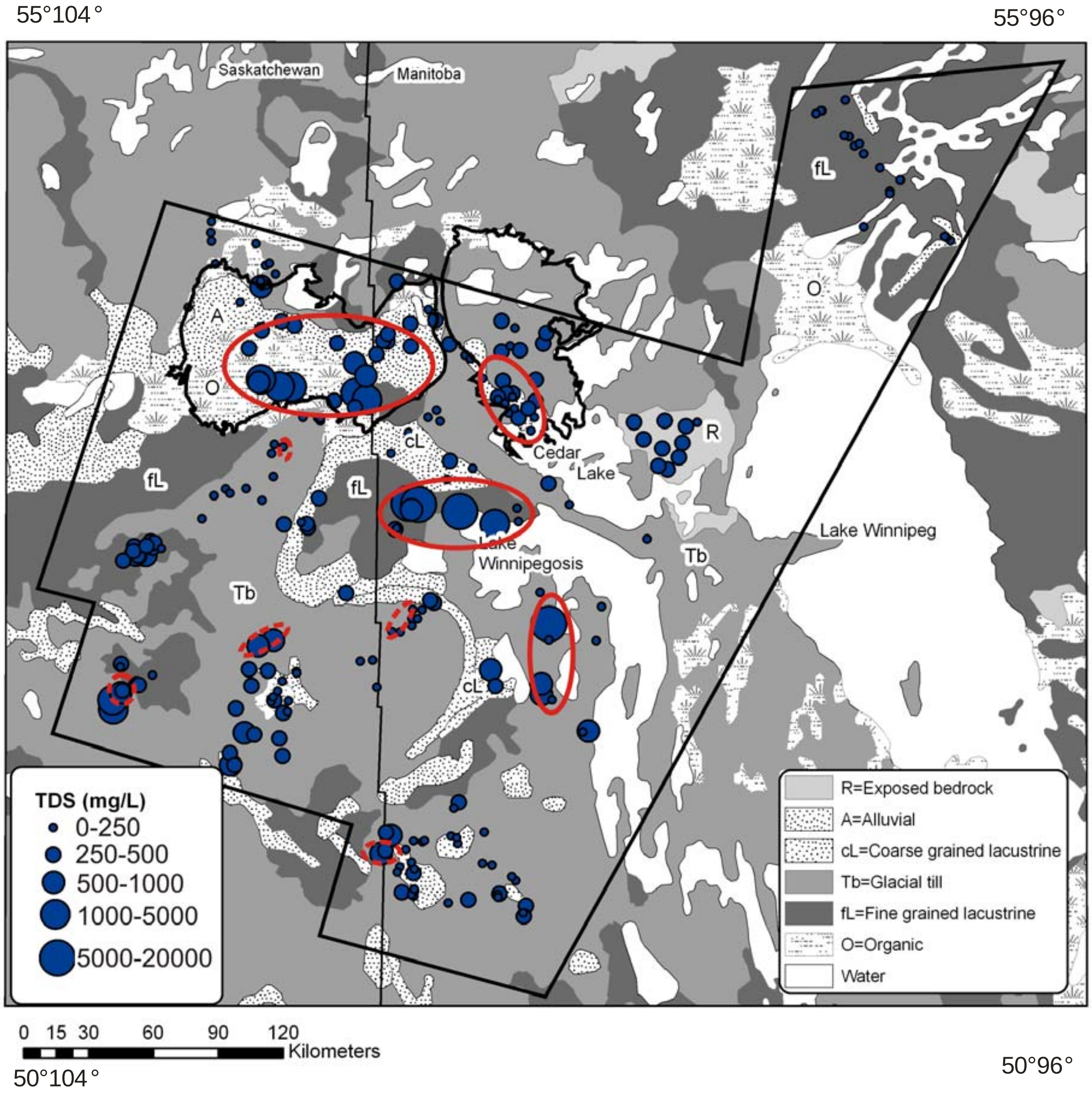


Figure 3.4. Location of ponds with chemically distinct characteristics within the study area stratified by surficial geology. Black line within study area represents SRD. Solid red line represents ponds that fell within the ascending limb of the Gibbs model (ponds/lakes within and outside envelope were removed for chapter 3 analysis). Red dotted line represents ponds that fell outside of the Gibbs model. Map revised from Fulton (1995).

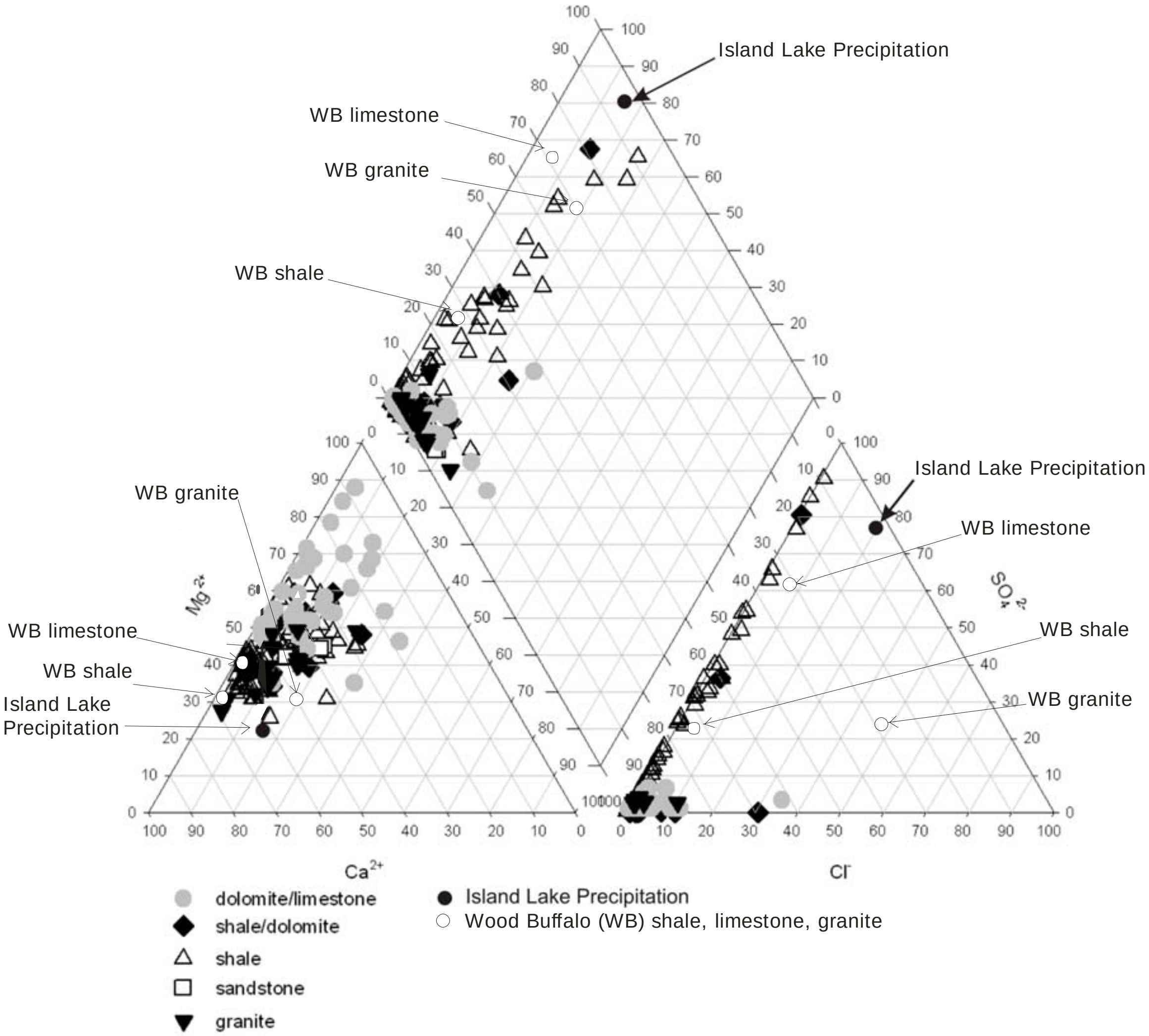


Figure 3.5. Major ion chemistry for 147 ponds from the study area further stratified by bedrock geology. Precipitation chemistry is from Island Lake, Manitoba located approximately 400 km east of The Pas, Manitoba (Krawchuck, 1998). Additional average surface water compositions relative to geology from Wood Buffalo, Alberta are reported from Moser et al. (1998). Classification diagram for cation and anion facies is included on Figure A.1 in Appendix A.

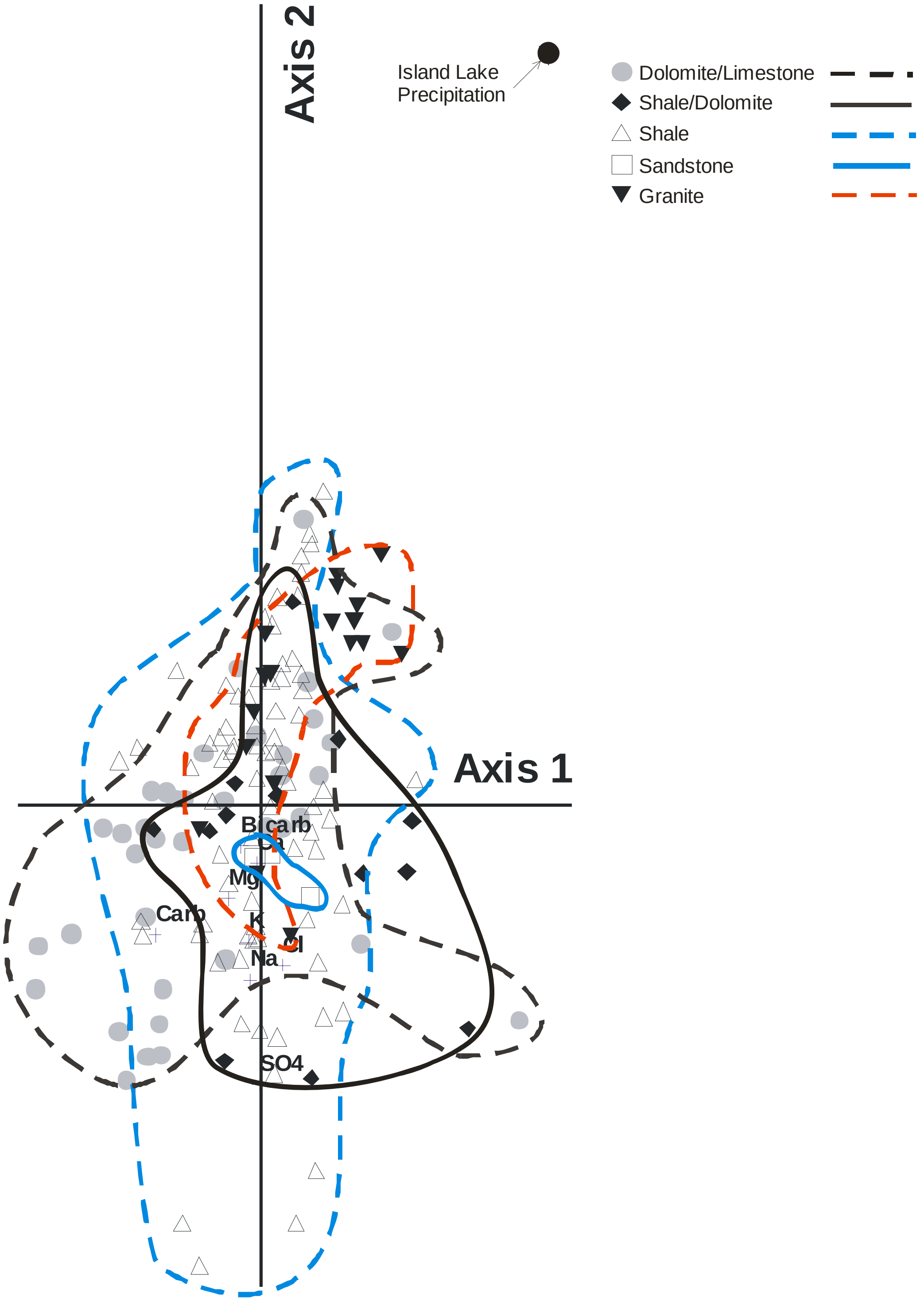


Figure 3.6. Ordination of major ion chemistry for 147 ponds within the study area. Ponds/lakes are stratified by underlying bedrock geology. Precipitation chemistry is from Island Lake, Manitoba located approximately 400 km east of The Pas, Manitoba (Krawchuck, 1998).

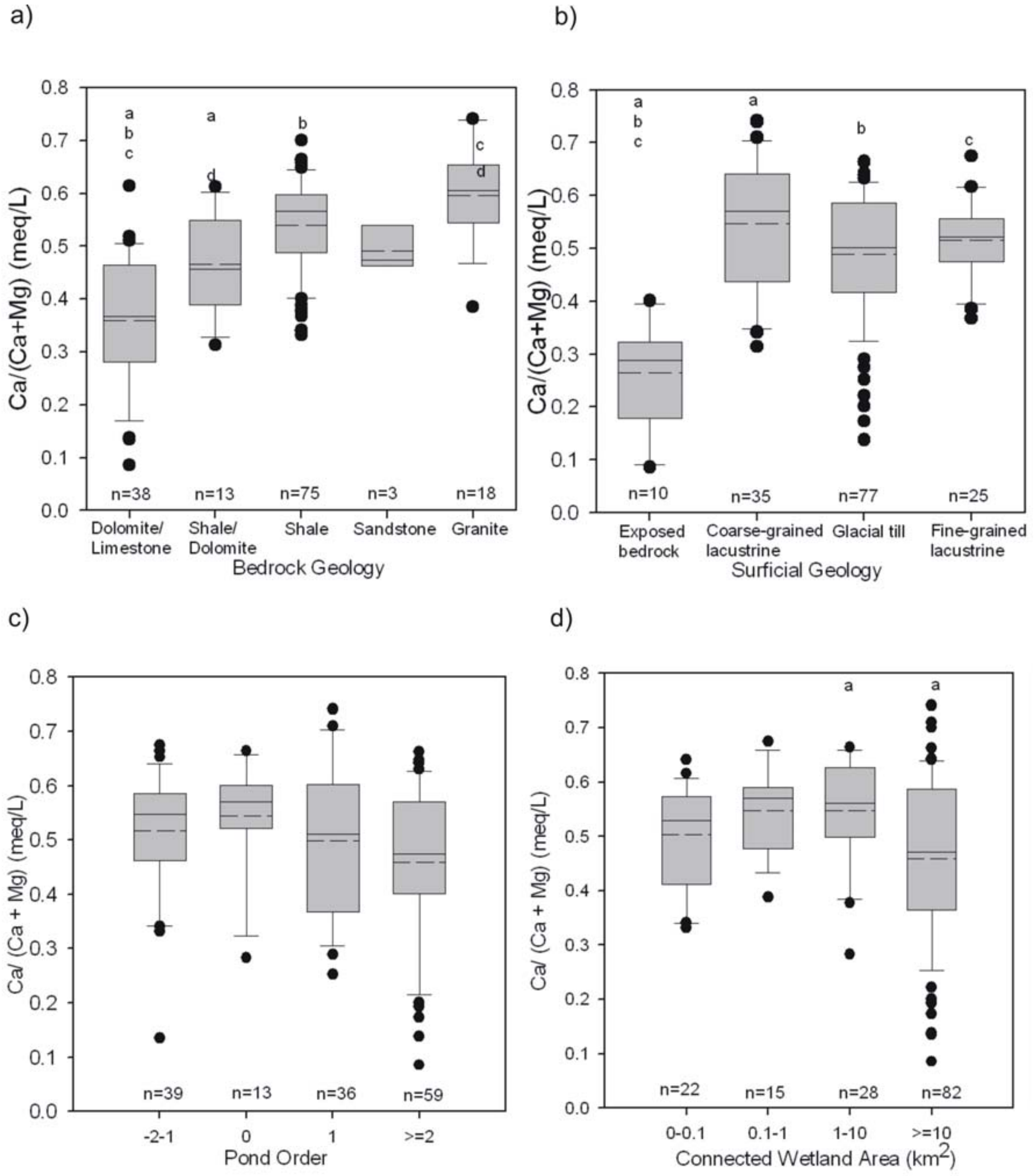


Figure 3.7. Box plots for the Ca/(Ca+Mg) ratio for 147 ponds within the study area (box = 50% of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

