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Characterization Of Phosphorus, Nitrogen, And Sulfur Concentrations In A Paired Disturbed And Natural Wetland In Northwest Minnesota

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CHARACTERIZATION OF PHOSPHORUS, NITROGEN, AND SULFUR CONCENTRATIONS IN A PAIRED DISTURBED AND NATURAL WETLAND IN NORTHWEST MINNESOTA

by

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This thesis, submitted by Nicolas H. Buer in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done, and is hereby approved.

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Title	Characterization of Phosphorus, Nitrogen, and Sulfur Concentrations in a Paired Disturbed and Natural Wetland in Northwest Minnesota
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ABSTRACT

A degraded wetland with a history of human-induced hydrologic alterations lies within northwestern Minnesota's Skull Lake Wildlife Management Area (WMA). Although conservation practices have been enacted by the Minnesota Department of Natural Resources (MNDNR), there remains interest in the wetland's potential for ecological restoration. Restoration should not be undertaken without an understanding of underlying factors leading to degradation. A paired study between the disturbed wetland at Skull Lake WMA and the relatively natural wetland in the nearby Caribou WMA was designed to help understand near surface pore water geochemistry in an effort to determine causes of degradation and the potential for reversal. Shallow groundwater samples collected along and perpendicular to a major ditch flowing through the wetland were analyzed for pH, Eh, sulfide (H_2S), soluble reactive phosphorus (SRP), sulfate (SO_4), nitrate (NO_3), and nitrite (NO_2). Data revealed nutrient gradients and characterized nutrient transport relative to State Ditch 84. Wetland geochemistry comparisons between the disturbed cattail marsh and undisturbed sedge meadow showed increased concentrations of SRP, Eh, and pH. This indicates that Caribou WMA is a low nutrient ecosystem and suggests that Skull Lake WMA has become a phosphorus sink. Correlation between distance to State Ditch 84 and geochemical constituents indicated increased acidity and nitrite concentrations and possible SRP export out of the system during the fall. Ecological restoration through prescribed burning and water level control

may reduce invasive macrophyte communities, but altered pore water chemistry and increased pore water SRP concentrations may inhibit the full restoration potential of Skull Lake WMAs wetland.

CHAPTER I

INTRODUCTION

During the last hundred years, ditching, draining, and increased agricultural pressure has degraded wetlands within Skull Lake Wildlife Management Area (WMA) compared to the largely undisturbed sedge meadows prevalent in Caribou WMA (Bradof, 1992), both of which lie in the heart of the Tallgrass Aspen Parkland (TAP) (Figure 1) eco-region (MNDNR, 2012). Drastically altered plant communities have also changed species richness and habitat quantity and quality. The MNDNR has identified 85 Species in Greatest Conservation Need (SGCN) in the eco-region with most specialist and non-specialist species depending upon wetland habitats. Loss and degradation prevention, preservation, and restoration of wetland habitats are important to SGCN. The avoidance of impoundment creation and invasive exotic plant management are keys to supporting these species (MNDNR, 2006). The possibility of restoration at Skull Lake WMA may offer some relief to SGCN; however the effort of restoring plant communities in Skull Lake WMA cannot be undertaken without a more complete understanding of how and why current conditions have been brought about.

The hydrology of Skull Lake WMA has been altered at least three times: original ditching and draining, dike construction and subsequent flooding, and draining after reopening the dike. Minor changes in average water depth or residence time have been shown to promote changes in macrophyte communities from native to invasive (Urban et al., 1993; Budelsky & Galatowitsch, 2000; Magee & Kentula, 2005; Richardson et al.,

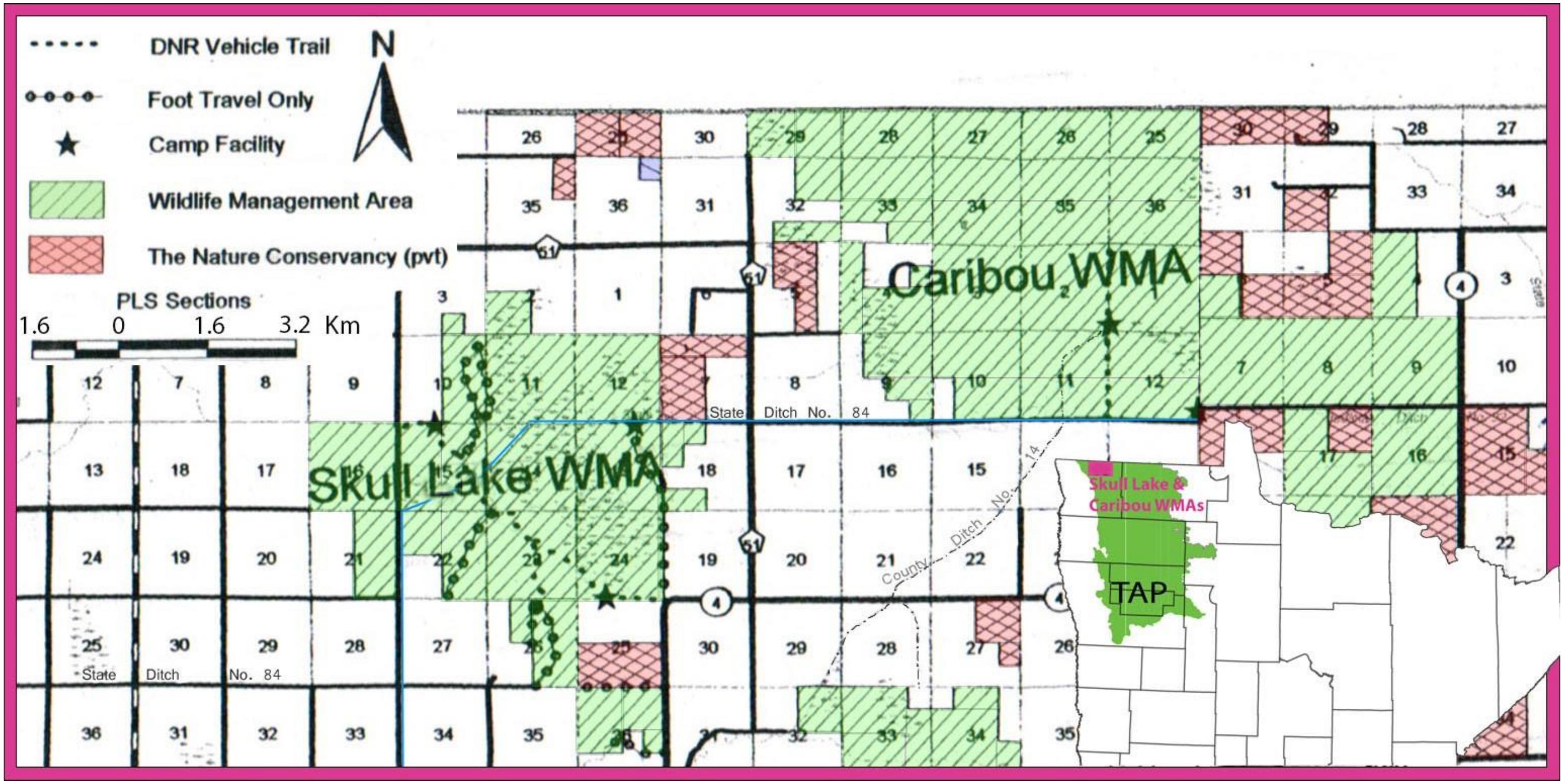

Figure 1: Location of Skull Lake and Caribou WMAs within the Tallgrass Aspen Parklands (TAP) eco-region, Minnesota. The overlay shows both WMAs, The Nature Conservancy (TNC) owned land, and their relationship to roads.

2008). Restoration of wetland hydrology after prolonged periods of such events (years to decades) may not be enough by itself to bring back native communities. Flooding and deposition of nutrients carried from upstream sources, compounded over decades, may change nutrient and soil profiles drastically, subsequently discouraging the return of native plant communities (Zedler, 2000). Comparison of nutrient concentration and distribution profiles between the hydrologically connected control wetland (Caribou WMA) and the downstream nutrient affected wetland (Skull Lake WMA) can help determine the basic factors that have led to degradation.

It is hypothesized that years of agricultural pressure, including ditching, draining, and flooding have led to increased nutrient concentrations and altered biogeochemistry in Skull Lake WMAs damaged wetlands when compared to the relatively natural wetlands of Caribou WMA. An overall difference in plant community composition (invasive versus native in Skull Lake and Caribou WMAs, respectively) and corresponding community nutrient requirements also suggest contrasting nutrient availabilities between the two wetlands.

The objectives of this research are to:

1) Compare and contrast nutrient concentrations between wetlands at Caribou and Skull Lake WMAs.
2) Determine vertical nutrient distribution in the wetland phreatic zone at Caribou WMA.
3) Characterize the horizontal and vertical nutrient distribution in the saturated subsurface, relative to the ditch at Skull Lake WMA.