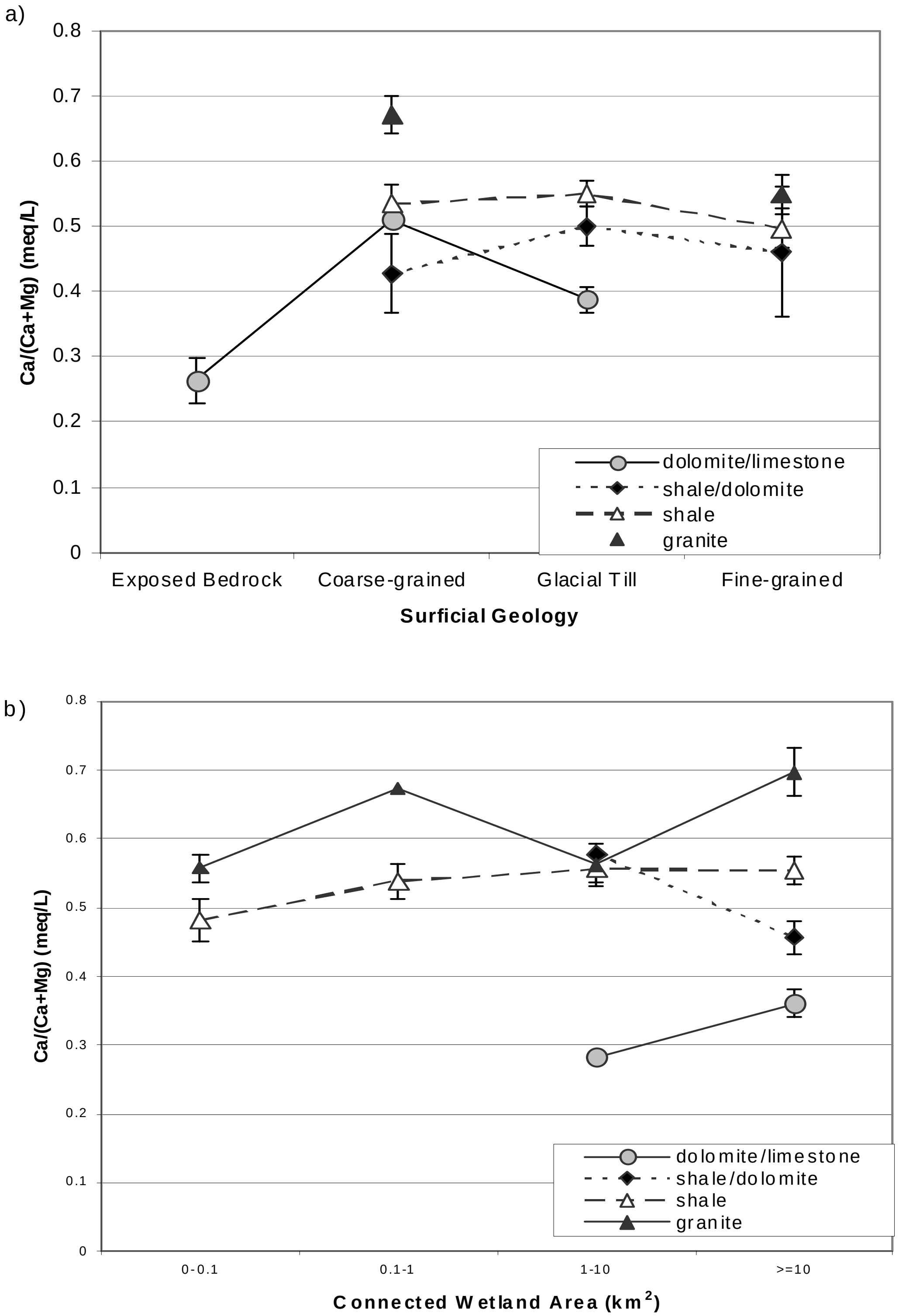


Figure 3.8. Interactions of bedrock geology and a) surficial geology and b) connected wetland area and their influence on the average Ca/(Ca + Mg) ratio. Error bars represent standard error.

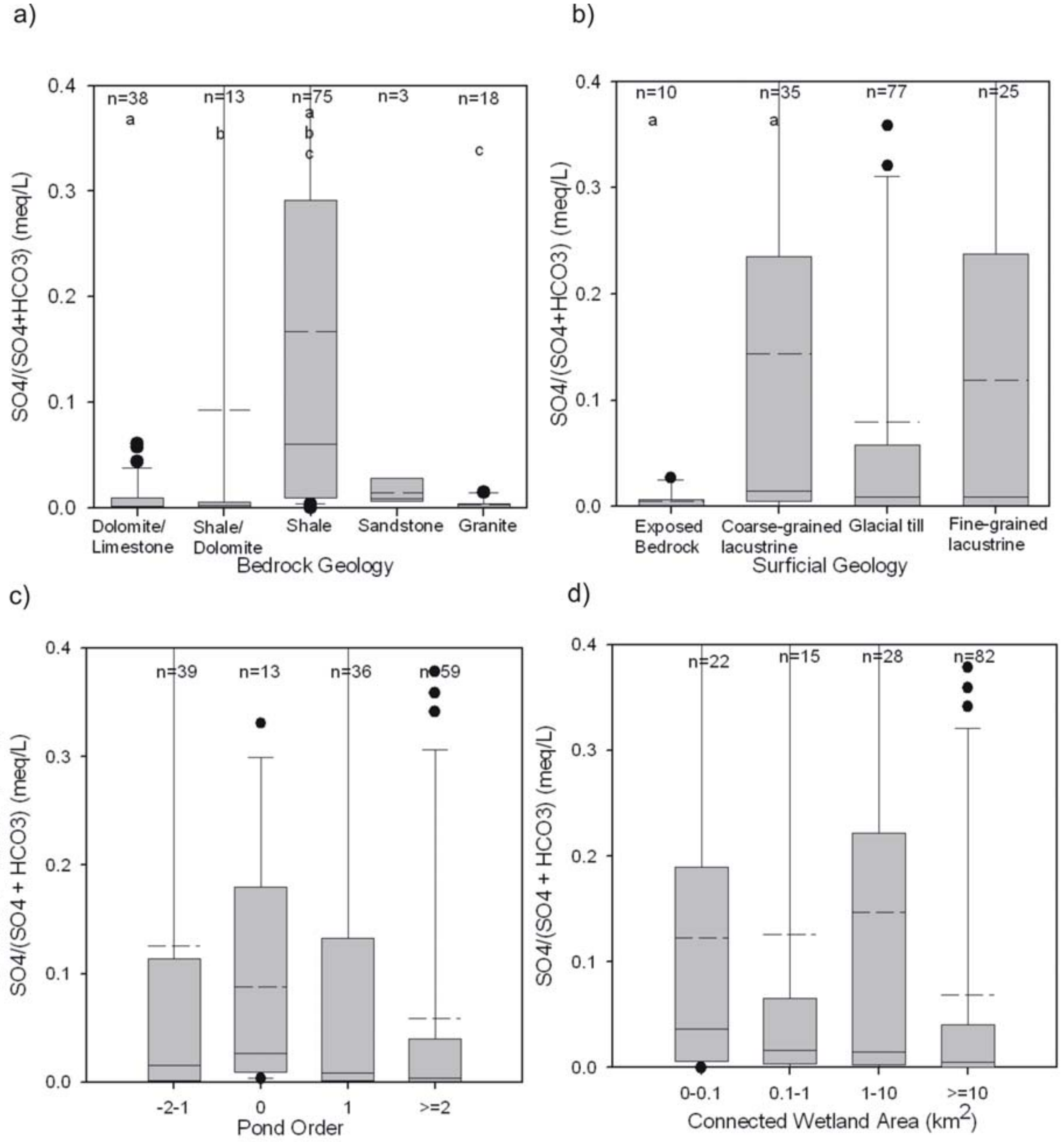


Figure 3.9. Box plots for the $SO_4/(SO_4 + HCO_3)$ ratio for a total of 147 ponds from the study area (box = 50%of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

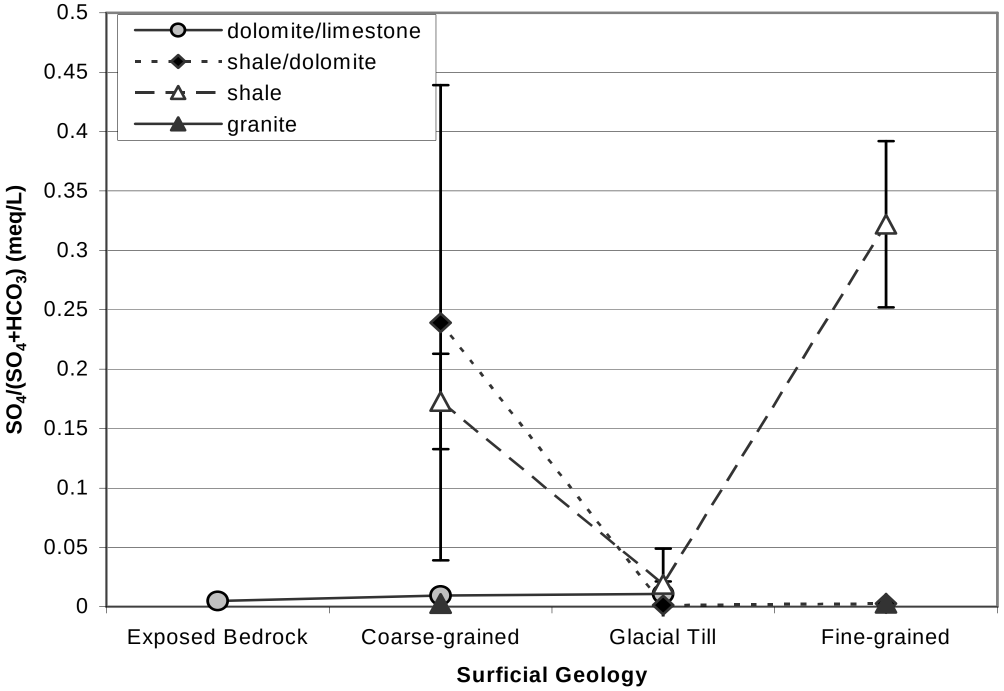


Figure 3.10. Interaction of bedrock geology and surficial geology and their influence on average $SO_4/(SO_4 + HCO_3)$ ratio. Error bars represent standard error.

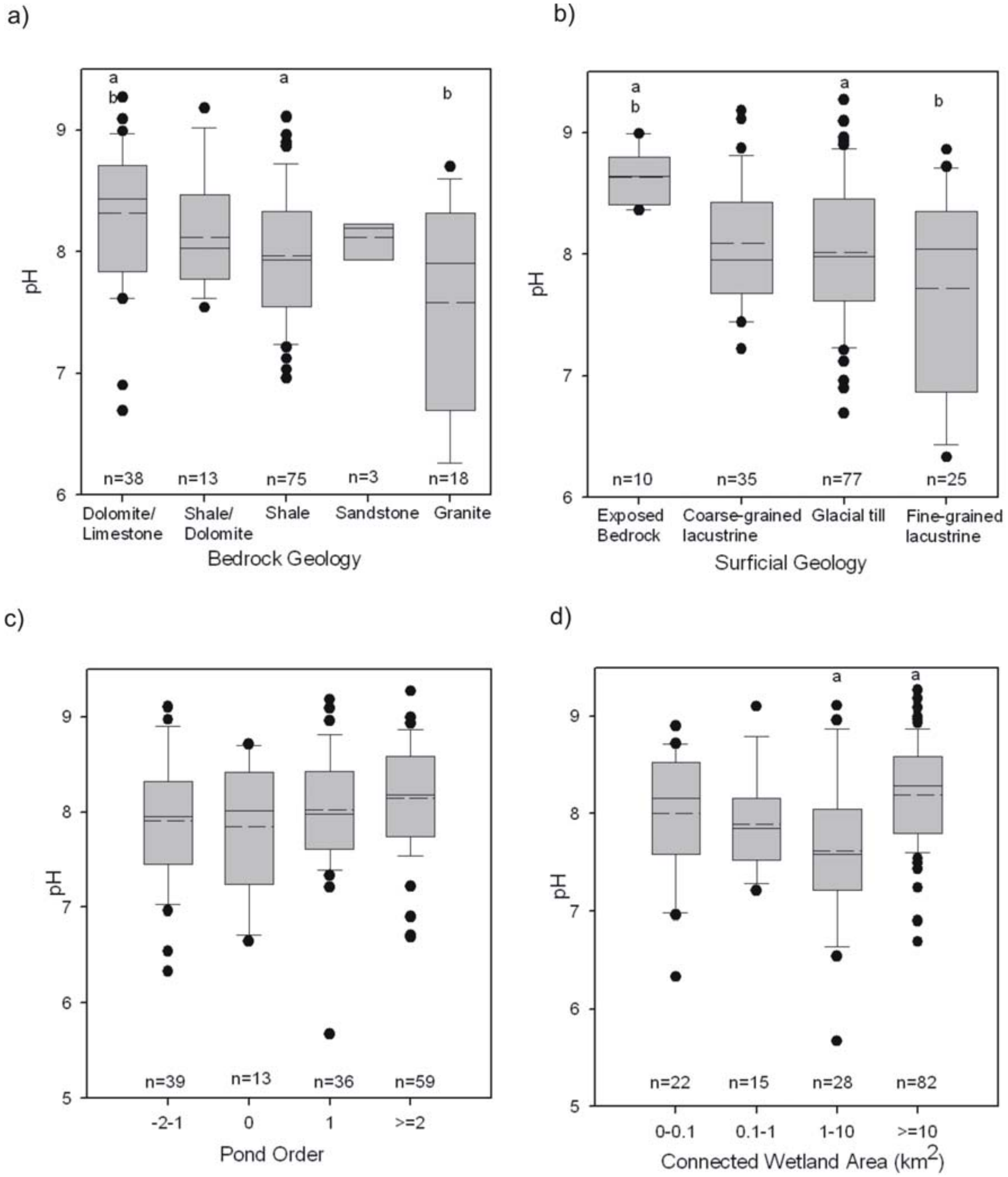


Figure 3.11. Box plots of pH for a total of 147 ponds from the study area (box = 50% of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

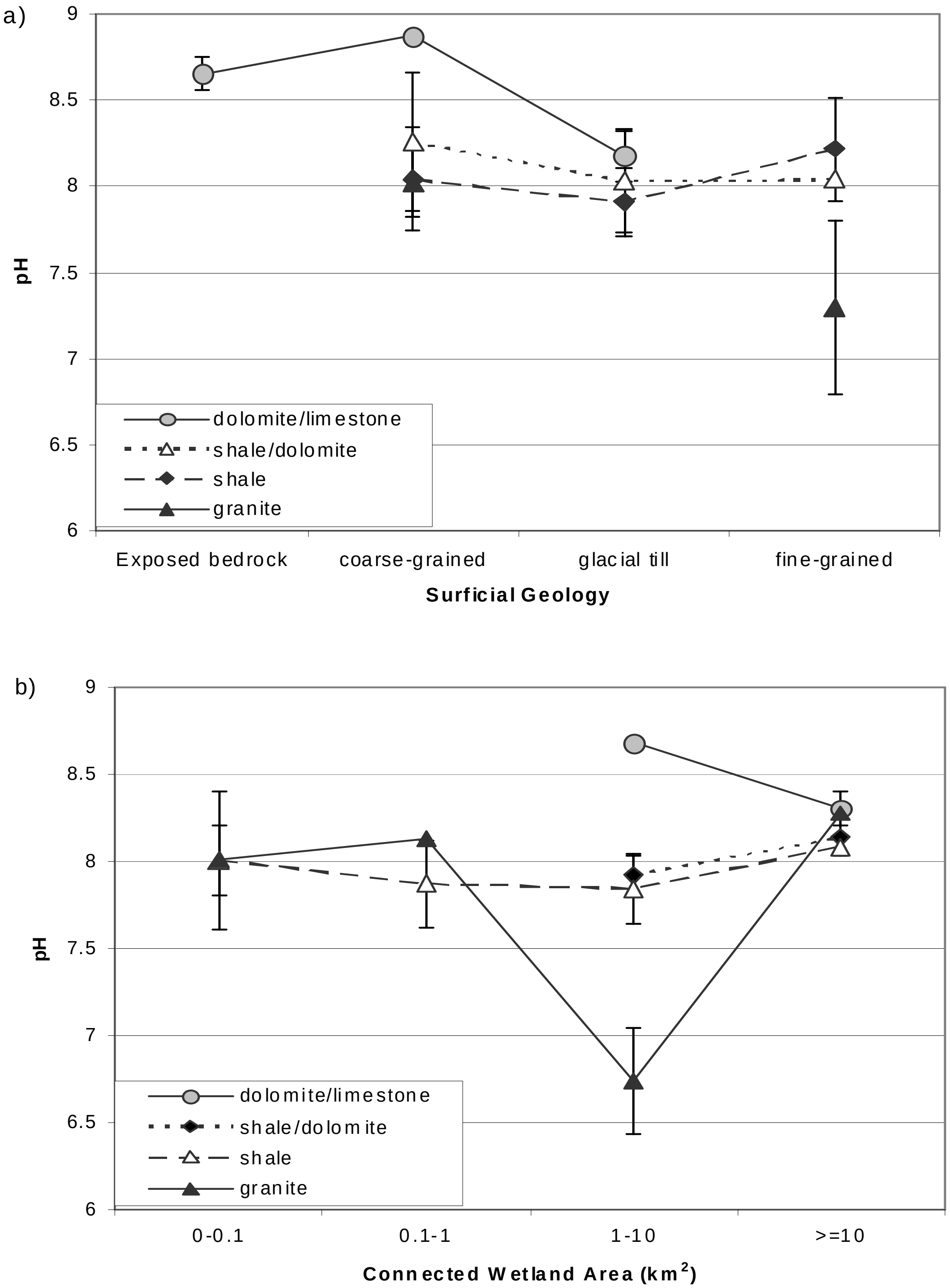


Figure 3.12. Interaction of bedrock geology and a) surficial geology and b) connected wetland area and their influence on average pH. Error bars represent standard error.