4) Define which key factors are responsible for the ecosystem change at Skull Lake WMA.
5) Recommend ways that ecological restoration may be implemented, if at all possible.

An absence of inflowing surface waters and associated anthropogenic nutrients (USGS, 2011) at Caribou WMA, as well as high native plant density (MNDNR, 2011a) relative to Skull Lake WMA indicate nutrient levels may be low in comparison to Skull Lake wetlands. *Carex* species adaptations to P limitation also indicate a probable lower nutrient ecosystem. Abundance of grass species with root-associated nitrogen fixing bacteria may be evidence of N and a lack of P (DiTomasso & Aarsen, 1989). Co-limitation of P and N may also be plausible in this system.

The overwhelming biomass of species with high nutrient requirements (e.g. *Typha, Phalaris*) (Craft et al., 2007), in comparison to Caribou WMA, may indicate higher nutrient levels throughout Skull Lake wetlands (Figures 5). Ecosystems with high nutrient availability have been shown to favor taller plant species (*Typha),* excluding shorter species due to light restrictions, thereby decreasing macrophyte biodiversity (Tilman, 1985; Moore & Keddy, 1989). The ditch system and downstream impoundment may indicate high nutrient and sediment accumulation from slowed agricultural runoff (Mitsch et al., 1995). P or N limitation may be possible throughout the marsh, but evidence has been shown that wetlands with high levels of P and low N favor macrophytes with nitrogen fixing bacteria present in the rhizosphere (*Typha)* (Bieboer, 1984; DiTomasso & Aarsen, 1989).

Subsurface nutrient gradients may be revealed through multi-depth sampling. Gradients between pore water P and water column P can be established through pore water P uptake by macrophyte roots (Reddy et al., 1999). It seems plausible that increasing organic burial depth and removal from surface oxidation would allow for an increase in reactive P concentrations at depth. Leakage of oxygen from *Typha* rhizospheres and uptake of reactive P throughout the root zone (Figure 2) may mask this process. The opposite may be true for N concentrations because of the direct relationship between the atmosphere, the rhizosphere, and nitrification processes, unless the system is being overwhelmed by allocthonous sources of N (Figure 3). Pore water P concentrations may increase with high P loading in the water column, and contribute P to the water column during periods of low P loading (Mitsch et al., 1995; Reddy et al., 1999; Richardson, 1985). Nutrient distribution in sub-surface waters could vary temporally with increased runoff and concentrations occurring in the spring or after large rain events, producing a decreasing gradient away from the ditch. Other times of the year may not show any significant variation due to years of nutrient loading and storage.

It is proposed that P may currently be the largest influence on Skull Lake wetland macrophyte communities, although N and S may also play roles in decreased native biodiversity (Li et al., 2009). Changes in hydrology due to human involvement as well as plant physiology may also factor into differences in biodiversity between the two wetlands. Comparative sampling and data analysis of the control and test wetlands will highlight differences in pore water geochemistry. Determination of the geochemical factors influencing wetland community biodiversity will help determine restoration potential. If sedge meadow restoration efforts prove to be difficult, functional wetland restoration could still be within grasp.

CHAPTER II

BACKGROUND

Recent History

From 1780 to 1980, Minnesota lost 42 percent of its wetlands (USEPA, 2011). From 1930 to 1993 alone, the TAP in Minnesota had a decrease in wetland coverage from 25 percent to 6 percent (MNDNR, 2006). Human activities continue to degrade wetlands, turning once biologically diverse native ecosystems into severely altered, near-monotypic stands of invasive species. Wetland mitigation resulting in the creation, restoration, or preservation of functioning wetlands has become common practice in the United States (Hunt, 2001; Spieles, 2005). The focus of these practices is to improve water quality, decrease erosion, and mitigate downstream floods (Hunt, 2001; USEPA, 2011). By slowing water flow and increasing its residence time within a wetland, most sediment and nutrients can be sequestered or assimilated by established macrophytes (Tanner, 1996; Carter, 1997; Novitzki, 1997). Unfortunately, ecological restoration is often overlooked when producing a wetland that is functional in all other respects (Zedler, 2000).

Extensive changes can occur in macrophyte communities over time due to excessive draining or extended flooding in natural wetlands (Newman et al., 1998; Magee & Kentula, 2005). A combination of one change after the other can prove deadly to many native species. Understanding the hydrologic regime and how it has changed complements any assessment of water quality (Hunt et al., 1999).

Biogeochemistry

Nonpoint nutrient contamination from urban, agricultural, and atmospheric sources can have detrimental effects on native wetlands (Carpenter et al., 1998; Zedler, 2000). Increased phosphorus (P) and nitrogen (N) availability favors highly competitive, invasive macrophytes (e.g. cattail and reed canary grass, *Typha* spp. and *Phalaris* spp. respectively) (Noe et al., 2001; Li et al., 2010). Increased reduction of sulfate (SO_4) and toxic sulfide (H_2S) in anoxic soils can increase available P (Lamers et al., 1998). In conjunction with increased P, excess SO_4 and H_2S can also produce higher native plant toxicity (Li et al., 2009). Addition of P to low nutrient systems can decrease Eh, adversely affecting wetland plant growth (Drake et al., 1996; Qualls et al., 2001; Colbert, 2000; Li et al., 2010). Eh decreases can subsequently be overcome by increased P availability and exploited by macrophytes that respond well to high P (*Typha, Phalaris*) (Li et al., 2010).

Phosphorus

Phosphorus (P) exists in both organic and inorganic forms of soluble and insoluble compounds in nature (Reddy et al., 1999; Mitsch & Gosselink, 2007). Organic forms of P are mostly associated with living organisms and can be a major portion of total phosphorus (TP) in anaerobic soils (Stevenson & Cole, 1999). These forms range from low to high molecular weight compounds and can generally be classified as either easily decomposable P compounds (nucleic acids, phospholipids, sugar phosphates) or slowly decomposable P compounds (inositol phosphates-phytin) (Reddy et al., 1999). Soluble unreactive P (SUP) is primarily made up of most organic non-particulate forms of P as well as chains of large inorganic P molecules (polyphosphates). This fraction is measured by subtracting soluble reactive P (SRP) from soluble P (SP) (SRP-SP=SUP) (Carlson & Simpson, 1996). Organic P of this nature only becomes bioavailable after conversion to orthophosphate via digestion or ultra-violet radiation (Carlson & Simpson, 1996; Reddy et al., 1999; Mitsch & Gosselink, 2007). However, many studies have focused on inorganic forms of P because of the slow decomposition rates of organic P sources and subsequent low bioavailability in anaerobic conditions (Reddy et al., 1999).

Particulate P (PP) is readily separated from the SP fraction via a 0.45 micron filter (cellulose membrane) (Carlson & Simpson, 1996; Reddy et al., 1999). PP can be obtained by subtracting SP from TP concentrations (TP-SP=PP). It contains both organic and inorganic forms of P usually stored in bacteria and detritus and often adsorbed to clays and other sediments by chemical bonding of negatively charged phosphates to positively charged broken edges of clays (Carlson & Simpson, 1996; Reddy et al., 1999; Mitsch & Gosselink, 2000). Al, Fe, and Mn can cause P precipitation in acidic soils, while Ca and Mg can cause precipitation in alkaline soils (Reddy et al., 1999).

Soluble reactive phosphorus (SRP) is the other part of a SP fraction and will be the focus of this research. SRP primarily consists of orthophosphate, which exists as the anion $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}; at pHs of 2 to 7, 8 to 12, and >13, respectively (Mitsch & Gosselink, 2007; Richardson & Vepraskas, 2001), but can contain small portions of other reactive P compounds. SRP is considered bioavailable because it is in a form that can be taken up directly by plants. It is generally used as an index of the amount of P immediately available for plant growth and in groundwater is usually the same as TP (Domagalski & Johnson, 2012; Mitsch & Gosselink, 2007; Carlson & Simpson, 1996).

Phosphorus goes through a sedimentary cycle and does not have a gaseous phase (Figure 2) like nitrogen (N) (Figure 3), or sulfur (S) (Figure 4) (Mitsch & Gosselink, 2007). P mobilization and fixation is controlled directly and indirectly by pH and redox conditions. Bioavailability is highest in circumneutral (pH 5.5 to 7.4), anaerobic conditions (Tiner, 1997; Reddy et al., 1999; Mitsch & Gosselink, 2007). Physical mobility is possible via the advective transport of adsorbed, precipitated, or organically bound P particles in the surface water (Kadlec, 1987; Reddy et al., 1999). Chemical mobility is possible during the soluble phase in anaerobic conditions. When ferric (Fe^{3+}) iron is reduced to more soluble ferrous (Fe^{2+}) compounds, bound P is released. Hydrolysis of ferric and aluminum phosphates as well as the release of P sorbed to clays and hydrous oxides can also be important anaerobic reactions (Mitsch & Gosselink, 2007). P bound to Al or Fe at low pH becomes increasingly available with increasing pH, while P bound to Ca and Mg at higher pH become more available as pH decreases. Sulfuric, nitric, and organic acids produced by chemosynthetic bacteria can also release P bound in insoluble salts (Reddy et al., 1999; Richardson & Vepraskas, 2001; Mitsch & Gosselink, 2007).