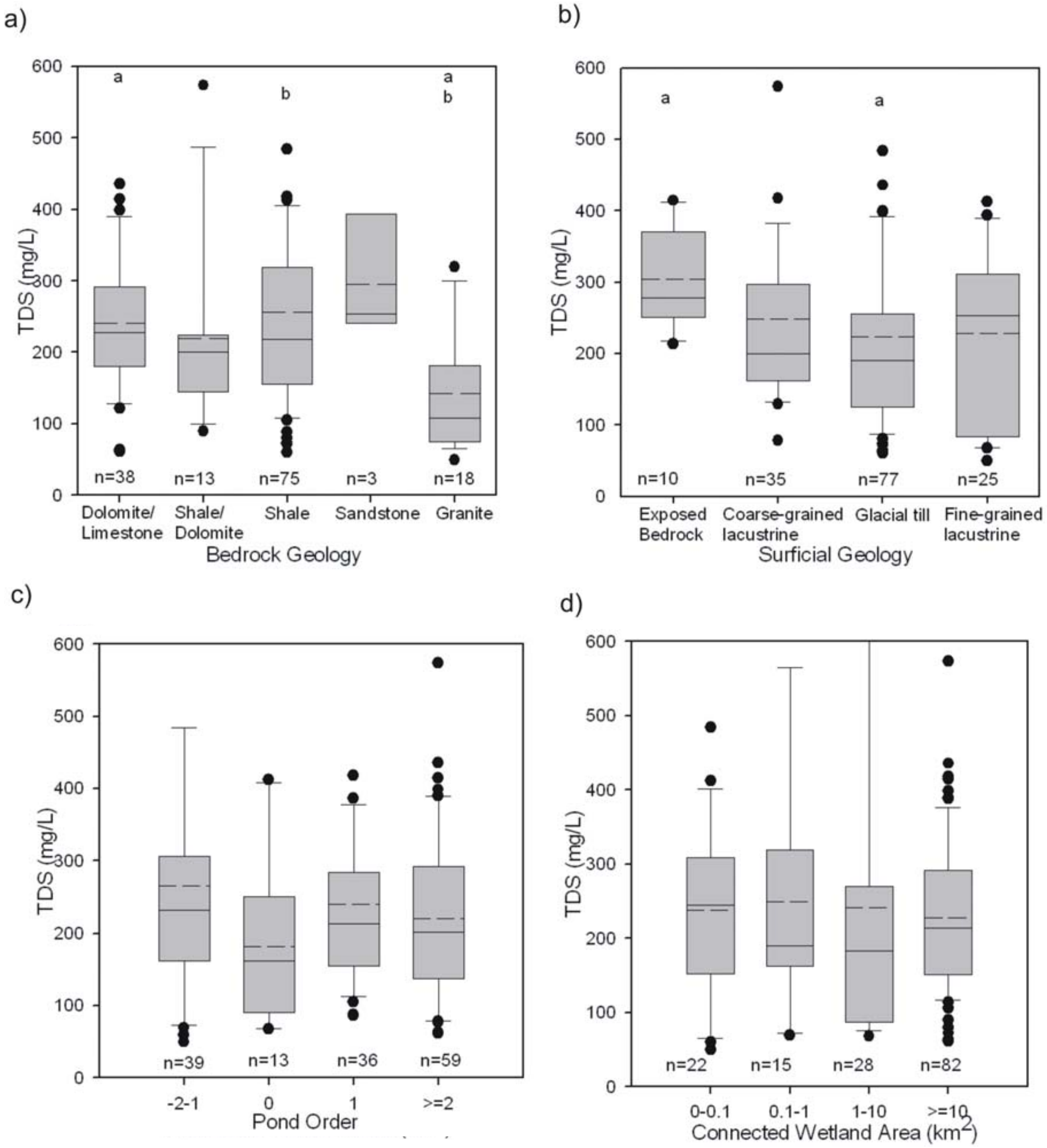


Figure 3.13. Box plots for TDS for a total of 147 ponds from the study area (box = 50% of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

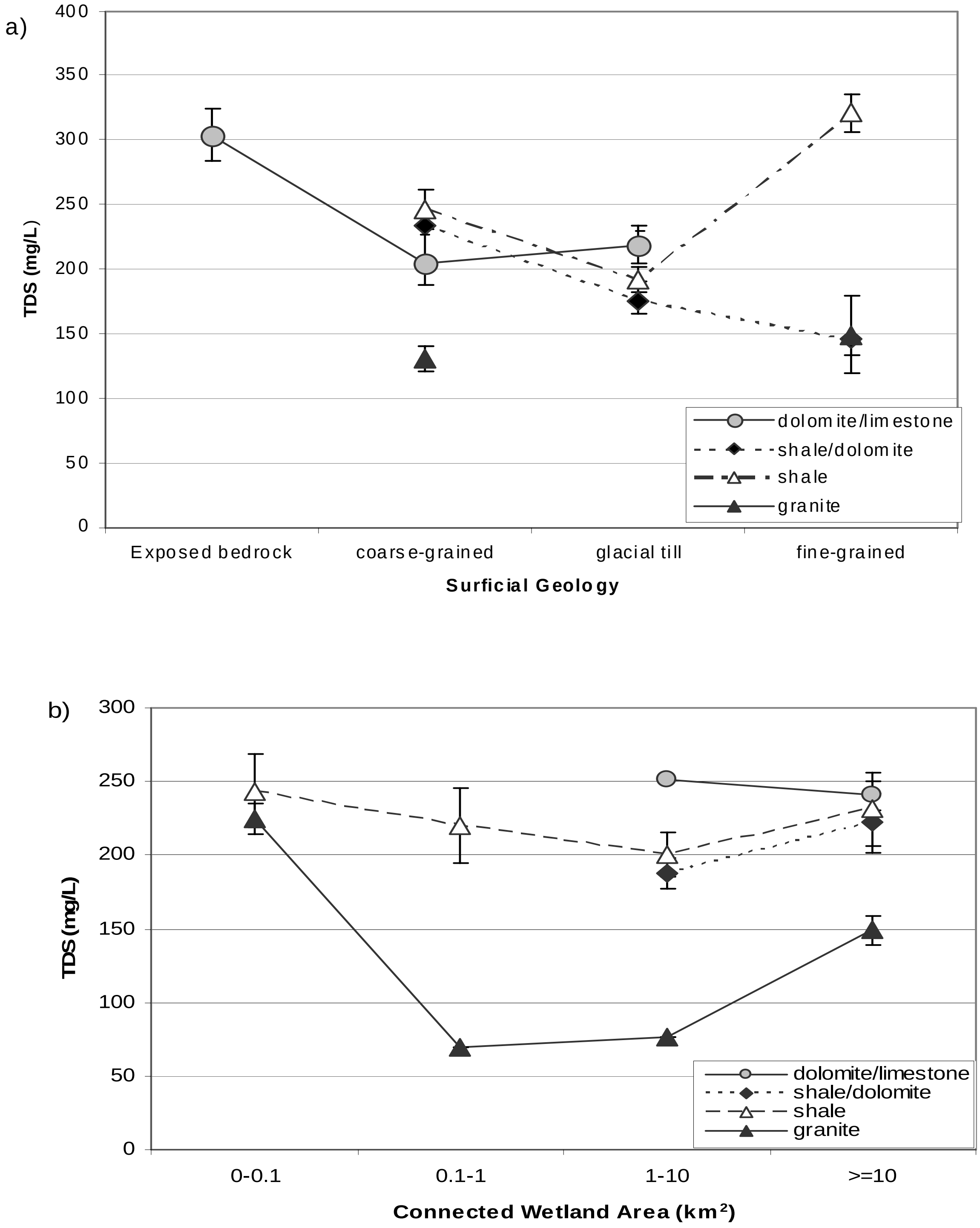
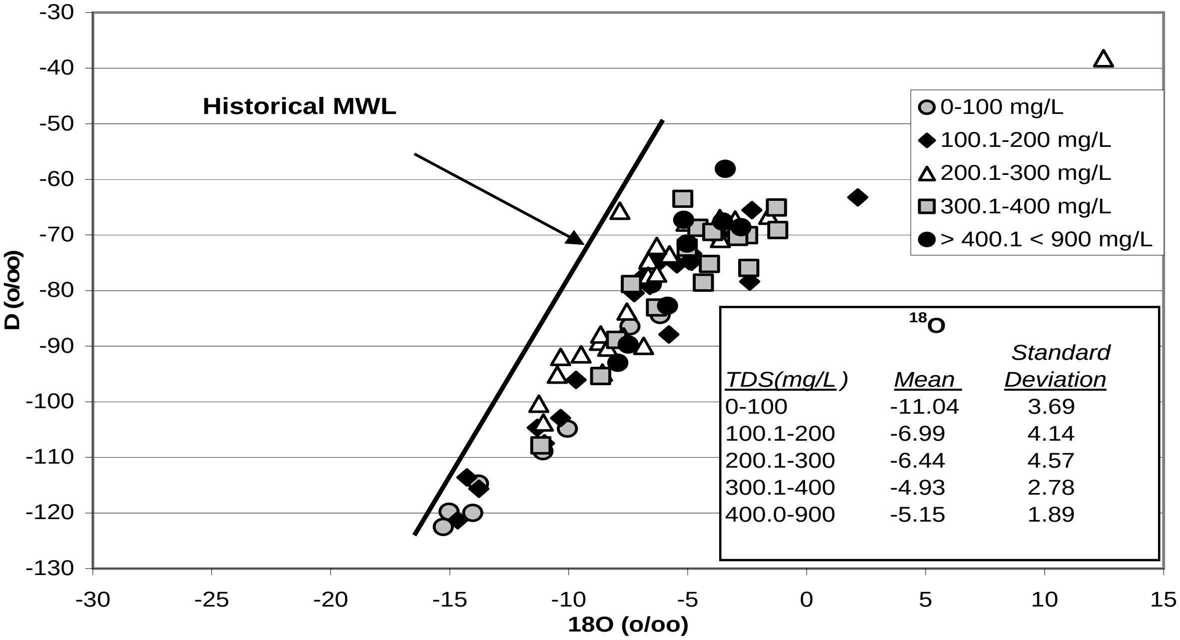


Figure 3.14. Interaction of bedrock geology and a) surficial geology and b) connected wetland area and their influence on average TDS. Error bars represent standard error.



	^{18}O	
TDS(mg/L)	*Mean*	*Standard Deviation*
0-100	-11.04	3.69
100.1-200	-6.99	4.14
200.1-300	-6.44	4.57
300.1-400	-4.93	2.78
400.0-900	-5.15	1.89

Figure 3.15. Oxygen 18 relative to deuterium with TDS concentrations for ponds within the study area.

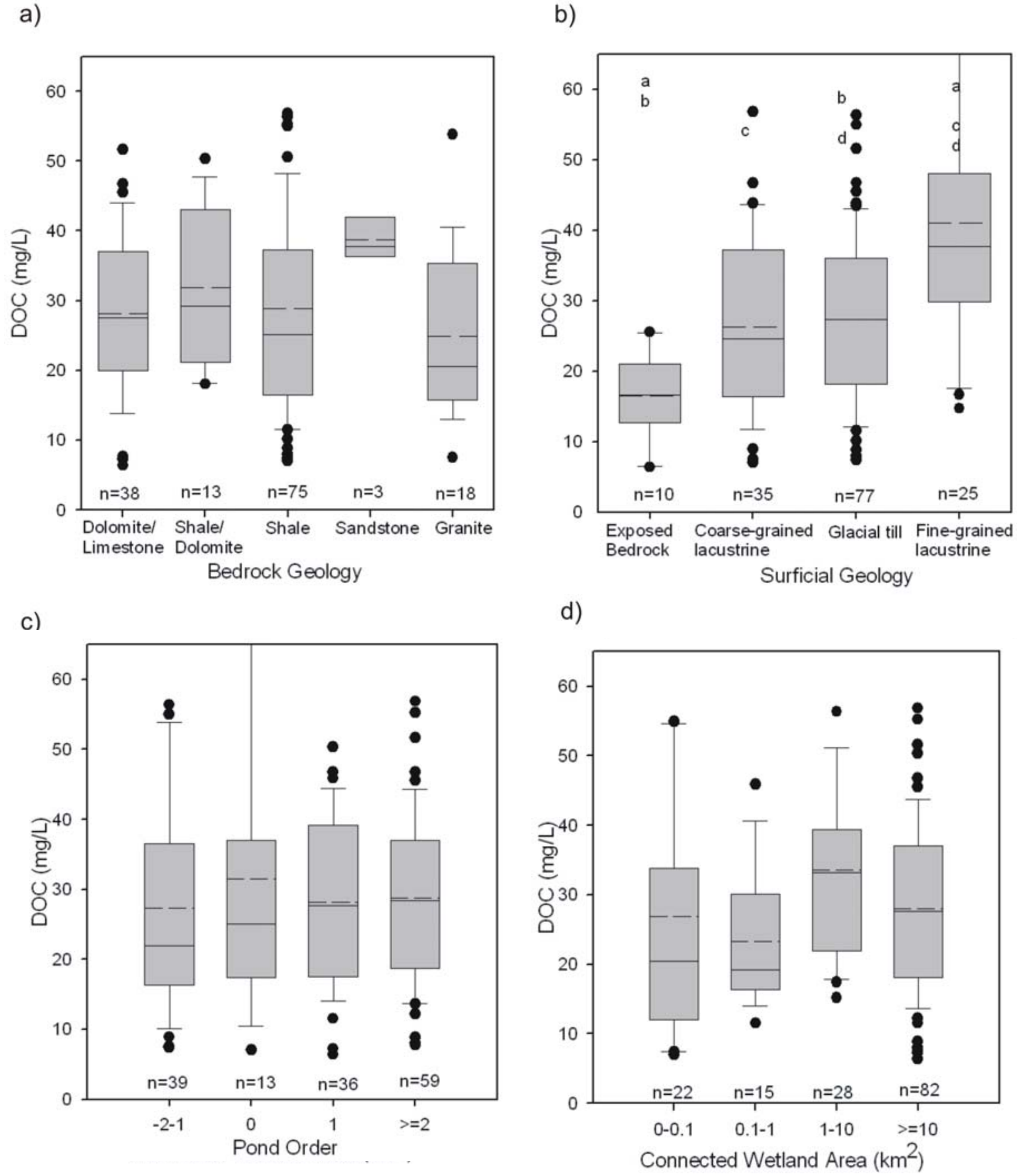


Figure 3.16. Box plots of DOC for a total of 147 ponds from the study area (box = 50% of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