Assimilation and fixation removes dissolved P ions from solution, lowering available soluble P concentrations (Brady & Weil, 2002). P retention in biologically unavailable forms can involve a variety of physical, biological and chemical processes (Reddy et al., 1999). Organic uptake of P can be significant in wetlands, but it is periodical and balanced by release of P during decomposition (Reddy & Debusk, 1987; Mitsch et al., 1995; Reddy et al., 1999).

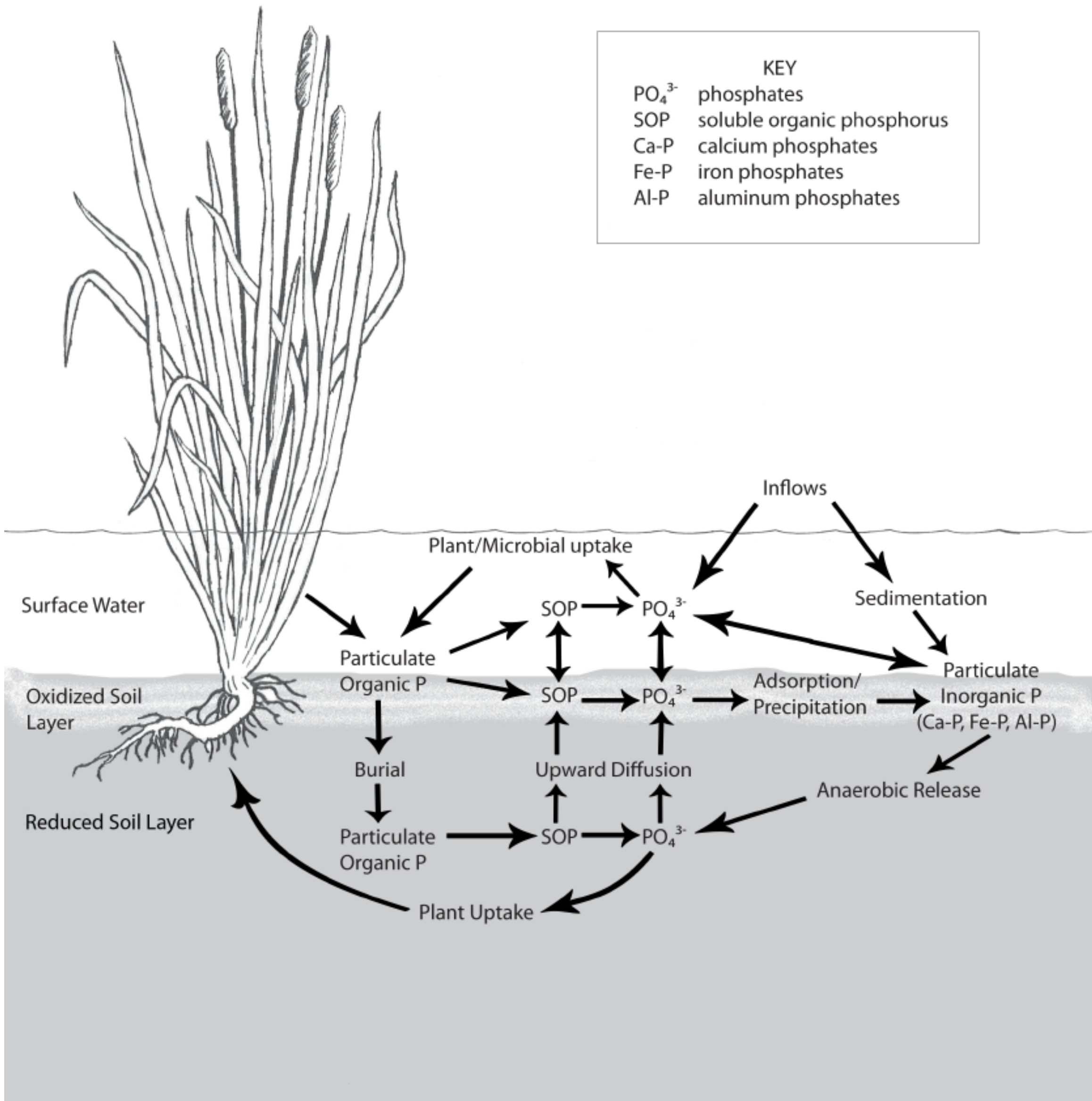

Figure 2: Phosphorus cycling in wetlands, adapted and modified from Mitsch & Gosselink, 2000.

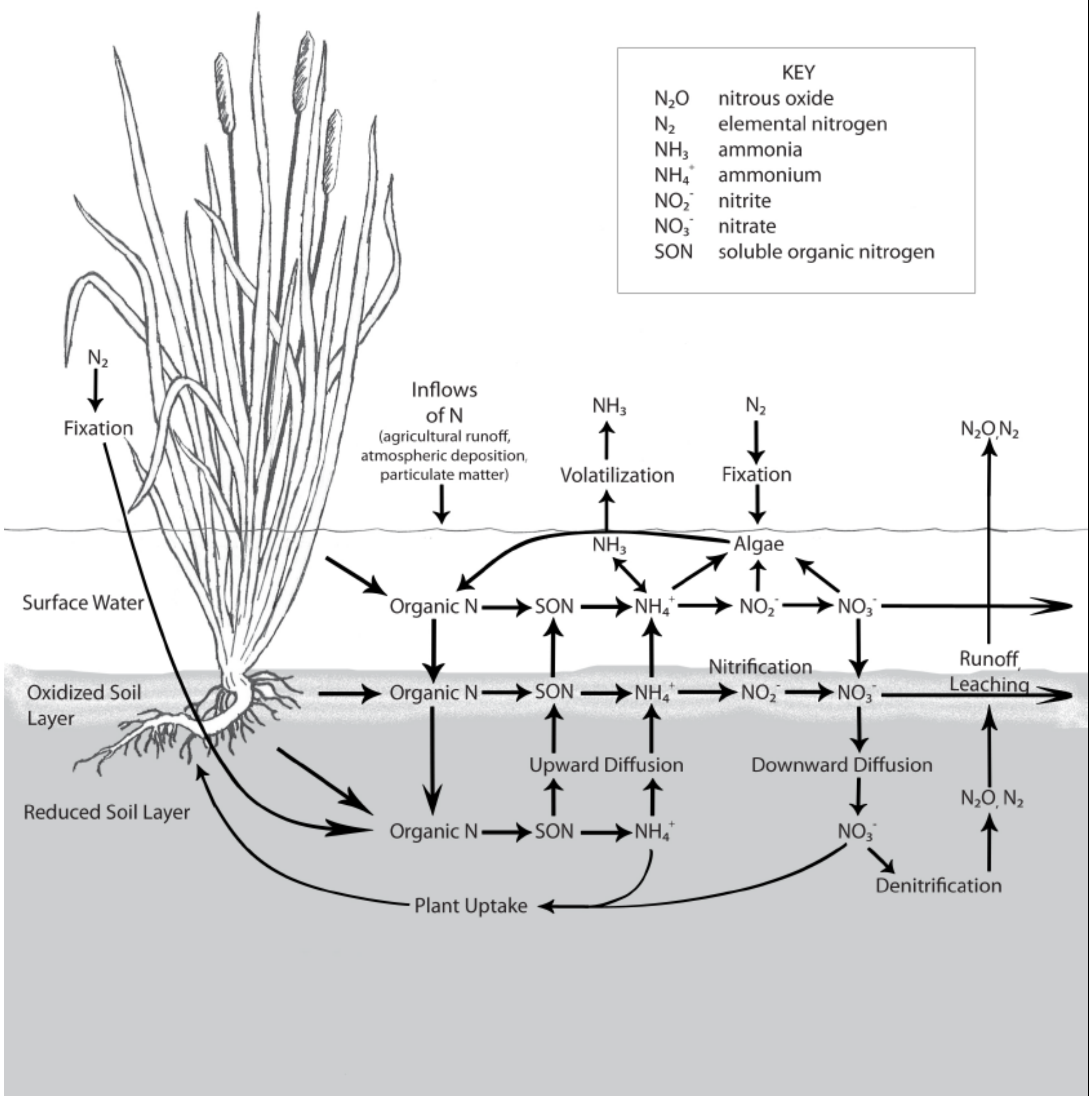

Figure 2: Nitrogen cycling in wetlands, adapted and modified from Mitsch & Gosselink, 2000.

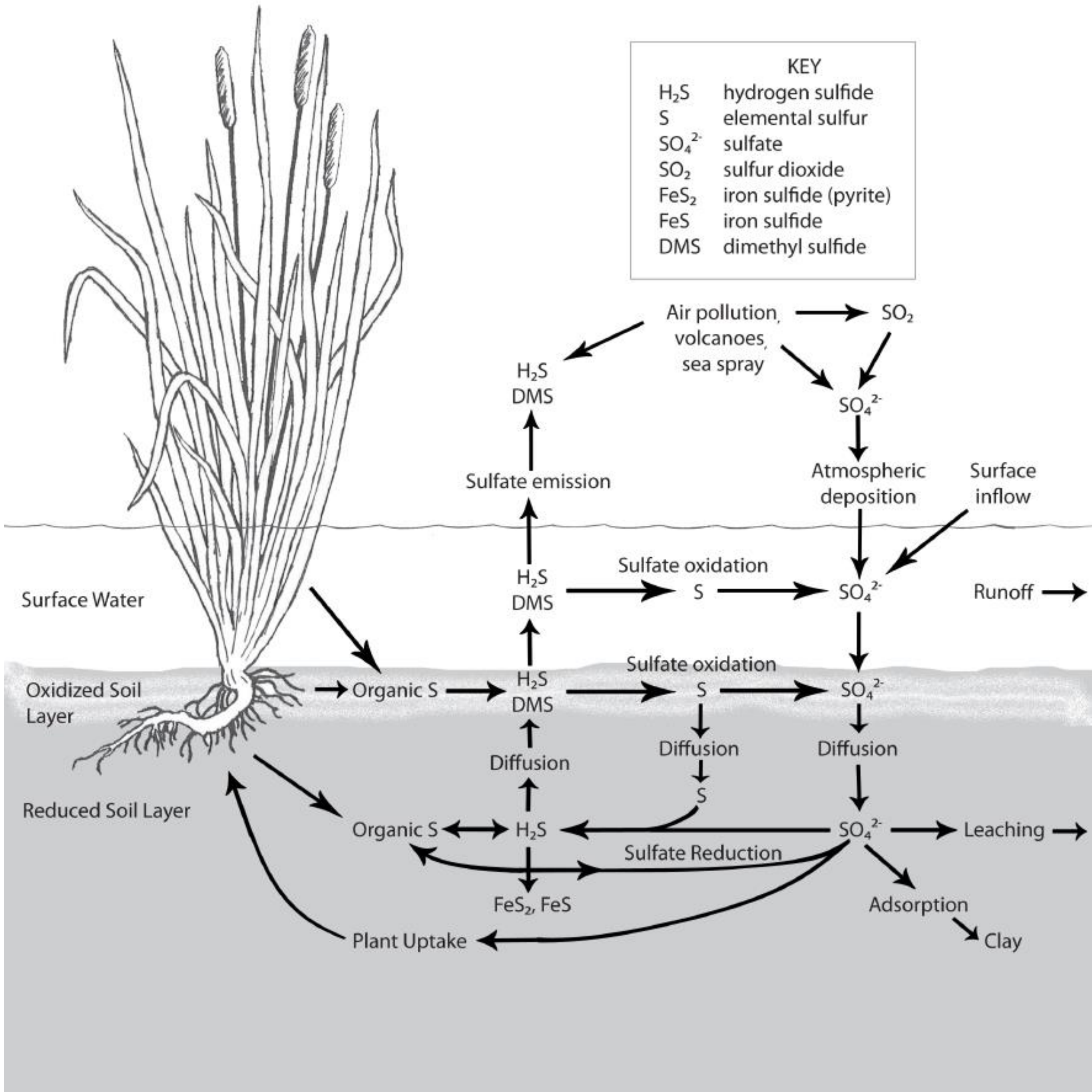

Figure 4: Sulfur cycling in wetlands, adapted and modified from Mitsch & Gosselink, 2000.

Nitrogen

Organic forms of nitrogen (N) are found in a variety of compounds including amino acids ($-NH_2$), urea (CNH_4O), uric acid ($C_4N_4H_4O_3$), purines, and pyrimidines. Amino acids, purines, and pyrimidines are the main building blocks of nucleotides that make up DNA in all living things. Urea and uric acid are essential to the excretion of toxic ammonia for all animals (Kadlec & Wallace, 2009). The most important inorganic forms of N in wetlands include ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O) and elemental nitrogen (N_2) (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008).

Nitrogen is often the most limiting nutrient of wetland productivity, even though it is the most abundant gas in the atmosphere (Mitsch & Gosselink, 2000). Highly mobile NH_4^+ and NO_3^- are the forms usable to plant life. For either of these forms to become available, N must be transformed either industrially through the Haber—Bosch process, forming nitrogen fertilizers, or biologically with the help of nitrogen-fixing bacteria found in soils and associated with certain plant rhizospheres. Even after transformation to a bioavailable form, NH_4^+ and NO_3^- are easily reduced back to forms such as N_2O and N_2 through denitrification or volatilization. Nitrogen taken up by plant matter is immobilized and unavailable until it is released back into the cycle through ammonification during decomposition (Figure 3) (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008).

Sulfur

Sulfur (S) cycling is functionally very similar to nitrogen cycling, with most sulfur tied to the lithosphere, as opposed to the atmosphere. In anaerobic soils of freshwater wetlands, the most oxidized form of sulfur, sulfate (SO_4^{2-}) is the next major electron acceptor after nitrates (NO_3^-), manganese (Mn^{4+}), and iron (Fe^{3+}). Reduction of sulfate can result in sulfur immobilization through precipitation of insoluble iron sulfide (FeS) and pyrite (FeS_2) or the volatilization of sulfide (H_2S) and dimethyl sulfide (DMS, $(CH_3)_2S$) (Figure 4) (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008). The most common forms of S at 25°C, one atmosphere of pressure, and neutral pH are SO_4 and H_2S, depending on redox conditions (Reddy & DeLaune, 2008).

Sulfate loading in highly reduced wetlands can lead to increases in H_2S production. Not only is H_2S toxic to plants, but it can re-oxidize when it is released, forming SO_4 and sulfuric acid (H_2SO_4), thereby acidifying the soil (Mitsch & Gosselink, 2000; Li et al., 2009).

Reduction and pH in Wetland Soils

Many wetland soils have a characteristic thin oxidized soil layer (~10 mm) at the soil water interface, overlying reduced soils (Mitsch & Gosselink, 2000). Reducing conditions occur in saturated soils because rates of oxygen diffusion are up to 10,000 times slower than through drained soils. In soils not permanently flooded, reducing conditions can start to occur within a few hours of inundation (Reddy & DeLaune, 2008). After depletion of oxygen as an electron (e^-) acceptor, e^- concentrations increase as organic matter in the soil continues to be oxidized, releasing electrons during decomposition.

Oxidation reduction potential (ORP), also referred to as redox potential or Eh (mV), is a measure of e^- availability or pressure in solution, determining reduction of wetland soils. Continued increasing electron concentrations, reflected by decreasing Eh values, allows for the reduction of other elements and compounds including nitrate, manganese, and iron indicating a continually reducing environment (Table 1). Eh measurements provide a quick and easy way to determine reduction intensity of saturated wetland soils (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008).

Table 1: Oxidized and reduced forms of several elements and corresponding approximate redox thresholds for transformation

Sequence of Reduction	Element	Oxidized Form	Reduced Form	Approximate Redox Potential for Transformation (mV)
1	Oxygen	O_2	H_2O	400-600
2	Nitrogen	NO_3	NO_2, NH_4, N_2O, N_2	250
2	Manganese	MnO_2	Mn^{2+}	225
3	Iron	Fe_2O_3	Fe^{2+}	+100 to -100
4	Sulfur	SO_4^{2-}	S^{2-}	-100 to -200
5	Carbon	CO_2	CH_4	below -200
5	Hydrogen	H_2O	H_2	below -200
6	Phosphate	PO_4^{3-}	PH_3	below -200
Adapted from Mitsch & Gosselink, 2000 and Reddy & DeLaune, 2008.				

The measure of the H^+ ion activity is defined as: $pH= -\log [H^+]$ (Reddy & DeLaune, 2008). In saturated soils this can be an important tool for wetland categorization and nutrient characterization (Cowardin et al., 1979). Circumneutral pH is typical in most types of wetlands (Table 2). Dry soils, even when previously basic or acidic, tend to become neutrally buffered through oxidation/reduction reactions when

Table 2: pH ranges of several freshwater flooded soils

Soil	pH
Floodwater	7.0-10.0
Flooded Soils	6.5-7.5
Freshwater Sediments	6.0-7.0
Marsh Soils	5.0-7.0
Nutrient Poor Peatlands	3.7-6.6
Adapted and modified from Mitsch & Gosselink, 2000 and Reddy & DeLaune, 2008.	

flooded. Initially acidic soils containing carbon and reducible oxidants will increase alkalinity through continuous consumption of protons and electrons. Stable neutral pH in alkaline soils can be produced by carbonates of iron and manganese, although buffering of alkaline systems occurs primarily by CO_2. Wetland Eh and pH are closely linked through chemical compound stability in reduced and oxidized conditions and specific pH (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008).