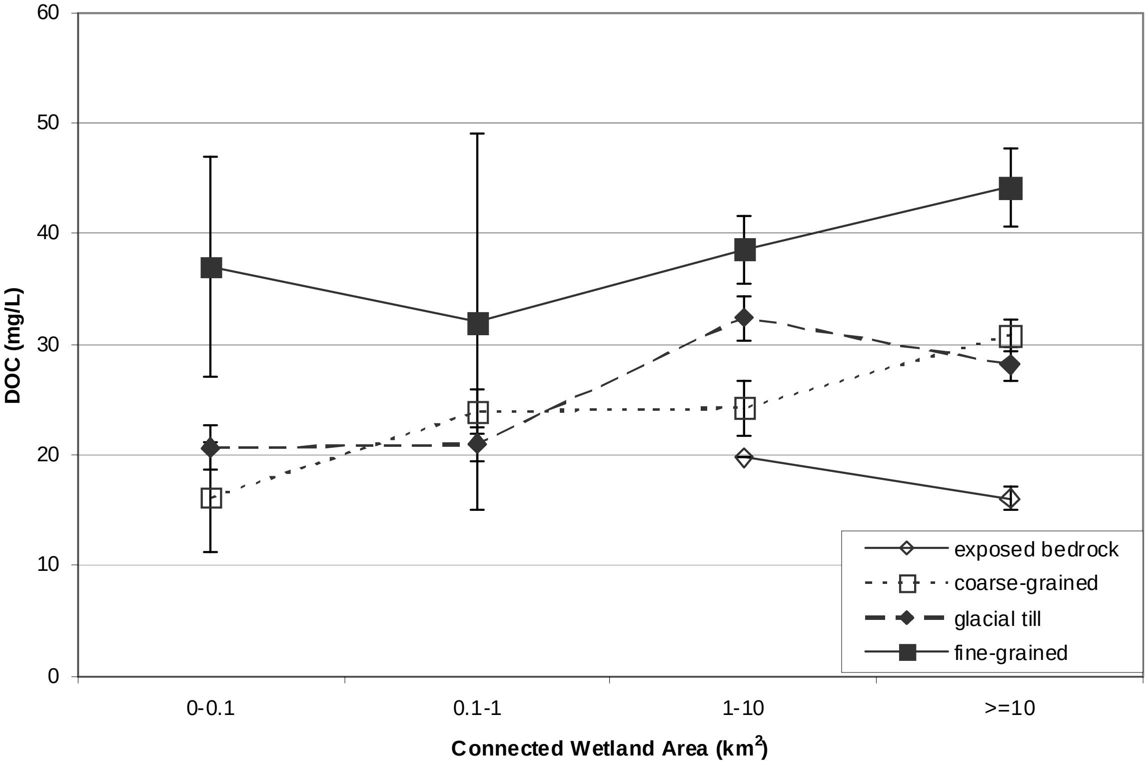
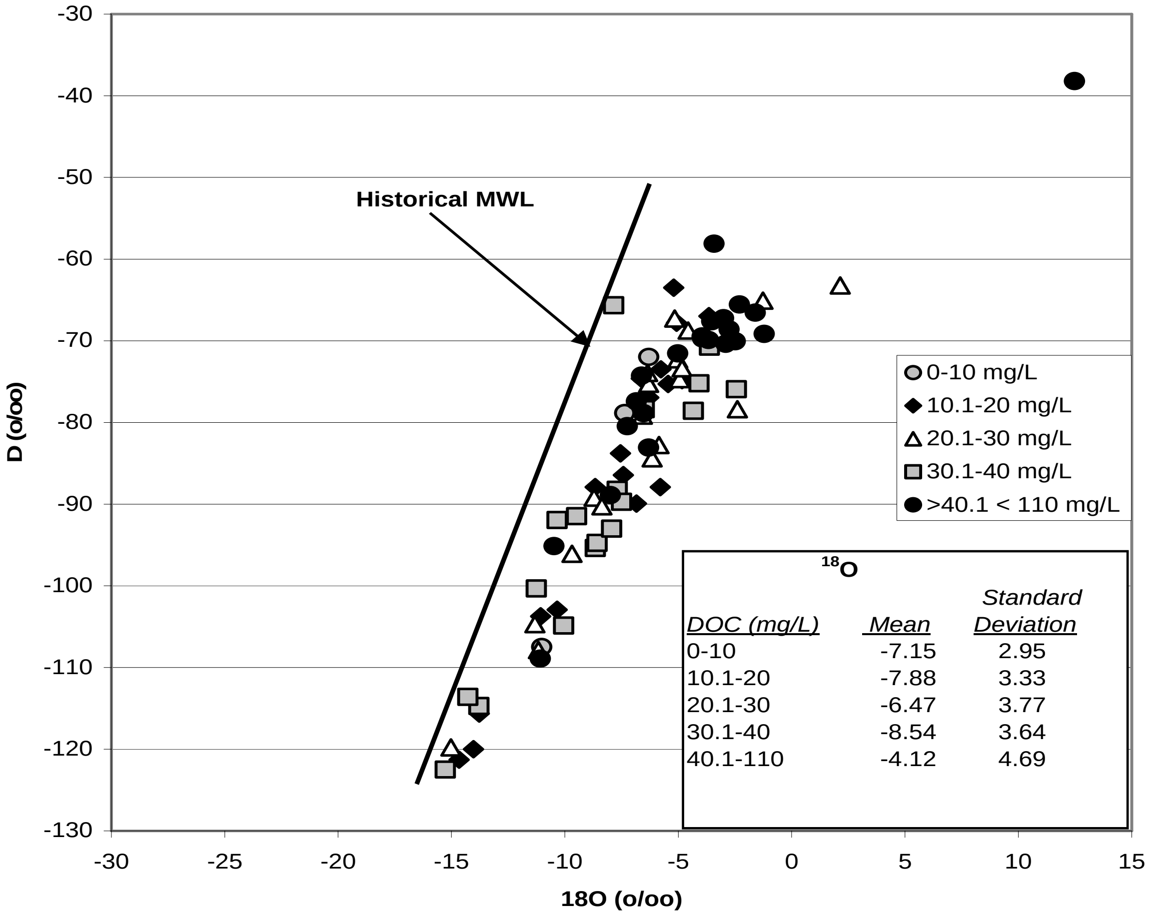


Figure 3.17. Interaction of surficial geology and connected wetland area and their influence on average DOC. Error bars represent standard error.



^{18}O

DOC (mg/L)	*Mean*	*Standard Deviation*
0-10	-7.15	2.95
10.1-20	-7.88	3.33
20.1-30	-6.47	3.77
30.1-40	-8.54	3.64
40.1-110	-4.12	4.69

Figure 3.18. Oxygen 18 relative to deuterium with DOC concentrations for ponds within the study area.

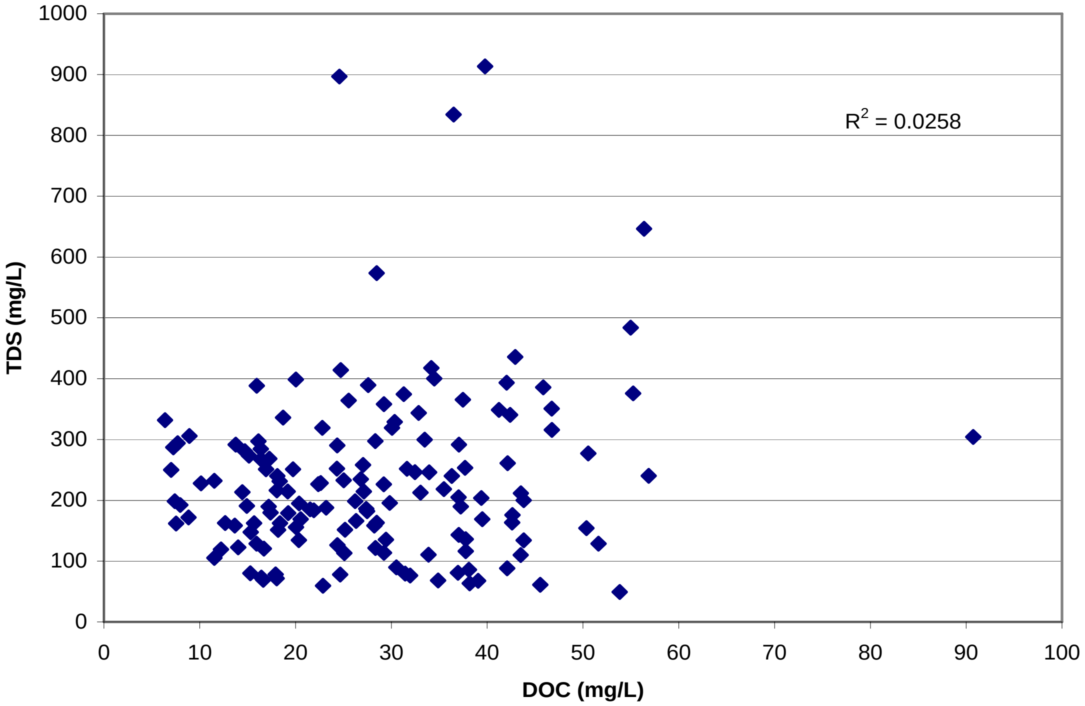


Figure 3.19. TDS relative to DOC concentrations for ponds within the study area

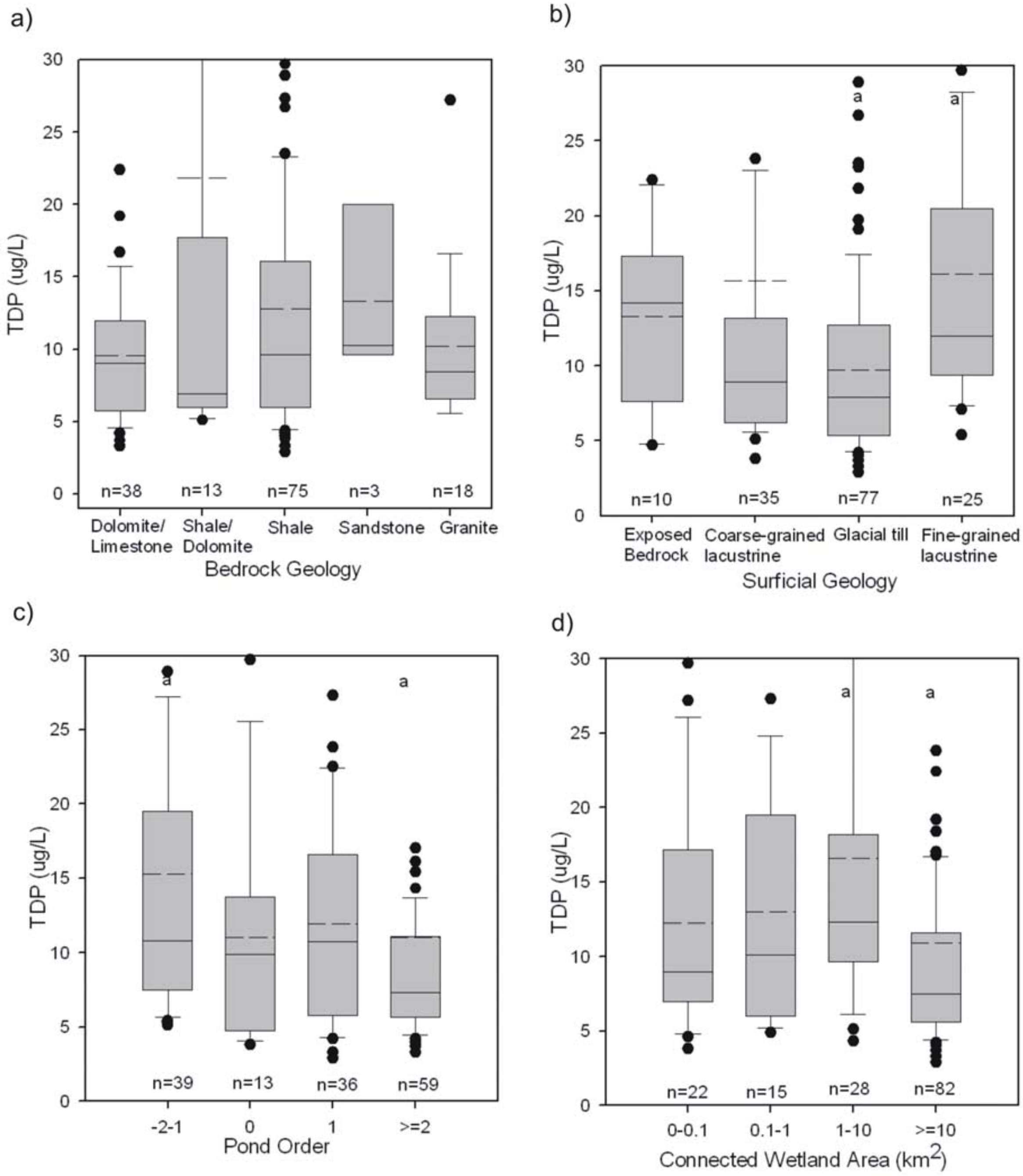


Figure 3.20. Box plots for TDP for a total of 147 ponds from the study area (box = 50% of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

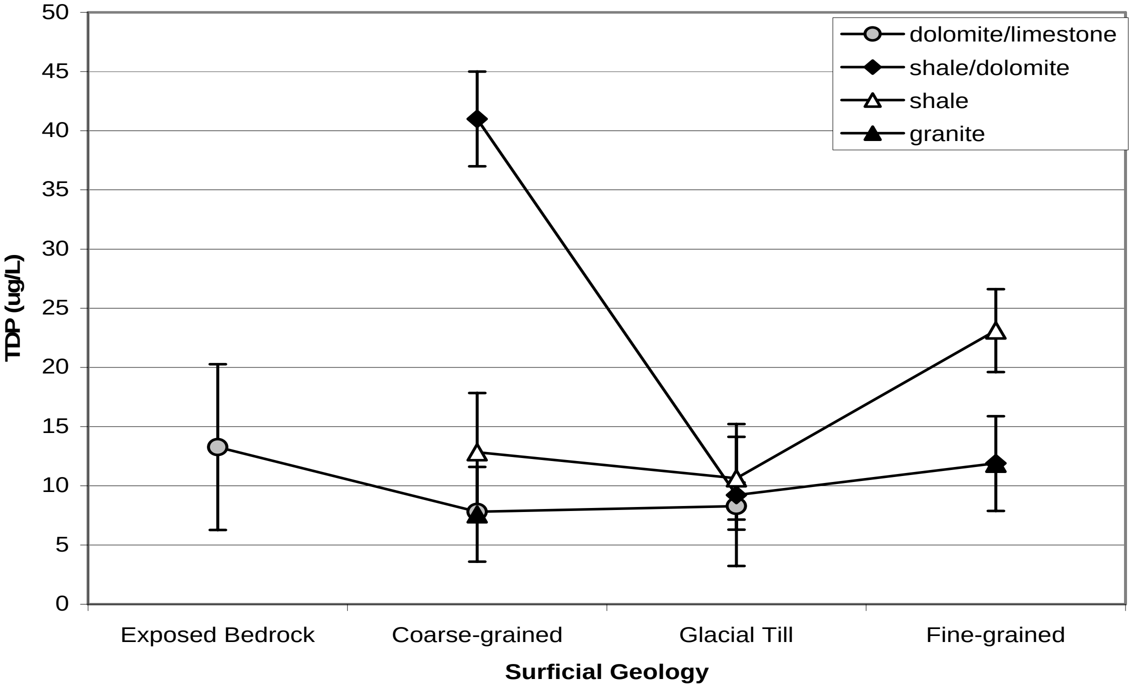


Figure 3.21. Interaction of bedrock geology and surficial geology and their influence on average TDP. Error bars represent standard error