Site Description

The study sites lie within the Aspen Parklands, a subsection of the larger Lake Agassiz Parkland (LAP) in the TAP eco-region, Minnesota (Figure 1) (MNDNR 2012). The LAP is defined by beach ridges, shoreline complexes and shallow sand regions of the Glacial Lake Agassiz basin. The Aspen Parklands are dominated by forested peatlands on the eastern edge and tallgrass prairie, low dunes, beach ridges, and wet swales to the west (MNDNR, 2012). Caribou Wildlife Management Area (WMA) and Skull Lake WMA are both found on the western edge of the Aspen Parklands, surrounded by private and Nature Conservancy (TNC) owned lands (NorthernMinnesota.org, 2006) (Figure 1). Wetlands in these WMAs were once part of the former glacial Lake Agassiz, and are characterized by level topography, interrupted by beach ridges and remnant sand dunes (Cummins & Grigal, 1981). Ordovician sedimentary deposits of dolomite, sandstone, and shale, including parts of the Red River and Winnipeg Formations on the eastern edge of the Williston Basin are overlain by 30 to 120 m of calcareous glacial drift (Ojakangas et al., 1979; Morey et al., 1982; Morey & Meints, 2000). Fine-sands deposited by Glacial Lake Agassiz underlie wetland soils classified as Histosol-Hemist (Cummins & Grigal, 1981; Albert, 1995). Moderately decomposed organic material varies in thickness from

30 to 90 cm in these palustrine wetlands, characterized by emergent vegetation and a saturated water regime for much of the growing season (MCBS, 2009b; USFWS, 2010). Mean annual precipitation is 48 cm/year with average temperatures ranging from -15°C in the winter to 18°C in the summer (MNDNR, 2013a; NCDC, 2013). Peatlands formed over calcareous drift and beach deposits with near-surface water tables allow mineral-rich groundwater to interact with the surface, keeping pH circumneutral and water table fluctuations minimal, with minor flooding after spring melt and heavy rain events (MCBS, 2009d).

Caribou WMA is classified as a Prairie Rich Fen (MCBS, 2009b). It is one of the last intact, unaltered remnants of the Aspen Parklands community in the state with only 0.2 km^2 of over 52.6 km^2 coming from abandoned cropland (MNDNR, 2011a). The WMA borders Canada, and lies approximately 19 km northeast of Lancaster, Kittson County, Minnesota with an equivalently large area of similar wetland existing north of the border (MNDNR, 2011a; USFWS, 2011). Terrain is generally level (USGS, 2011) with a series of low ridges running northwest to southeast (Figure 5). Wet sedge meadows dominate the areas between the ridges, making up about 13.8 km^2 of the WMA (MNDNR, 2011a). An area on the southern edge of the wetland is ditched and drained by a 0.4 km ditch flowing southwest, exiting into State Ditch 84, along the southern border of the wetland (USFWS, 2010). Mineral-rich, nutrient poor waters of these communities are dominated by graminoids adapted to full sun, high mineral concentrations, sustained water levels, and low nutrients. Adaptations include intercellular air spaces (aerenchyma) that carry oxygen to the roots, stunted growth patterns, and narrower leaves to tolerate the low amount of nutrients in the system. The most prevalent graminoid species in undisturbed Prairie Rich Fens are Narrow Reedgrass (*Calamagrostis stricta*), Fen Wiregrass Sedge (*Carex lasiocarpa*), Buxbaum's Sedge (*Carex buxbaumii*), and Tall Cottongrass (*Eriophorum polystachion*) (MCBS, 2009b; MCBS, 2009d).

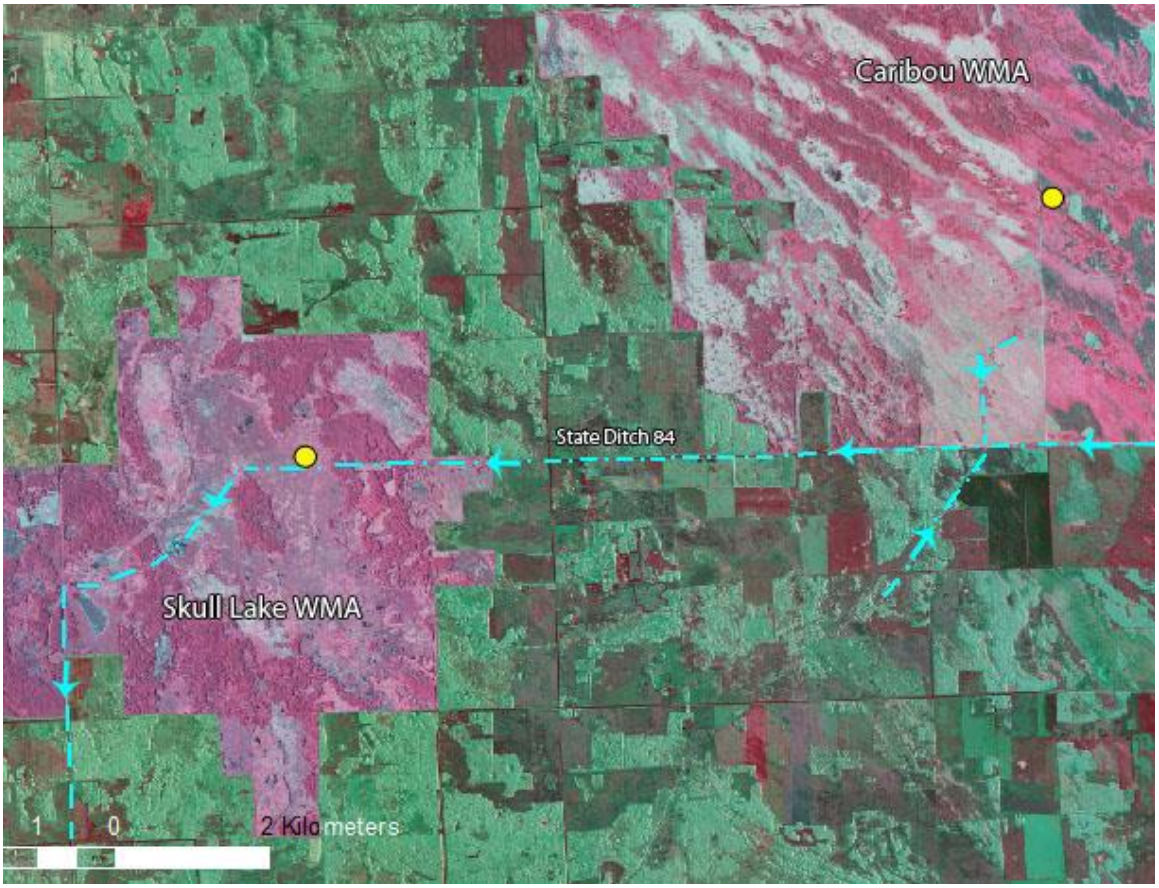

Figure 5: Caribou and Skull Lake WMA sample locations shown on a color-infrared aerial image, taken while the sedge was senescent, revealing areas of sedge meadow (light blue) and cattail marsh (light violet). A series of low ridges (pink) are remnants of glacial activity, in between the sedge meadow. Green indicates areas outside of the two WMAs. Comparative sites sampled are shown by yellow dots. Blue arrows indicate direction of flow along State Ditch 84 (USDA, 2008).

Skull Lake WMA covers 30.4 km^2 and lies about 5 km west of Caribou WMA (Figure 1) (MNDNR, 2011b). There are 15.4 km^2 of wetland in the unit (MNDNR, 2011b). The main part of the wetland unit is transected by a ditch flowing west into the impoundment (USDA, 2008; USFWS, 2011) (Figure 5). Impoundment control is achieved through removal of large wood blocks in a stop-log structure approximately 1.2 m wide. All blocks except for the bottom one were removed to decrease water levels to pre-dike levels. Ditch walls are generally higher than the surrounding wetlands and consist of bed materials (fine sands) (Cummins & Grigal, 1981; Albert, 1995). Breaks and degradation of the ditch walls are evident in person and in air photos (Figure 6). These may be due to beaver dams, scouring, erosion, and a lack of bed material cohesiveness along the margins of the ditch over time. Hydrology and plant communities

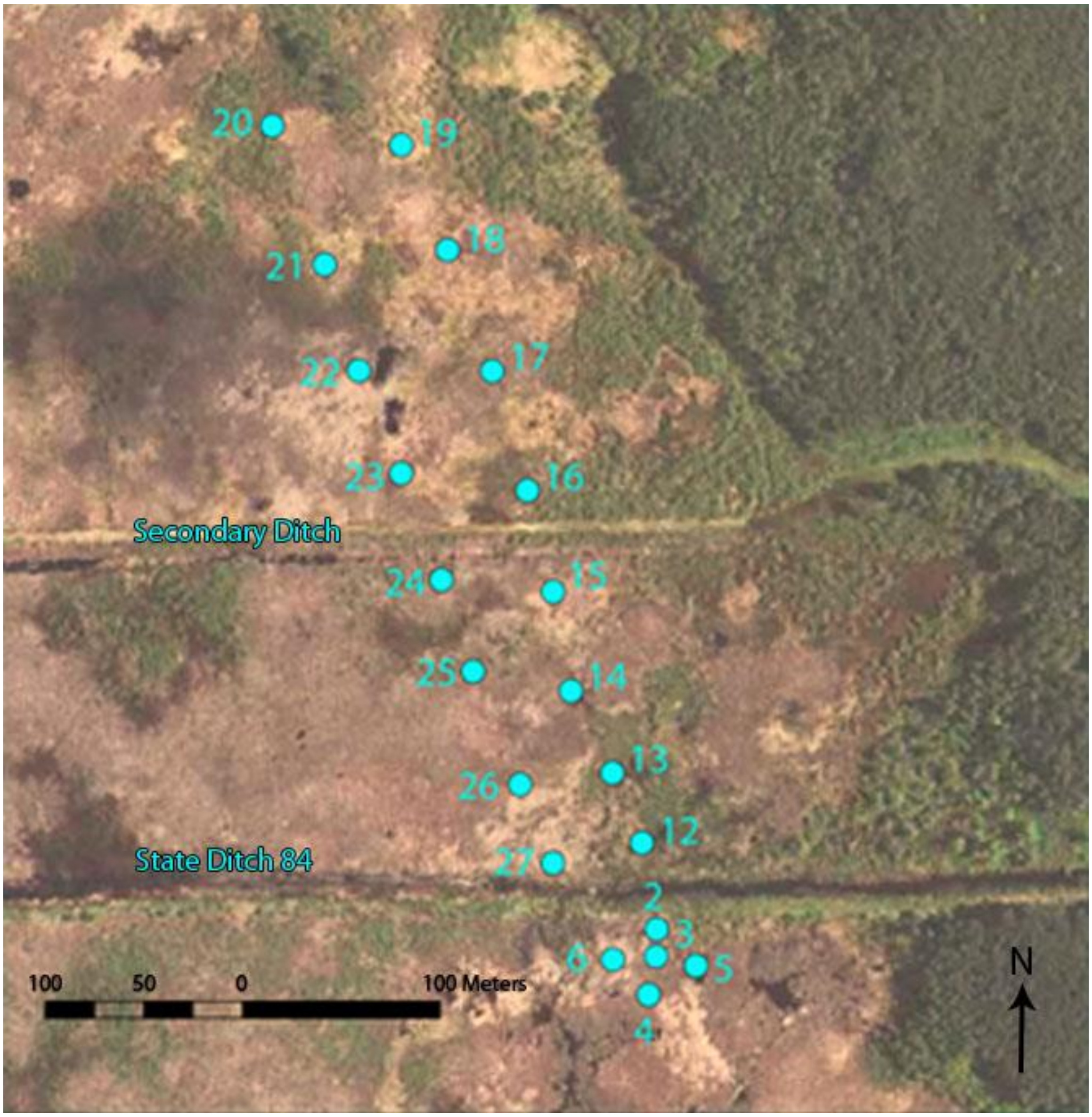

Figure 6: Skull Lake WMA sample location shown on an air photo. Sample points are indicated by blue dots. Numbers correspond to site IDs listed in Appendix 1. State Ditch 84 and a secondary non-functioning ditch are intersected by the sampling transects (USDA, 2008).

indicate Skull Lake WMA may be a low quality Prairie Mixed Cattail Marsh (MCBS, 2009a). Typical water depth in these types of communities is maintained at 50 to 100 cm (MCBS 2009c). Mineral rich waters are typically nutrient rich, due to anthropogenic sources (MCBS, 2009c). Marsh communities are dominated by over 50 percent cattails (*Typha*), which are adapted to sustained high water levels and high nutrient levels (MCBS, 2009a; Li et al., 2010). Adaptations include well developed aerenchyma to distribute oxygen to the roots and rapid clonal expansion through an extensive rhizome network (MCBS, 2009a; MCBS, 2009c).

CHAPTER III

METHODS

Water Sampling

Initial pore water sampling began in the summer of 2010 with cross-shaped test plots (Figure 7). Samples were taken at 15-cm intervals starting 15 cm below the soil

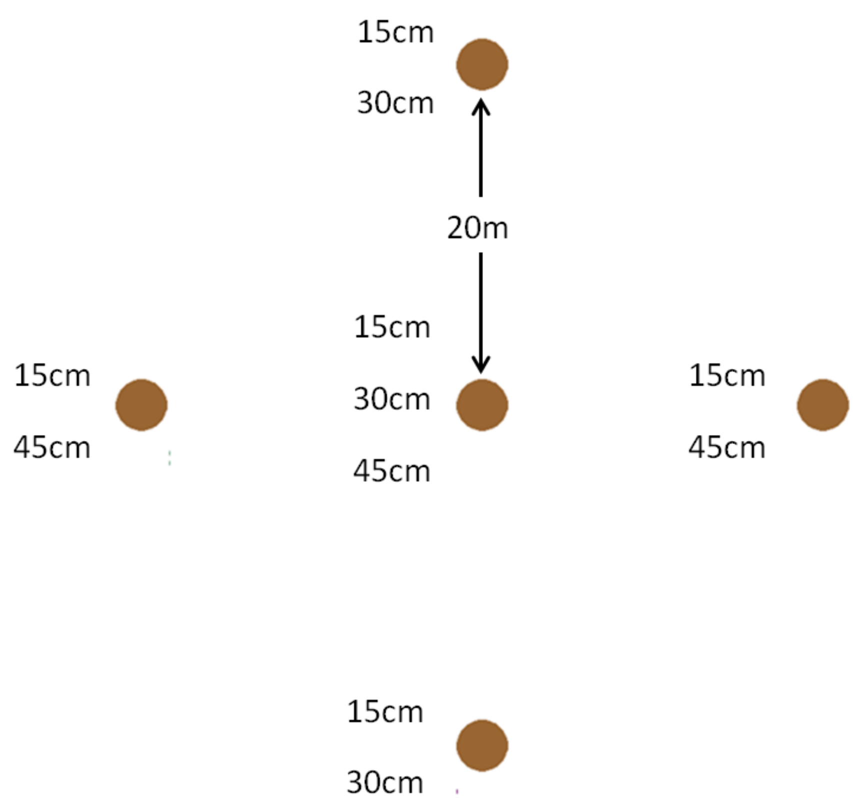

Figure 7: An example of the initial water sampling strategy at Caribou WMA and Skull Lake WMA. Samples were taken at 15, 30, and 45 centimeter depths, as indicated. Grid spacing is approximately 20 meters.

surface and terminating at 45 cm. All five sample sites in a test plot were sampled at 15 cm of depth, three sites in a line were sampled at 30 cm and a different three were sampled in a line at 45 cm to help determine vertical and horizontal variation (Figure 7). Sample sites within a test plot were 20 m apart.

The sample site at Caribou WMA (Figure 8) was chosen as an example of an apparently undisturbed sedge meadow, determined by an absence of invasive species, ditches, and allocthonous surface water inputs. Records suggest this site was never grazed nor hayed (MNDNR, 2011a; USGS 2011). The Skull Lake WMA site (Figure 6) was chosen to determine nutrient input near the ditch in a damaged, invasive dominated wetland. Both initial sample plots were sampled in the same manner, using the same sampling pattern. Pore-water samples were collected with a Soilmoisture Equipment Corp. Model 1900 soil moisture sampler (Santa Barbara, California) with 1.3 µm-pore