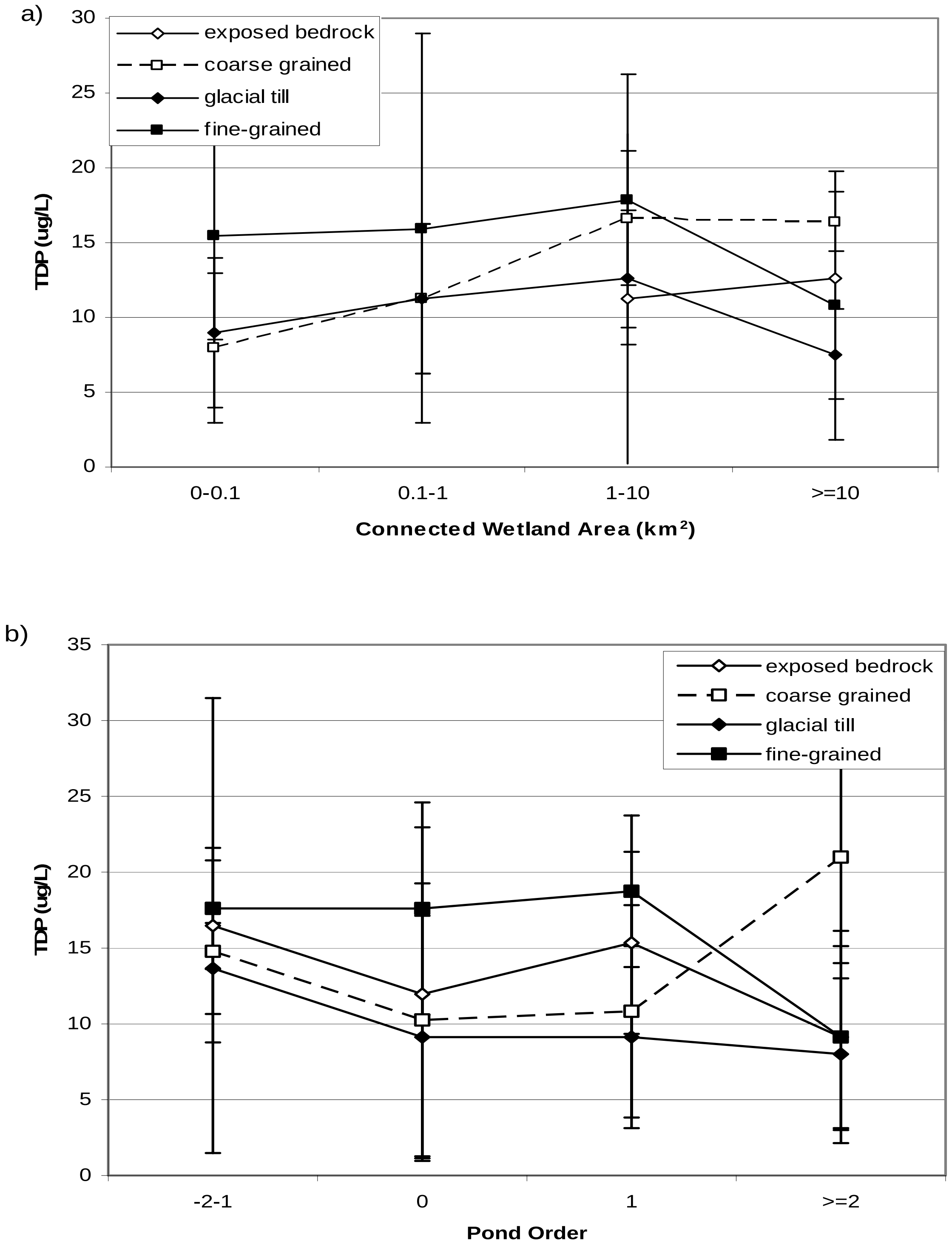
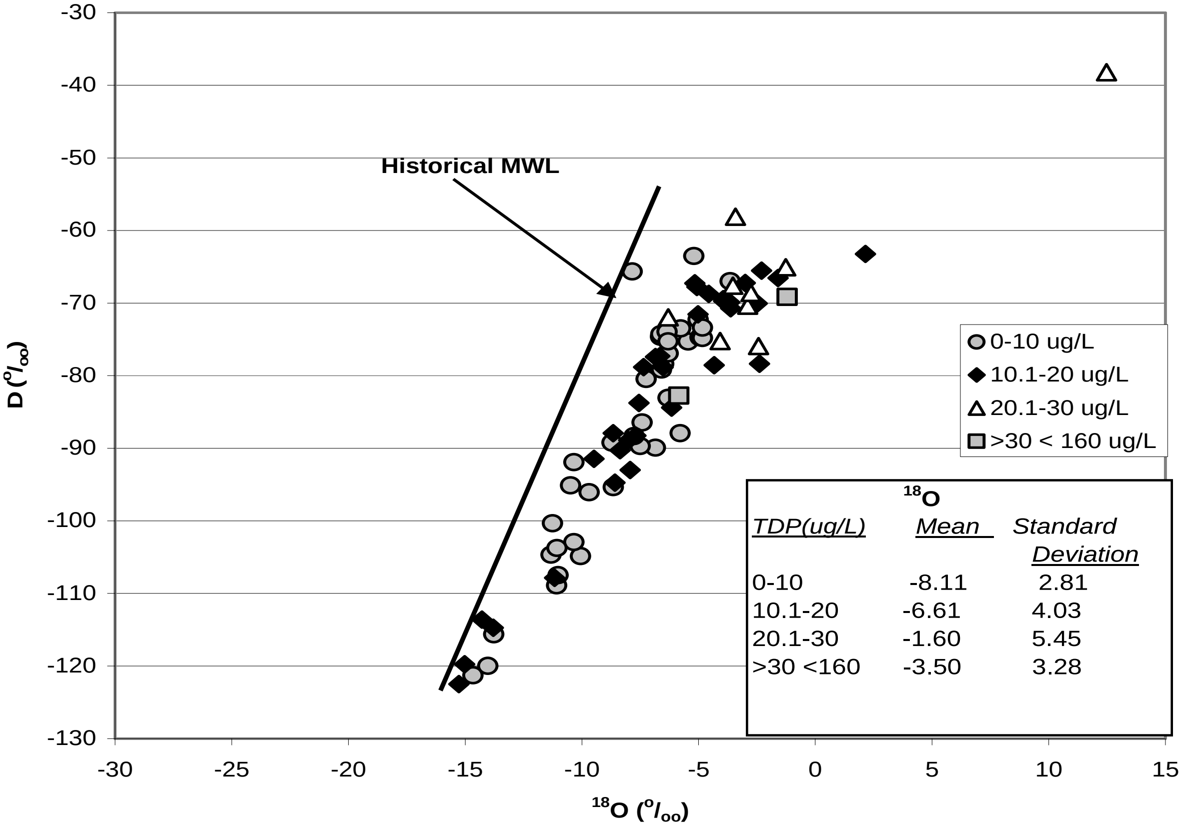


Figure 3.22. Interaction of surficial geology and a) connected wetland area and b) pond order and their influence on TDP. Error bars represent standard error.



TDP(ug/L)	^{18}O *Mean*	*Standard Deviation*
0-10	-8.11	2.81
10.1-20	-6.61	4.03
20.1-30	-1.60	5.45
>30 <160	-3.50	3.28

Figure 3.23. Oxygen 18 relative to deuterium with TDP concentrations for ponds within the study area.

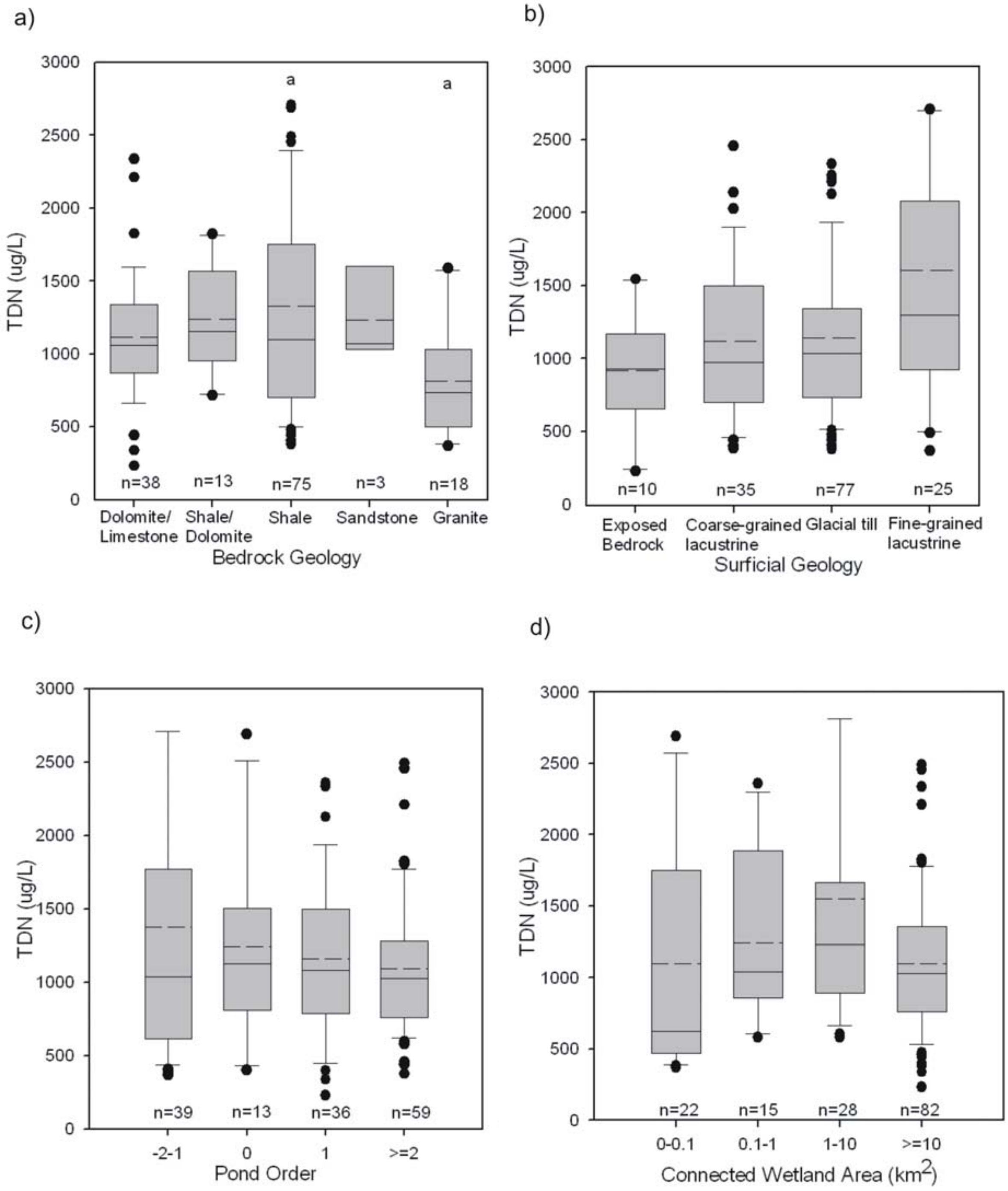


Figure 3.24. Box plots of TDN for a total of 147 ponds from the study area (box = 50% of data, whisker = 40% of data and dots = 10% of data). X-axis represents a) bedrock geology, b) surficial geology, c) pond order and d) connected wetland area. Solid line in box represents median value, dotted line represents the mean. Lower case letters indicate significant differences between groups using the Bonferroni Test. Significance of overall trends and polynomial models are shown on Tables 3.3 and 3.4.

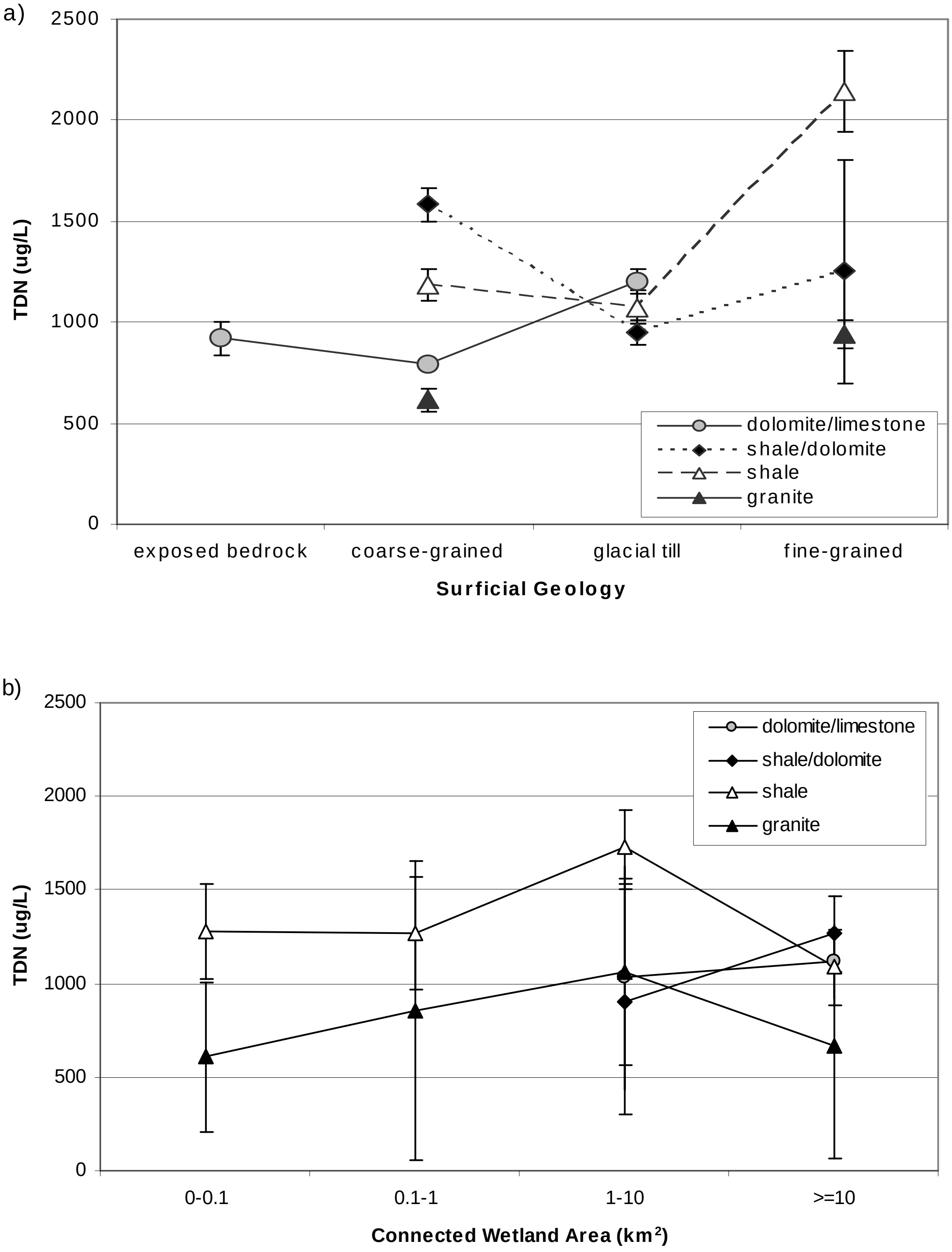
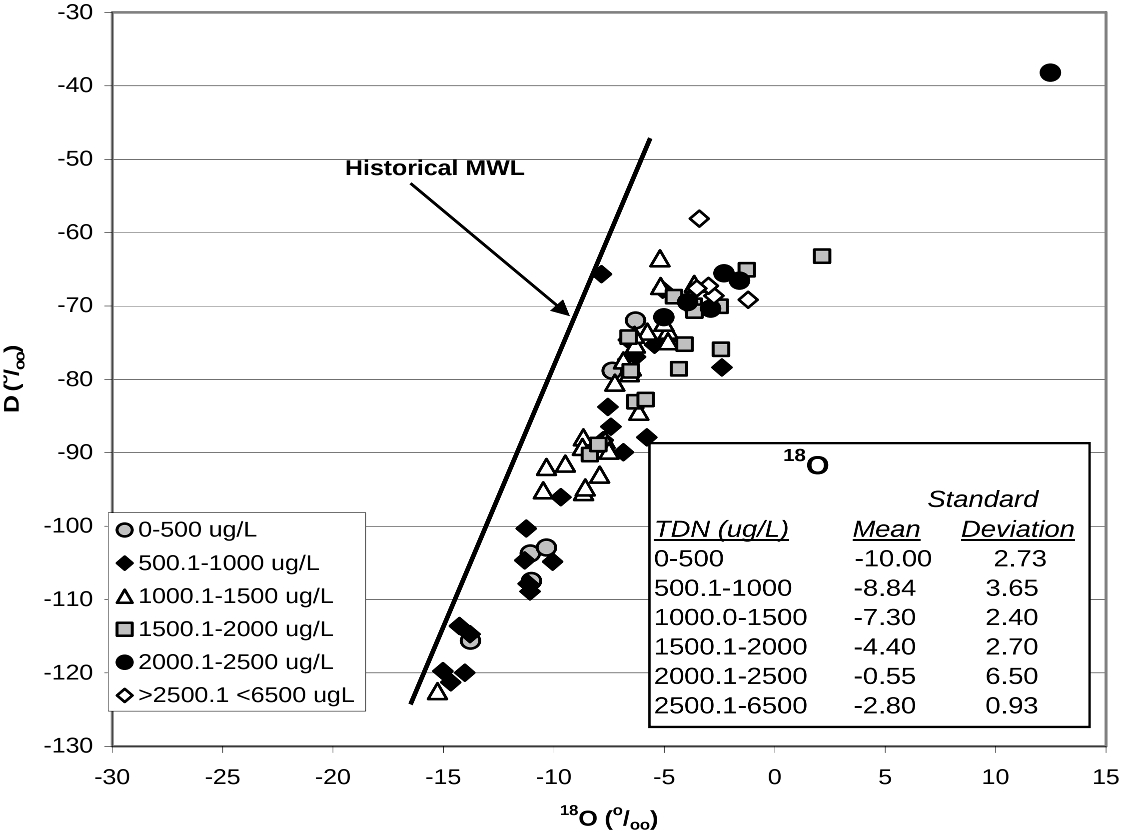


Figure 3.25. Interaction of bedrock geology and a) surficial geology and b) connected wetland area and their influence on TDN. Error bars represent standard error.