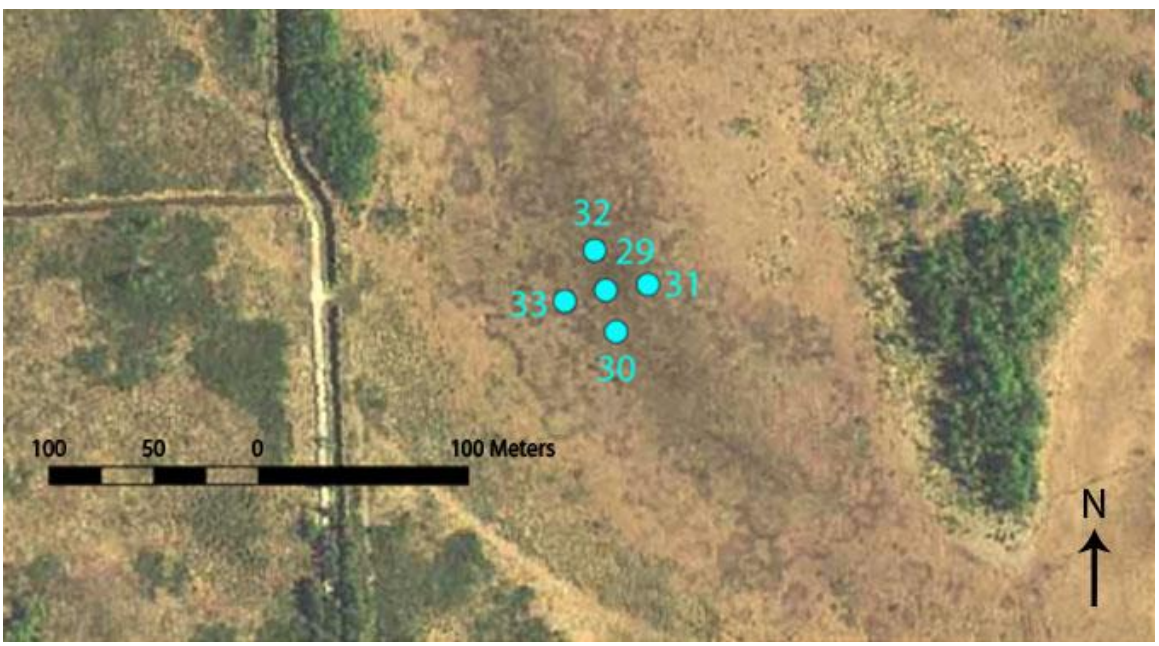

Figure 8: Caribou WMA sample location shown on an air photo. Sample points are indicated by blue dots. Numbers correspond to site IDs listed in Appendix 1 (USDA, 2008).

ceramic cups. These samplers were used to target a specific depth. Samplers were put under 60-65 cbars of tension for six to ten hours. A long sampling time was required because of fine particulate organic matter (FPOM) decreasing flow into the ceramic cups. Universal Transverse Mercator (UTM) coordinates of each site were recorded with a location uncertainty of +/- three meters using a Garmin Etrex Vista HCx handheld Global Positioning Satellite (GPS) unit (Appendix 1). Distances from each sample site to the edge of the main drainage ditch (County Ditch 84) were calculated using GPS coordinates. Geochemical parameters for all depths at each sample point were compared to distances to analyze the correlation, if any, between distance and constituent concentration.

Eleven samples were collected from each sample plot and analyzed for reduction-oxidation potential (Eh) and hydrogen ion concentration (pH) in the field using an Extech Instruments ExStik RE300 (Waltham, Massachusetts) and an Extech Instruments ExStik EC500 (Waltham, Massachusetts), respectively. Samples were immediately put on ice in a cooler for transport. All samples were filtered in the lab, within 6 hours of collection, through a Geotech 0.45 µm disposable cellulose acetate geofilter (Denver, Colorado) into clean 250 mL Nalgene plastic bottles before analysis. Sulfate, nitrate, nitrite, and soluble reactive phosphate (SRP) were analyzed in the Environmental Analytical Research Laboratory (EARL) at the University of North Dakota (UND).

A second and third set of samples from Skull Lake were collected and analyzed in the fall of 2011. Two offset transects perpendicular to the north side of the ditch were established (Figure 6). Twenty-eight samples were taken including 16 samples at 15 cm below the soil surface and 12 samples at 45 cm below the soil surface (Appendix 1). All samples were tested for Eh, pH, and HS in the field and transported on ice as described previously. Nitrate, nitrite, and SRP analysis were performed in EARL.

SRP concentrations were determined via spectrophotometry within 48 hours of sample collection. A HACH DREL/2010 spectrometer (Loveland, Colorado) was used with HACH Method 8048, PhosVer3 Method (Hach, 2010). This method is able to detect SRP in the range of 0.00 to 5.00 mg/L and is an accepted method by the United States Environmental Protection Agency (USEPA) (Hach, 1999).

Nitrite, nitrate, and sulfate levels were analyzed using the Dionex DX-120 ion chromatograph and the Dionex AS50 auto-sampler (Sunnyvale, California). Six calibration standards with increasing concentrations were prepared using stock solutions of Na_2SO_4, KNO_3, and KNO_2 (Table 3). All field samples, field blanks, duplicates, calibration standards, and lab blanks were tested in duplicate and averaged. Calibration curves were calculated by plotting area versus concentration of the known standards, and then used to determine pore-water concentrations.

Table 3: Concentration of nitrate, nitrite, and sulfate standards used in ion chromatography to produce a calibration curve.

Standard	NO_2 conc. mg/L	NO_3 conc. mg/L	SO_4 conc. mg/L
1	0.1	0.1	1
2	0.2	0.2	2
3	0.5	0.5	10
4	1	1	20
5	5	5	50
6	10	10	100

Statistical Analysis

Suspected outliers for each parameter (pH, Eh, HS, NO_2-N, NO_3-N, SRP, and S) at each depth (15, 30, and 45 cm) were determined by calculating the interquartile ranges

(IQRs) using a 5 number summary of each dataset (minimum, Q1, median (M), Q3, maximum). Suspected outliers were determined using the 1.5×IQR rule where: suspected outlier ≥ (1.5×IQR)+Q3 or suspected outlier ≤ (1.5×IQR)-Q1. A modified box and whisker plot was used to visualize this where Q1 and Q3 were represented by a box with line M running through it. Minimum and maximum values are represented by lines extending from the box, except where the 1.5×IQR rule is exceeded, in which case suspected outliers are represented by dots. This method is used because the IQR is resistant to changes in the tails of the distribution (Moore & McCabe, 2004).

Mean and standard deviations were calculated for each test parameter at all depths for both sites before and after suspected outlier removal to determine if this significantly changed the statistical results. Maximum, minimum, and average values were also calculated and plotted in the same manner. Standard deviations were calculated for each dataset (parameter and depth) before and after outlier removal.

A two-tailed heteroscedastic t-test was used to determine the statistical significance of data across all depths and between wetlands. T-test p-values less than 0.05 were considered significant indicating a difference between comparative parameters or depths. Correlation between water quality parameters and distance from the ditch were determined by a Pearson correlation and the associated best fit lines with R^2 values. A Spearman rank correlation (ρ) was also used to determine water quality parameter and distance correlations of non-linear data (pH, Eh, phosphate).

Quality Assurance Quality Control (QAQC)

Multiple field blanks were taken and processed in conjunction with all other samples to ensure methods were good and contamination was not present. Multiple duplicate samples were also taken to make sure methods were repeatable. Field blank and duplicate results are published with all other results (Appendix 1). Blanks were used during spectrophotometry and ion chromatography to ensure data accuracy. Samples in which a parameter was not detected or was below the detection limit were recorded as such. For statistical purposes, concentrations below the detection limit were used if available, and were treated as zeros where not available.

CHAPTER IV

RESULTS

Field (Table 4) and lab (Table 5) results from the control wetland (Caribou WMA) and the degraded wetland (Skull Lake WMA) were generated from all of the raw data collected (Appendix 1). A comparison of vertical constituent concentrations of both sites followed by a horizontal nutrient profile is important in characterizing geochemical distribution across both WMAs. Coupled with other knowledge of the wetlands, these data will help determine factors that have led to degradation and the ecological restoration potential of Skull Lake WMA.

Table 4: Mean, minimum, maximum, and standard deviations for Caribou and Skull Lake WMAs for constituents measured in the field at all depths before and after outlier removal.

		Skull Lake WMA			Caribou WMA		
		15 cm	30 cm	45 cm	15 cm	30 cm	45 cm
pH	# samples	23	3	16/14*	5	3	3
	mean	6.91	6.69	6.78/6.66*	6.06	6.05	6.07
	min	6.27	6.64	6.15	5.98	6.03	5.96
	max	7.36	6.78	7.66/7.21*	6.22	6.07	6.20
	std. dev.	0.32	0.08	0.39/0.24*	0.10	0.02	0.12
Eh (mV)	# samples	23/20*	3	16/14*	5/3*	3	3
	mean	180/187*	152	161/150*	35/38*	39	30
	min	133/162*	140	113	12/36*	10	13
	max	208	159	245/171*	48/40*	85	56
	std. dev.	20/11*	10	35/19*	14/2*	40	23
HS (mg/L)	# samples	23/21*	3	16	5	3	3
	mean	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
	min	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
	max	0.3/0.1	0.1	0.1	<0.1	<0.1	<0.1
	std. dev.	0.09	1.7E-17	0.03	0.00	0.00	0.00

* Indicates values affected by removal of outliers.
ND (no detect) indicates no detection of the constituent

Table 5: Mean, minimum, maximum, and standard deviations for Caribou and Skull Lake WMAs for constituents measured in the lab at all depths before and after outlier removal.