TDN (ug/L)	Mean	Standard Deviation
0-500	-10.00	2.73
500.1-1000	-8.84	3.65
1000.0-1500	-7.30	2.40
1500.1-2000	-4.40	2.70
2000.1-2500	-0.55	6.50
2500.1-6500	-2.80	0.93

Figure 3.26. Oxygen 18 relative to deuterium with TDN concentrations for ponds within the study area.

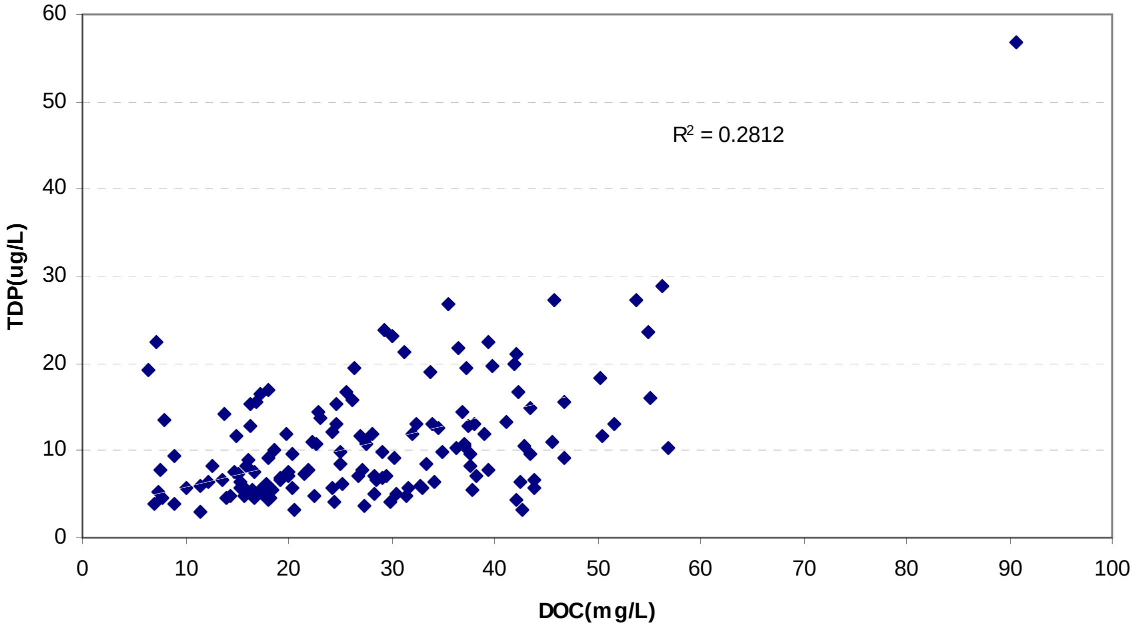


Figure 3.27. DOC relative to TDP concentrations for ponds within the study area.

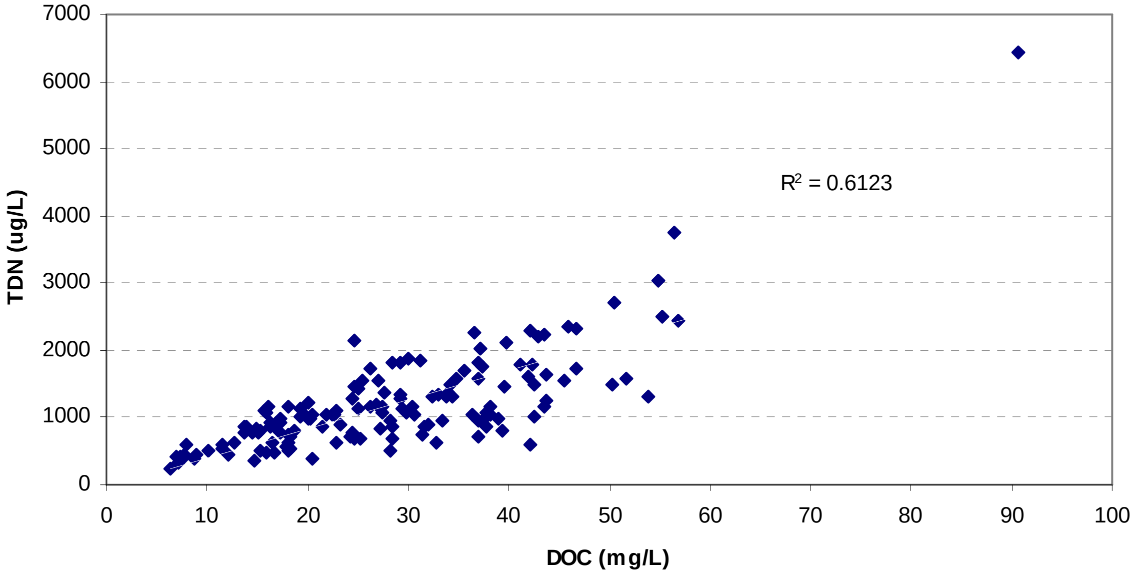


Figure 3.28. DOC relative to TDN concentrations for ponds within the study area.

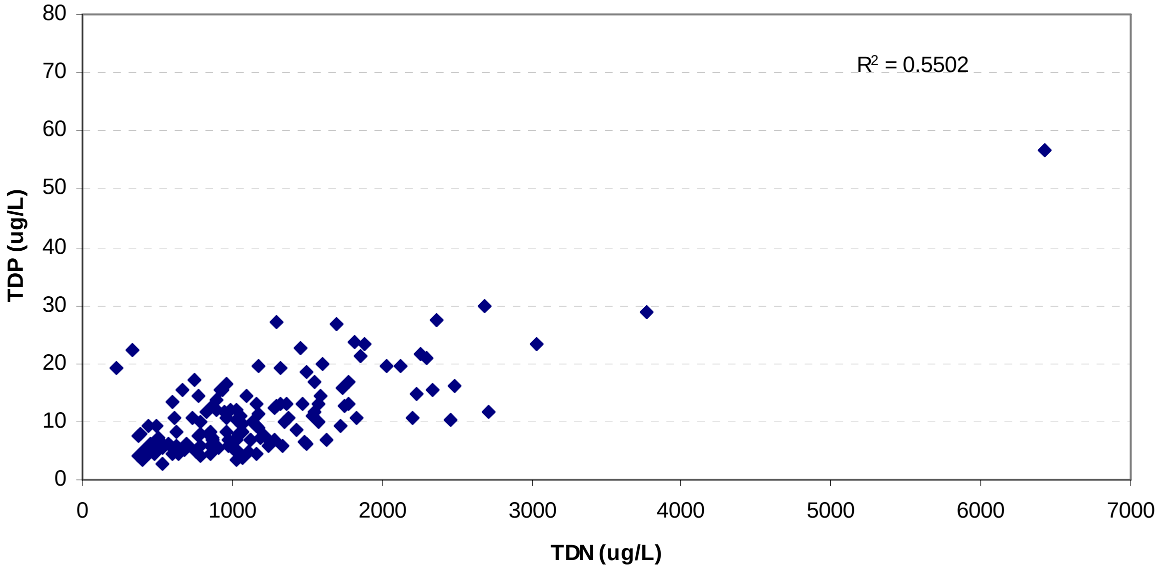


Figure 3.29. TDP relative to TDN concentrations for ponds within the study area.

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Chapter 4

Summary and Management Implications

4.1 Summary and Conclusion of the Gibbs Model

The preceding chapters provide data and interpretation to increase the knowledge of processes controlling either the hydrologic function or nutrient and solute chemistry of ponds of the Western Boreal Forest (WBF). Globally, there are few models except the Gibbs model that can be used to explain or predict the variability of surface water chemistry of major lakes and rivers across the world (Wetzel, 1983, Jorgensen and Vollenweider, 1989). There are fewer models for predicting water chemistry of small ponds and wetlands which are ubiquitous across continental North America and are important ecosystems for water birds and other aquatic organisms (DUC, 2006). Currently, more research is needed to determine the processes controlling the hydrologic function and the spatial variability of nutrient and solute chemistry of wetland-ponds in the WBF, and to assess or predict current impacts of landuse and climate change to develop models for assessing the susceptibility of wetlands (Buttle et al., 2000). The preceding chapters examined major controls of surface water chemistry at a continental scale as hypothesized initially by Gibbs (1970). The relative roles of the climate and geology interactions on surface water composition and concentration in ponds of the WBF of central North America were assessed by examining the potential for dilution by atmospheric precipitation, the dominance of geology and dissolution, and the evaporation-crystallization processes. Best management practices (BMP) and assessment of landuse and climate impacts will also be required at a finer scale. The research examined regional to local scale hydrologic interactions and thus their influence on surface water chemistry.

Application of the Gibbs (1970) model to a total of two-hundred and ten ponds surveyed from the Boreal Plain and transition to the Boreal Shield of Saskatchewan and Manitoba shows that most ponds fell within the rock dominance mechanism proposed by the Gibbs model (Figures 4.1 and 4.2). This is expected due to the moderate climate and high weathering rates of the dominant sedimentary bedrock. However, three distinct groups of ponds had surface water chemistry with salinities and chemical composition that clearly fell outside the range predicted by the Gibbs model. These groups reflect the regional heterogeneity in bedrock geology and complex surface-groundwater interactions.

The first group of ponds, characterized by moderately saline waters and relatively larger proportions of sodium and chloride were associated with topographic lows and and an outcrop belt of lower Silurian dolomites, and middle and upper Devonian red shales. These findings also correspond with the spatial locations of some of the saline springs and brackish waters identified by Grasby and Betcher (2002). Therefore low topographic position and the degree of mixing between intermediate scale freshwater flow systems and deep basin scale regional flow systems likely influence these waters. The very saline water in this area is the result of the dissolution process along long groundwater flow systems and not the evaporation-crystallization process that would be predicted by the Gibb's model. The Gibb's model does not consider continental scale or intermediate scale groundwater interactions, and interpreting surface water chemistry, and assessing susceptibility of aquatic ecosystems to land use would be misleading without an understanding of the regional hydrogeology. The Saskatchewan River Delta (SRD) is also associated with these hydrogeologic phenomena, and this has large implications for maintenance and management of this important boreal ecosystem, which will be expanded on later.

The second groups of ponds, was characterized by dilute surface water and a relatively lower proportion of sodium than would be expected from the Gibbs model if precipitation from oceanic sources dominates. Although these ponds were located in moderate to highly calcareous glacial deposits of the Pasquia Hills and Porcupine Hills, they were also located at the relatively highest positions within the local hydrologic flow system and may result in hydraulically mounded lakes that receive virtually all of their water from direct precipitation (Winter, 2001). The isolated and elevated position may result in the relatively low measures of TDS and the higher proportion of calcium to sodium reflects the inland precipitation ionic signature identified by Krawchuck (1998). The chemical composition may indicate some interaction with Ca rich surface geology in lake sediments of very short local flowpaths, but the relatively higher landscape position likely result in short flowpaths through calcareous till and maintain dilute water reflecting precipitation (Webster et al., 1996). These ponds were also generally small in size and may agree with findings of Eilers (1992) in that smaller lakes are more influenced by local geologic setting and flowpaths. Modifications of global models such as the Gibb's model need to reflect inter-continental precipitation chemistry. Without such, one may fail to classify isolated lakes which are more susceptible to climate change and landuse impacts.

The third group of ponds has moderately saline waters associated with much lower proportions of chloride predicted from initial bedrock weathering or evaporation-crystallization process. These ponds were also associated with relatively higher concentrations of sulphate and sodium. In general the ponds overlaid shales, commonly associated with gypsum and sedimentary pyrite which can be a major source of sulphate to surface waters (Cole, 1994).The ponds were located at a low topographic position at the toe of the regional upland slopes, typically associated with intermediate to regional flow systems as defined by Tóth (1999). These moderately saline waters agree with the hypothesis of intermediate flowpaths influencing these waters, and suggest an alternative control of surface water through mixing with intermediate to regional groundwater flow. This may be expected or typical in complex geology such as the Canadian sedimentary basin.

The variance in pond surface water chemistry in a region of moderate climate, are dominated by geologic process with moderate flushing and the interaction of local to regional surface-groundwater interactions. This results in increased concentrations of waters and variability in composition due to groundwater and dissolution, exclusive of evaporation process. In contrast, we see reduced concentrations and reduced variation in composition associated with isolated systems relative to rock dominated systems due to Ca^{2+} and HCO_3^- rich precipitation. Both of these need to be considered when assessing the influence of land use and climate change on intercontinental regions.

The initial analyses illustrate the importance of the interaction of geology and regional groundwater flow systems in explaining large variation in surface water concentration and composition. The majority of the ponds surveyed had surface waters that indicate dominance of geologic processes. While the surface waters concentration and composition generally fall within the boundary predicted for waters controlled by geology, the considerable variation observed requires further resolution to effectively predict surface water chemistry and apply BMP in this region. All ponds from the SRD or ponds that were influenced by regional scale groundwater flow and plotted on the ascending limb of Gibbs model were removed in the following analyses. Given that the climatic gradient across the study area was minimal (gross evaporation generally exceeded precipitation) and generally not confounding the relationships, a subset of one-hundred and forty-seven ponds were used to test influence of bedrock geology relative to more local controls of surficial geology and surface and shallow groundwater flowpath interactions on surface nutrient and solute chemistry.

4.2 Summary and Conclusion of Hydrologic Flowpaths and their Influence on Nutrient and Solute Chemistry

At a regional scale, and not considering larger continental scale groundwater inputs, bedrock geology was the best estimator of major ion composition, weathering parameters (TDS and pH) and to a lesser extent total dissolved nitrogen (TDN). Bedrock geology influenced the relative proportion of ions, pH and TDS by one of two mechanisms. The first mechanism is by direct mineral weathering of the bedrock; and the second mechanism is the permeability of the bedrock influencing the relative control of flowpath and flowlength and scale of flow systems on the proportion and concentration of ions in surface waters. Ponds overlying granite bedrock were characterized by lower concentrations of solutes, ionic composition similar to local precipitation and lower measures of pH and TDS. These results can be associated with more surface dominated flowpaths as influenced by the permeability of the bedrock or reduced weathering rates. Ponds overlying more permeable sedimentary bedrock were characterized by higher measures of pH and TDS, and ionic composition of the waters reflected the underlying bedrock geology. Accurate mapping of bedrock geology is imperative to predict impacts of landuse and climate change to develop models for assessing the susceptibility of wetlands.

At the local scale, the texture of surficial deposits influenced the nature and type of flowpath connecting slopes to ponds of the study area within geologic units. Ponds overlying a fine-grained surficial geologic environment appeared to have more potential to generate overland flow as concentrations of total dissolved phosphorus (TDP), TDN and dissolved organic carbon (DOC) increased and pH and TDS concentrations decreased. The increased concentrations of nutrients resulted from the increased potential for overland flow through organic layers of catchments as they can be major sources of nutrients (Macrae et al, 2005 and Macrae et al., 2006). Measures of pH were generally lower in ponds overlying the fine-grained sediments. This can result in a lower pH, similar to precipitation and dilution of nutrients. Ponds overlying coarse-grained lacustrine sediments appeared to reflect more groundwater contributions and were likely located in intermediate to regional flowpaths as concentrations of TDP, TDN and DOC were respectively lower and pH measures were relatively higher. The lower concentrations of TDP and DOC were the result of nutrient poor groundwater to the ponds or dilution via increased groundwater (Williams, 1985). The hydrologic residence time of water-soil interactions as influenced by the texture of surficial geology did not have a significant influence on solute concentrations.

With an increase in connected wetlands, there is potentially an increase in overland flow and quick flow generation during precipitation events similar to flow on fine-grained material. This resulted in a general increase in TDP, TDN and DOC concentrations across similar bedrock and surficial geologic settings. The increase of nutrients is likely the result of overland flow through nutrient rich organic layers or wetlands within the catchments (Macrae et al., 2005 and Macrae et al., 2006). Large wetland complexes connected to the ponds resulted in reduced TDP and TDN concentrations and indicates increased nutrient poor groundwater or dilution from increased flow into the pond (Williams, 1985). DOC concentrations were largely related to surficial geology and there was some relationship with connected wetland area. The lack of a strong relationship indicates complex interaction between wetland connectivity and the subsurface geologic connection to the ponds of the study.

Landscape position (pond order) was a relatively poor measure to characterize nutrient and solute chemistry of the study area. A decrease in TDP concentrations with increasing pond order was the only significant trend observed at a local scale. There was a decreasing trend in pH and TDN with increasing pond order, but they were not significant. Ponds located lower in the landscape did not show increased solute concentrations from increased groundwater contributions. Rather, they had lower concentrations of nutrients that was likely the result of nutrient retention (removal by deposition into sediments) or dilution from increased groundwater (Rechkow and Chapra, 1983 and Williams, 1985). The lack of relationship between landscape position and the parameters tested indicate that the distribution of wetlands and this, in turn, is potentially related to geomorphology are potentially greater controls on nutrient and solute chemistry of the study area.

4.3 Management Implications

In applying global models, such as that of Gibbs (1970) to estimate the dominant mechanisms influencing surface waters in continental Canada, consideration of regional groundwater and composition of intercontinental precipitation is required. Some changes are required and modifications to the empirical model are shown on Figures 4.3 and 4.4. Greater variability in salinity and composition within regions of moderate climate should be expected. The ascending limb of the model should likely reflect the degree of local meteoric waters mixing with regional to basin scale flow systems, rather than the evaporation-crystallization mechanism. Also, the descending limb should trend towards dilute waters with relatively lower proportions of sodium and chloride which resemble intercontinental precipitation.

Management policies and assessments of background chemistry across the boreal should be variable in regions with moderate climates, particularly if geology and thus hydrogeology is complex. When applying BMP, there is little separation between precipitation dominated systems as continental precipitation trends to a Ca^{2+} and HCO_3^-composition, which is similar to many bedrock dominated systems. Techniques must be developed to better identify more isolated and rain dominated systems as these may be more susceptible to climate variation and adjacent landuse.

The SRD is geologically considered a flood plain, alluvial silts deposited throughout by retreating glacial meltwater together with periodic flooding of the Saskatchewan River have left behind a fertile landscape that attracts a variety of waterfowl and wildlife (DUC, 2006). In addition to these ecologically distinct characteristics, most of the SRD also differs in relation to water chemistry with respect to the rest of the surrounding landscape. A combination of low topographic position, located within geological interfaces between sandstones and dolomites associated with large deep basin-scale discharge areas and alluvial sediments has led to proportionately different solute characteristics of surface waters. With respect to a water chemistry perspective and potentially a water quantity perspective of the SRD, the existing boundary of the lower delta could be revised to reflect the surficial geology of the area, as waters were influenced more by local controls. Moderate to high salinity waters within the SRD indicate that the application of management strategies to either control water quality or quantity would need to be at a regional to Williston basin scale in comparison to the remainder of the study area. Also, the SRD is located within a regional discharge area, therefore the relative role of local precipitation on pond permanence is likely minimal. Further, the role of ice damming and river flooding characteristics of large north flowing rivers, in maintaining ponds in the SRD may be different or limited capacity, requiring different management consideration compared to other large delta systems such as the Peace-Athabasca Delta. However, water quality within the SRD is likely dependent on local precipitation and seasonal flooding to dilute these waters. Without seasonal flooding, some of the ponds associated with the SRD may be driven to more saline conditions which will alter vegetation and thus habitat for waterfowl.

Climate is the primary driver of controls used in the Gibb's (1970) model and also suggested in distinguishing Fundamental Hydrologic Landscape Units (FHLU) among landscapes (Winter 2001, Devito et al. 2005). In moderate climates such as continental boreal, processes of evaporation-crystallization or dilution by excessive flushing from rain are not expected to dominate. Thus, climate influences are reduced and geology dominates and the application of an FHLU applies directly to continental boreal. However, understanding of regional bedrock lithology, hydrogeology and groundwater-surface water interactions is important to explain the variation in pond composition and concentration, not expected from previous global surface chemistry models. Further, within geology dominated regions, some understanding of local surficial geology is required to evaluate the influence of local and intermediate flowpaths and its influence on surface water salinity, composition and nutrient dynamics. Thus, to evaluate the susceptibility of pond water chemistry or water levels to land use or climatic changes, management policy may need to be set specific to geologic units.

In contrast, more local controls of hydrologic flow path, notably surface flow via surficial geology and wetland connectivity appear to influence nutrient dynamics, in addition to pond-sediment interactions, to a greater extent than geology. Application of local management practices may be applied across geologic units when considering nutrient dynamics of these ecosystems.

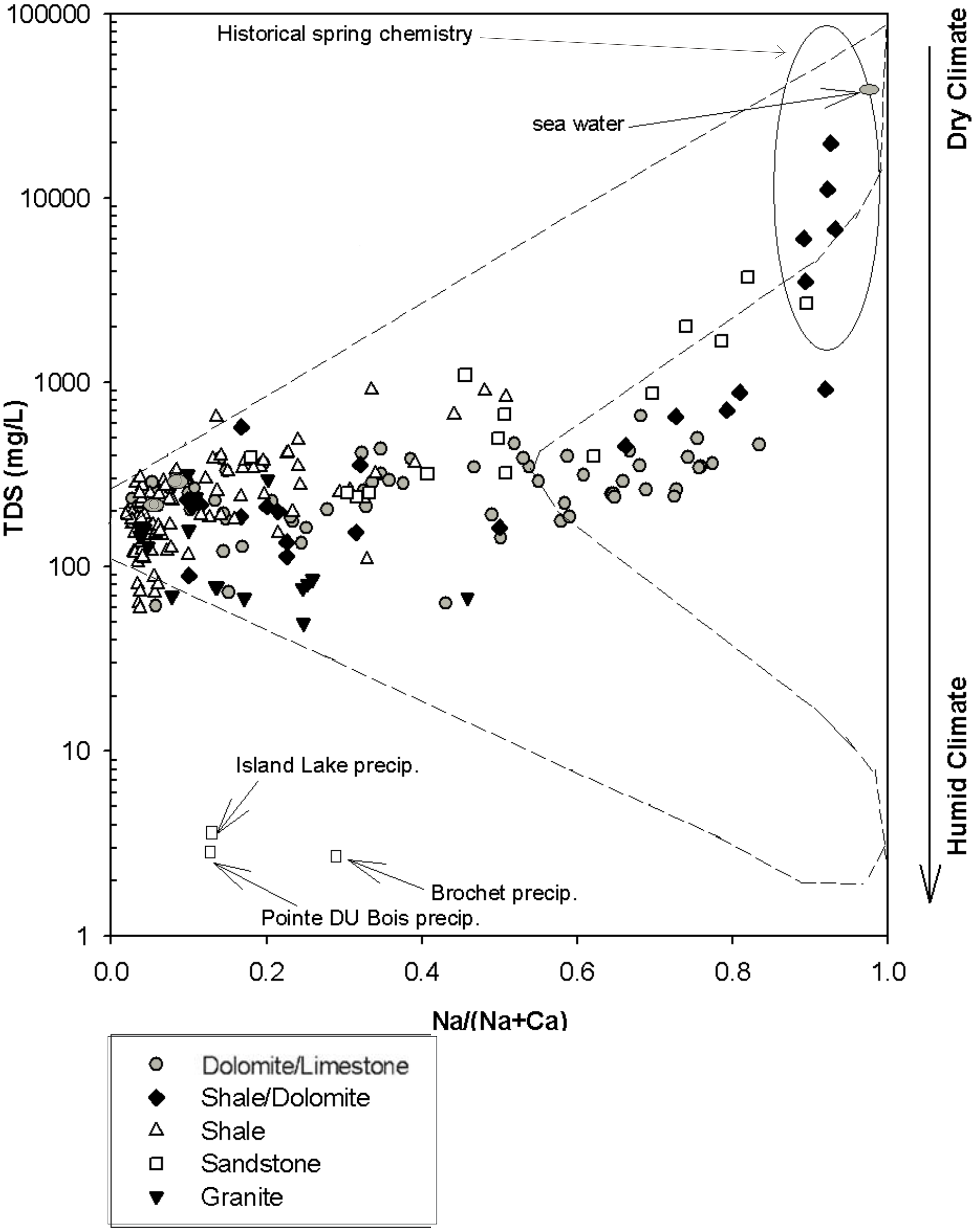

Figure 4.1. Variation of the weight ratio Na/(Na + Ca) as a function of TDS of ponds, and then stratified by major bedrock geological units of the study area. Dashed line represents the best approximation of the empirical boundary of world waters as delineated by Gibbs (1970). Precipitation chemistry reported from Krawchuk (1998), Island Lake (53°51'N 94°44'W), Brochet (57°54'N 101° 33'W), and Pointe Du Bois (50°18'N, 95°35'W). Ellipse displays the approximate range of Na/(Na+Ca) as a function of TDS for the brackish to saline springs West of Lake Winnepegosis (Grasby and Betcher, 2002).

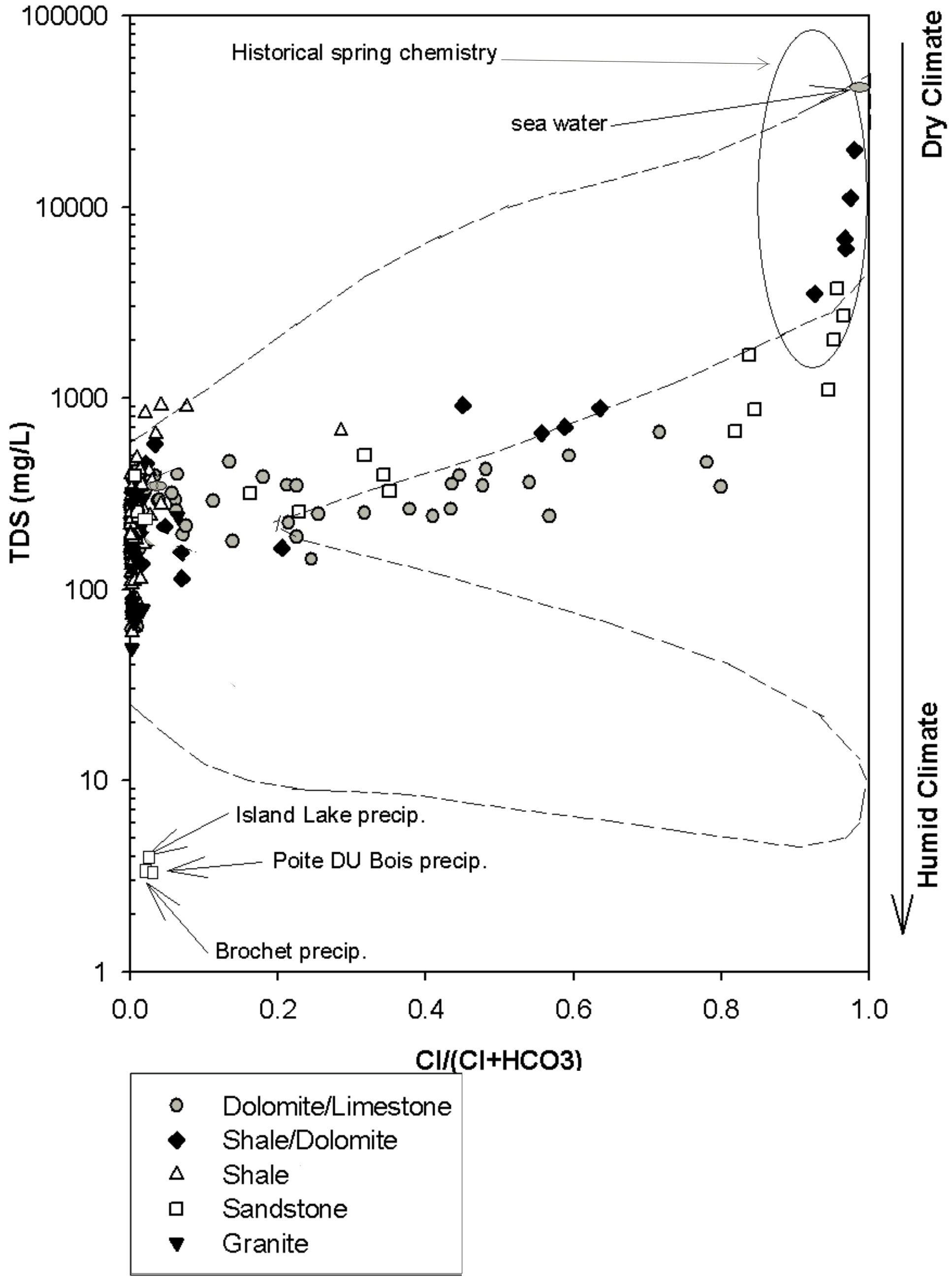

Figure 4.2. Variation of the weight ratio Cl/(Cl + HCO_3) as a function of TDS of ponds, then stratified by major bedrock geological units of the study area. Dashed line represents the best approximation of the empirical boundary of world waters as delineated by Gibbs (1970). Precipitation chemistry reported from Krawchuk (1998), Island Lake (53°51'N 94°44'W), Brochet (57°54'N 101° 33'W), and Pointe Du Bois (50°18'N, 95°35'W). Ellipse displays the approximate range of Cl /(Cl + HCO_3) as a function of TDS for the brackish to saline springs West of Lake Winnepegosis (Grasby and Betcher, 2002).

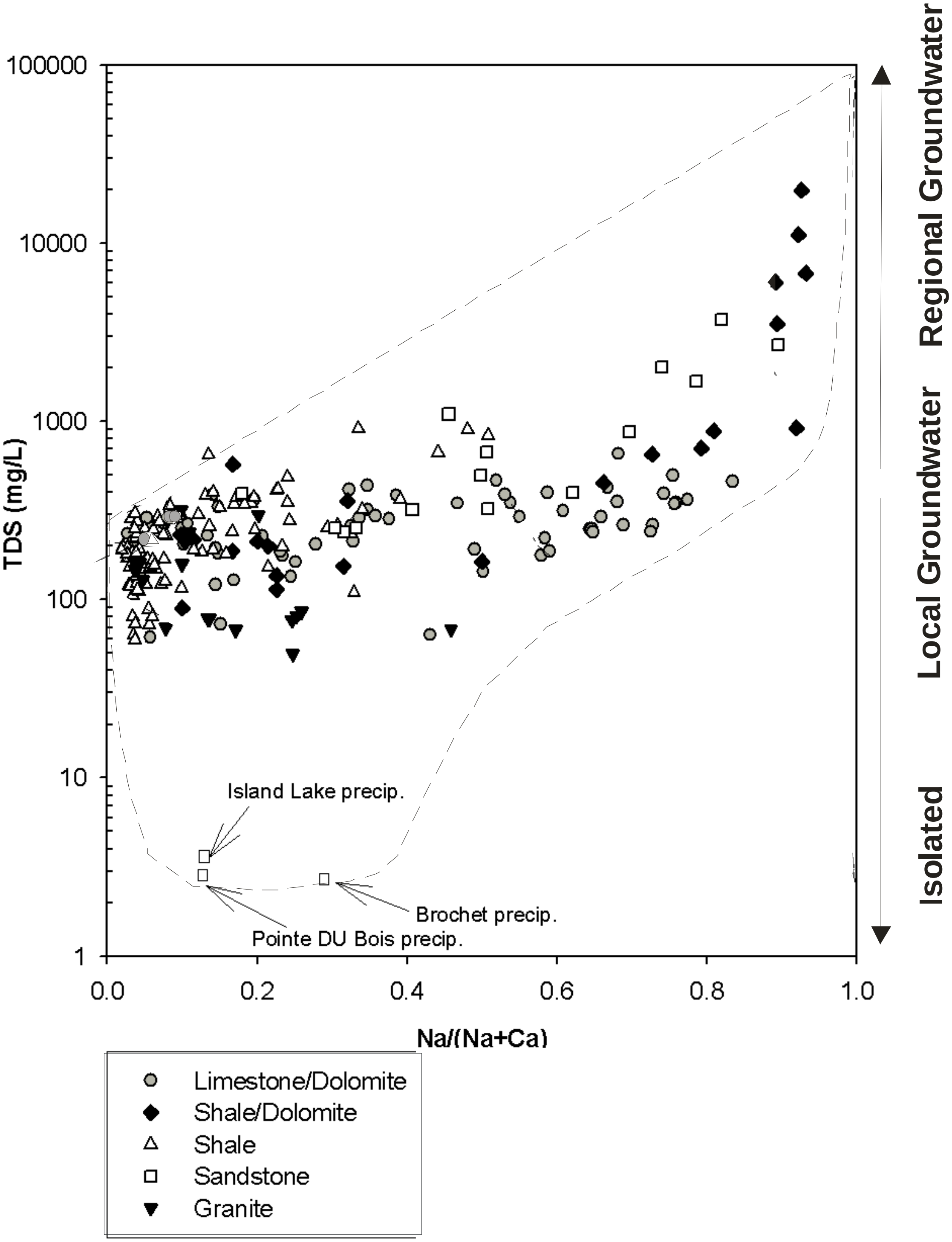

Figure 4.3. Proposed envelope of the weight ratio Na/(Na + Ca) as a function of TDS to improve the applicability of the Gibbs (1970) model for continental waters of Canada. Precipitation chemistry reported from Krawchuk (1998), Island Lake (53°51’N 94°44’W), Brochet (57°54’N 101° 33’W), and Pointe Du Bois (50°18’N, 95°35’W).

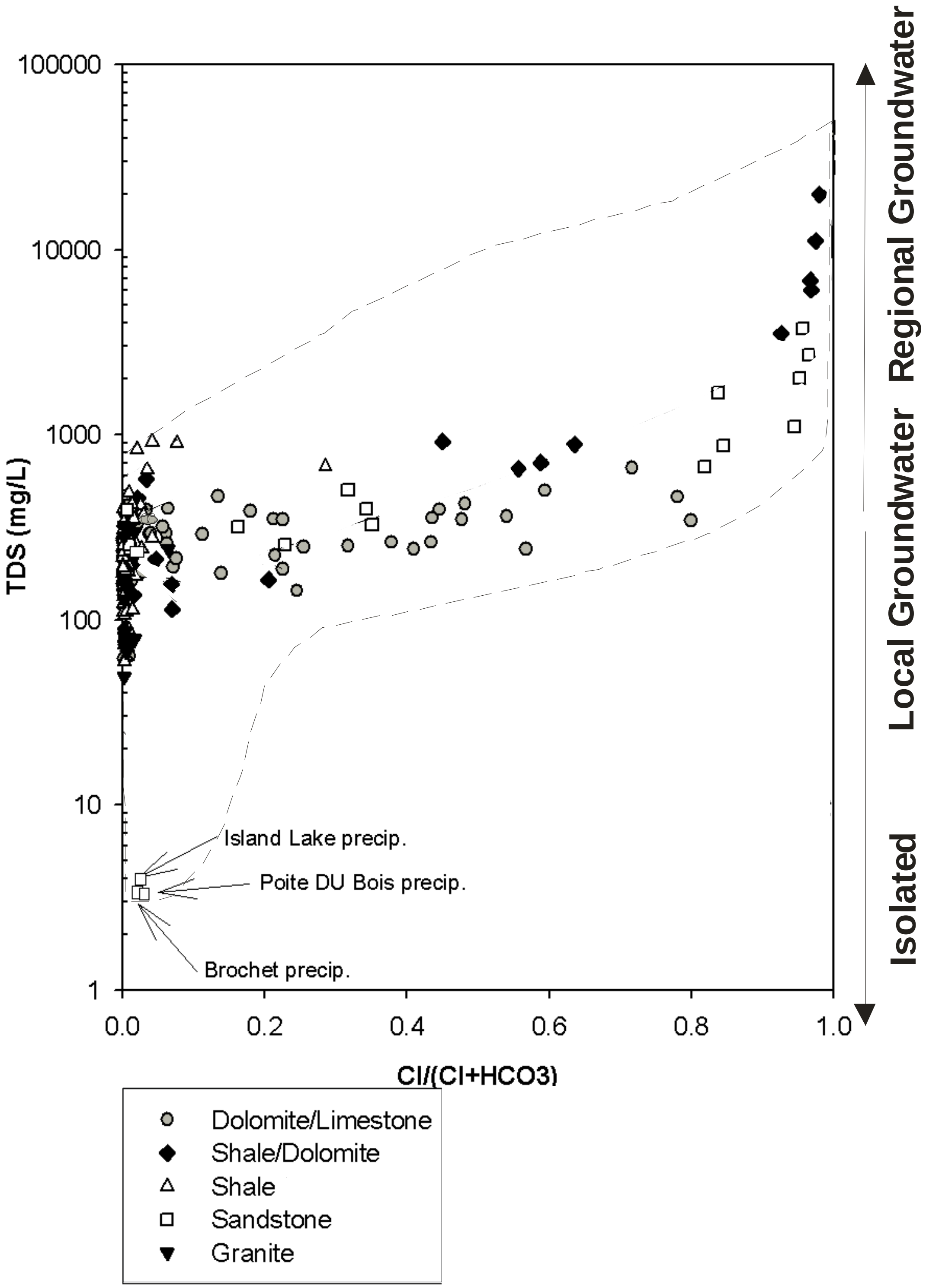

Figure 4.4. Proposed envelope of the weight ratio Cl/(Cl + HCO_3) as a function of TDS to improve the applicability of the Gibbs (1970) model for continental waters of Canada. Precipitation chemistry reported from Krawchuk (1998), Island Lake (53°51'N 94°44'W), Brochet (57°54'N 101° 33'W), and Pointe Du Bois (50°18'N, 95°35'W).

4.4 References

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Appendix A

Table A.1. One-way ANOVA for the ratio of Ca/(Ca + Mg) in ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of connected wetland area (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >=10 km^2) as shown on Figure 3.7.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	1.045	3	0.348	34.736	0.000
Error	1.403	140	0.01		
Squared multiple R=.427					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	0.639	3	0.213	16.486	0.000
Error	1.809	140	0.013		
Squared Multiple R=.261					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	0.038	3	0.013	0.735	0.533
Error	2.410	140	0.017		
Squared Multiple R=.016					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	0.238	3	0.079	5.018	0.002
Error	2.210	140	0.016		
Squared Multiple R=.093					

Table A.2. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of the ratio of Ca/(Ca + Mg) across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) as shown on Figure 3.7. Linear regression was conducted on the associated trends described.

Ca/(Ca+Mg)	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.000	0.238	0.839	0.421	0.120	0.016
Surficial Geology	0.000	0.000	0.000	0.049	0.046	0.036
Pond Order	0.008	0.142	0.293	0.014	0.001	0.000
Connected Wetland Area	0.025	0.001	0.081	0.035	0.078	0.006

Table A.3. One-way ANOVA for the ratio of $SO_4/(SO_4 + HCO_3)$ in ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of wetland area connected to the pond (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >=10 km^2) as shown on Figure 3.9. Data were log transformed.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	492.228	3	164.076	29.822	0.000
Error	771.265	140	5.502		
Squared Multiple R=.390					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	77.040	3	25.680	3.033	0.031
Error	1185.454	140	5.468		
Squared Multiple R=.061					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	0.177	3	0.059	1.662	0.178
Error	4.980	140	0.036		
Squared Multiple R=.034					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	0.143	3	0.048	1.326	0.258
Error	5.015	140	0.036		
Squared Multiple R=.028					

Table A.4. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of the ratio of $SO_4/(SO_4 + HCO_3)$ across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) and as shown on Figure 3.11. Linear regression was conducted on the associated trends described.

SO_4/SO_4+HCO_3	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.783	0.000	0.034	0.111	0.293	0.178
Surficial Geology	0.098	0.150	0.012	0.001	0.001	0.031
Pond Order	0.289	0.708	0.954	0.010	0.001	0.001
Connected Wetland Area	0.187	0.266	0.278	0.016	0.012	0.011

Table A.5. One-way ANOVA for pH of ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of connected wetland area (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >10 km^2) as shown on Figure 3.11.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	7.111	3	2.37	0.358	0.000
Error	50.185	140			
Squared Multiple R=.124					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	6.394	3	2.131	5.862	0.001
Error	50.903	140	0.364		
Squared Multiple R=.112					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	0.873	3	0.291	0.722	0.540
Error	56.423	140	0.403		
Squared Multiple R=.015					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	7.701	3	2.567	7.247	0.000
Error	49.595	140	0.354		
Squared Multiple R=.137					

Table A.6. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of pH across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) and as shown on Figure 3.11. Linear regression was conducted on the associated trends described.

pH	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.000	0.443	0.541	0.115	0.005	0.000
Surficial Geology	0.000	0.472	0.091	0.094	0.001	0.000
Pond Order	0.051	0.438	0.511	0.014	0.001	0.000
Connected Wetland Area	0.046	0.000	0.004	0.028	0.107	0.057

Table A.7. One-way ANOVA for TDS (mg/L) of ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of connected wetland area (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >10km^2) as shown on Figure 3.13.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	135384.053	3	45128.018	5.058	0.002
Error	1204526.226	135	8922.416		
Squared Multiple R=.101					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	95819.740	3	31939.913	3.466	0.018
Error	1244090.539	135	9215.485		
Squared Multiple R=.072					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	14304.225	3	4768.075	0.486	0.693
Error	1325606.054	135	9819.304		
Squared Multiple R=.011					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	77939.206	3	25979.735	2.779	0.044
Error	1261971.073	135	9347.934		
Squared Multiple R=.058					

Table A.8. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of TDS across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) as shown on Figure 3.13. Linear regression was conducted on the associated trends described.

TDS	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.003	0.433	0.061	0.045	0.003	0.038
Surficial Geology	0.016	0.014	0.685	0.028	0.029	0.007
Pond Order	0.787	0.683	0.232	0.000	0.001	0.007
Connected Wetland Area	0.847	0.024	0.729	0.000	0.037	0.016

Table A.9. One-way ANOVA for DOC of ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of connected wetland area (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >10 km^2) as shown on Figure 3.16.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	407.298	3	135.766	0.910	0.438
Error	20587.286	138	149.183		
Squared Multiple R=.012					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	2527.124	3	842.375	6.295	0.000
Error	18467.460	138	133.822		
Squared Multiple R=.120					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	307.050	3	102.350	0.683	0.564
Error	20687.534	138	149.910		
Squared Multiple R=.015					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	1053.756	3	351.252	2.431	0.068
Error	19940.828	138	144.499		
Squared Multiple R=.050					

Table A.10. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of DOC across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) as shown on Figure 3.16. Linear regression was conducted on the associated trends described.

DOC	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.190	0.253	0.318	0.008	0.000	0.004
Surficial Geology	0.000	0.732	0.065	0.098	0.005	0.001
Pond Order	0.187	0.840	0.599	0.013	0.000	0.000
Connected Wetland Area	0.067	0.491	0.168	0.024	0.003	0.014

Table A.11. One-way ANOVA for TDP of ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of wetland area connected to the pond (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >10 km^2) as shown on Figure 3.20.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	0.722	3	0.241	0.714	0.545
Error	46.818	139	0.337		
Squared Multiple R=.015					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	5.040	3	1.680	5.494	0.001
Error	42.500	139	0.306		
Squared Multiple R=.106					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	4.939	3	1.646	5.372	0.002
Error	42.601	139	0.306		
Squared Multiple R=.104					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	5.180	3	1.727	5.666	0.001
Error	42.360	139	0.305		
Squared Multiple R=.109					

Table A.12. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of TDP across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) as shown on Figure 3.20. Linear regression was conducted on the associated trends described.

TDP	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.835	0.165	0.499	0.005	0.015	0.000
Surficial Geology	0.694	0.010	0.091	0.001	0.073	0.039
Pond Order	0.010	0.862	0.372	0.061	0.000	0.023
Connected Wetland Area	0.041	0.001	0.010	0.029	0.069	0.045

Table A.13. One-way ANOVA for TDN of ponds overlying four different bedrock units (dolomite/limestone, shale/dolomite, shale, and granite), four different surficial geological units (exposed bedrock, coarse-grained, glacial till, and fine-grained), four different classifications of pond order (-2 &–1, 0, 1, >=2) and four different classifications of connected wetland area (0-0.1 km^2, 0.1-1 km^2, 1-10 km^2, and >10 km^2) as shown on Figure 3.24.

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Bedrock Geology	4212248.23	3	865372.029	2.782	0.043
Error	7.56E+07	138	311031.902		
Squared Multiple R=.057					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Surficial Geology	2284396.699	3	761465.566	2.431	0.068
Error	4.32341E+07	138	313290.738		
Squared Multiple R=.050					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Pond Order	715372.865	3	238457.622	0.734	0.533
Error	4.48031E+07	138	324660.476		
Squared Multiple R=.016					

Source	Sum-of-squares	df	Mean-square	F-ratio	P
Connected Wetland Area	648832.532	3	216277.511	0.665	0.575
Error	4.48697E+07	138	325142.652		
Squared Multiple R=.014					

Table A.14. Orthogonal polynomial contrasts were used to test linear, quadratic, cubic trends of TDN across ordered categories or levels of bedrock geology (weathering gradient from high to low), surficial geology (coarse grained to fine grained), pond order (low to high) and connected wetland area (low to high) as shown on Figure 3.24. Linear regression was conducted on the associated trends described.

TDN	Contrasts			Least squares regression		
Factor	**linear (p-value)**	**quadratic (p-value)**	**cubic (p-value)**	**linear r2**	**quadratic r2**	**cubic r2**
Bedrock Geology	0.071	0.023	0.520	0.004	0.032	0.014
Surficial Geology	0.023	0.525	0.194	0.032	0.012	0.004
Pond Order	0.370	0.219	0.657	0.004	0.002	0.000
Connected Wetland Area	0.677	0.112	0.482	0.001	0.018	0.004

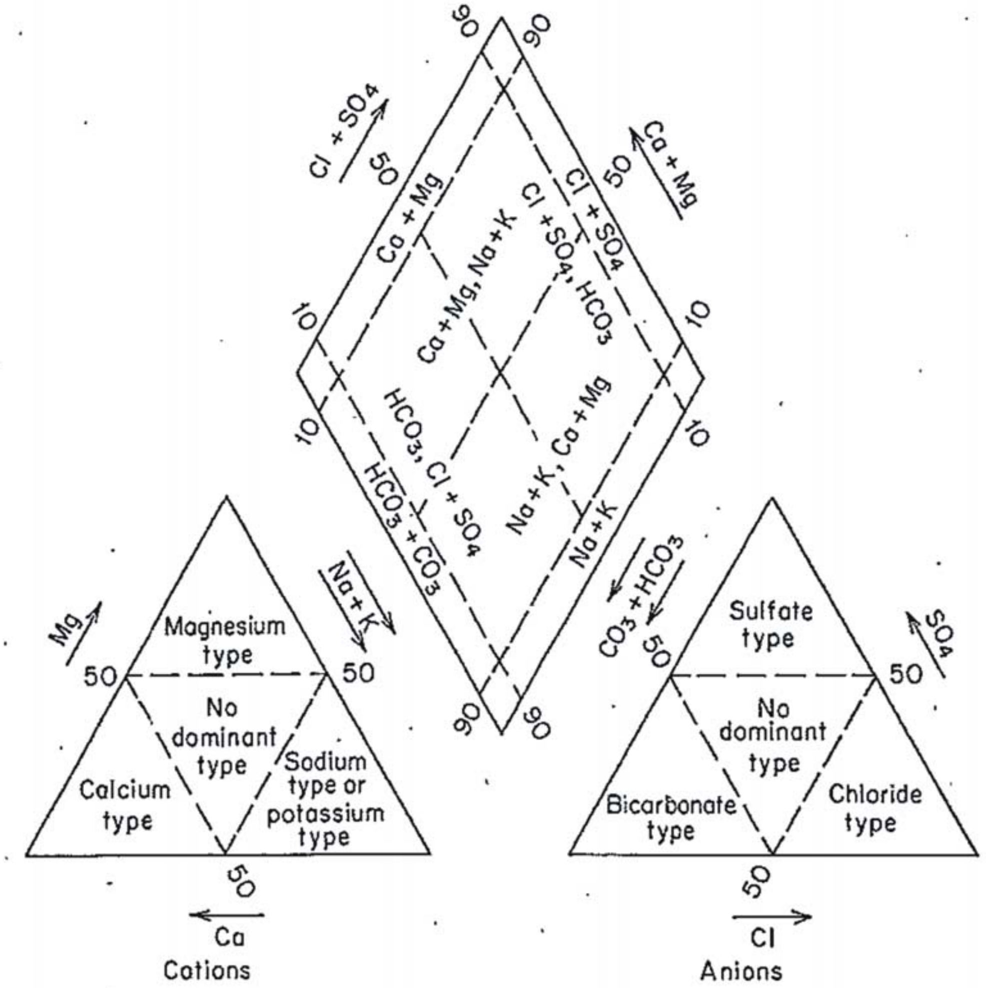

Figure A.1. Classification diagram for cation and anion facies. Figure obtained from Freeze and Cherry (1979).