		Skull Lake WMA			Caribou WMA		
		15 cm	30 cm	45 cm	15 cm	30 cm	45 cm
SRP (mg/L)	# samples	23/21*	3	16/11**	5	3	3
	mean	0.26/0.17*	1.05	0.45/0.68**	<0.01	0.01	0.01
	min	0.01	0.92	<0.01/0.28**	<0.01	<0.01	0.01
	max	1.30/0.60*	1.30	1.26	0.01	0.01	0.01
	std. dev.	0.34/0.15*	0.21	0.45/0.32**	0.01	0.01	0.00
NO_2-N (mg/L)	# samples	23	3	16/15*	5	3	3
	mean	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	min	ND	ND	ND	<0.1	<0.1	<0.1
	max	<0.1	<0.1	0.2/0.16*	<0.1	0.12	<0.1
	std. dev.	0.03	0.03	0.05/0.04*	0.00	0.05	0.01
NO_3-N (mg/L)	# samples	23/21*	3	16	5	3	3
	mean	<0.1/ND*	<0.1	<0.1	ND	<0.1	<0.1
	min	ND	ND	ND	ND	ND	ND
	max	<0.1/ND*	ND	0.1	ND	<0.1	<0.1
	std. dev.	0.01/0.00*	0.00	0.03	0.00	0.04	0.01
SO_4 (mg/L)	# samples	5/4*	3	3	5/4*	3	3
	mean	3.5/1.7*	2.0	1.5	1.8/<1.0*	4.6	24.7
	min	1.3	1.7	<1.0	<1.0	1.1	8.9
	max	10.8/2.1*	2.1	2.3	6.9/1.6*	9.9	51.1
	std. dev.	4.1/0.3*	0.2	1.0	2.9/0.7	4.7	23.0

* Indicates values affected by removal of outliers.

** Indicates values affected by removal of data from cloudy samples taken from a sand layer near 45cm. Affected samples are highlighted yellow in Appendix 1.
ND (no detect) indicates no detection of the constituent

Caribou WMA

Circumneutral pHs were measured at the site with a site mean of 6.06 (Table 6). A site mean of 35 millivolts (mv) was detected for Eh (Table 6). Hydrogen sulfide (HS) was not detected in any samples at the site. Mean soluble reactive phosphorus (SRP) was less than 0.01 mg/L with a maximum of 0.01 mg/L (Table 5), but four of the eleven samples were below the detection limit (Appendix 1). Mean nitrite-N values were below

Table 6: Overall site mean, standard deviation, and number of samples taken for Caribou and Skull Lake WMAs before and after outlier removal.

		Skull Lake WMA	Caribou WMA
pH	# samples	42/40*	11
	site mean	6.84/6.81*	6.06
	site standard deviation	0.35/0.31*	0.08
Eh (mV)	# samples	42/37*	11/9*
	site mean	161/170*	35/36*
	site standard deviation	28/23*	23/24*
HS (mg/L)	# samples	42/40*	11
	site mean	<0.1	<0.1
	site standard deviation	0.07/0.04*	0.00
SRP (mg/L)	# samples	42/35*,**	11
	site mean	0.39/0.40*,**	<0.01
	site standard deviation	0.42/0.38*,**	0.01
NO_2-N (mg/L)	# samples	42/41*	11
	site mean	<0.1	<0.1
	site standard deviation	0.02/0.04*	0.02
NO_3-N (mg/L)	# samples	42/40*	11
	site mean	<0.1	<0.1
	site standard deviation	0.02	0.00
SO_4 (mg/L)	# samples	11/10*	11/10*
	mean	2.5/1.7*	8.8/9.0*
	std. dev.	2.8/0.5*	14.8/15.6*

* Indicates values affected by removal of outliers.

** Indicates values affected by removal of data from cloudy samples taken from a sand layer near 45cm. Affected samples are highlighted yellow in Appendix 1.

the detection limit, with a maximum of 0.1 mg/L (Table 5). Nitrite-N was detected at a concentration of 0.1 mg/L in all five samples taken at a depth of 15 cm, but was undetectable in four of the six samples taken below that depth (Appendix 1). Nitrate-N mean values were also below the detection limit with a maximum of 0.1 mg/L (Table 5), but only one of 12 samples had detectable nitrate-N at a depth of 30 cm (Appendix 1). Mean site sulfate concentrations were 8.8 mg/L (Table 6). Three samples at 15 cm deep were the only ones with undetectable levels of sulfate (Appendix 1).

Vertical Constituent Concentrations

Comparison of pH at all depths using a t-test showed no significant variations and no suspected outliers. Comparisons of Eh across all depths also showed no significant variation, but two suspected outliers were identified in the 15 cm samples using boxplots (Figure 9). Removal of the suspected outliers resulted in a smaller standard deviation at 15 cm (Table 4) and increased the overall site mean from 35 mV to 36 mV (Table 6), but did not significantly alter Eh. HS, SRP, nitrite-N, and nitrate-N had insignificant changes in concentration across all depth and no outliers. Analysis of sulfate concentrations indicated the possibility of one outlier in the 15 cm samples. Removal of the suspected outlier decreased the mean to <1.0 mg/L (Table 5) and decreased standard deviation from

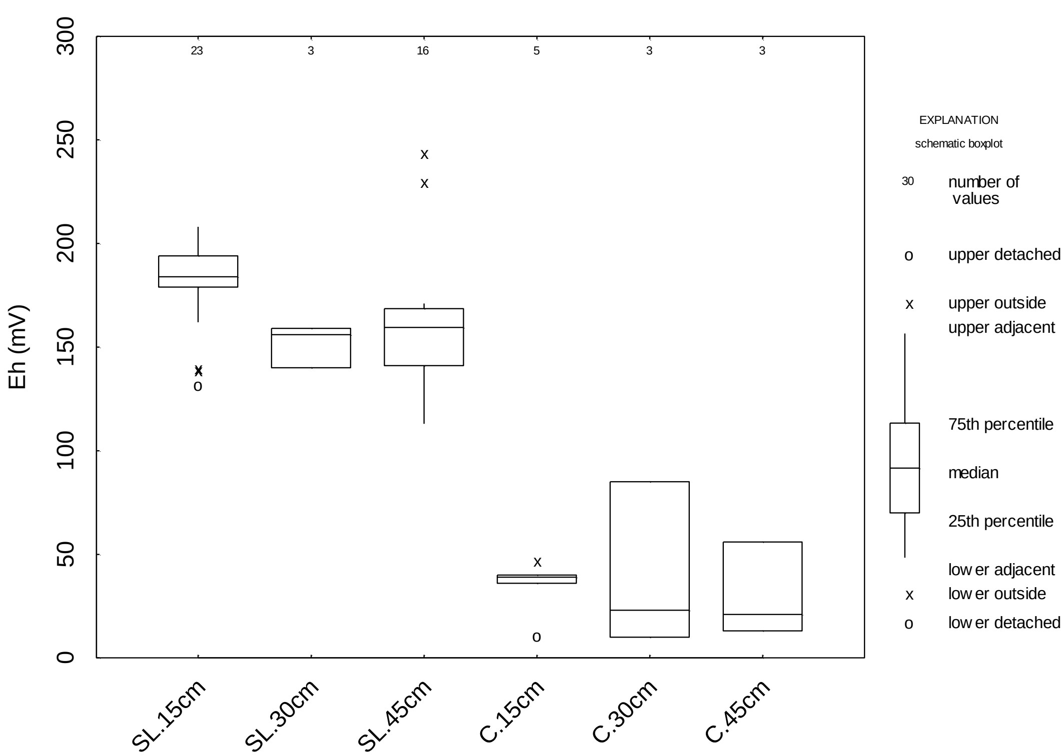

Figure 9: Boxplot of Eh showing outliers at 15 and 45 cm depth at Skull Lake WMA and 15 cm at Caribou WMA.

2.9 to 0.7 (Table 5). P-values greater than 0.05 indicated there was no significant difference in sulfate concentration across all depths before or after suspected outlier removal.

Skull Lake WMA

Circumneutral pH values were recorded at Skull Lake WMA with a site mean of 6.84 (Table 6). Mean Eh was 171 mV at the site (Table 6). Average hydrogen sulfide (HS) was below the detection limit. HS was only detected in small amounts (0.1 to 0.3 mg/L) in the initial sampling (Appendix 1). Mean site SRP concentration was 0.39 mg/L (Table 6) with a maximum of 1.30 mg/L (Table 5). Three of the 42 samples had undetectable amounts of SRP at 45 cm (Appendix 1). Average site nitrite-N values were less than 0.1 mg/L (detection limit) (Table 6) because only nine of 42 samples had detectable nitrite-N at or below a concentration of 0.2 mg/L, seven of which were collected at 45 cm (Appendix 1). Nitrate-N concentrations were below the detection limit for all samples but one with a concentration of 0.1 mg/L (Appendix 1). Low concentrations of sulfate were detected in all samples but one (Appendix 1).

Vertical Constituent Concentrations

Comparison of pH for all depths showed significant variation in concentrations between 15 and 30 cm with a p-value of 0.017. Three suspected outliers were identified in the 45 cm data (Figure 10). Removal of these data changed mean concentration from 6.78 to 6.66, and decreased the standard deviation for 45 cm samples (Table 4). Concentration variation between the 15 and 45 cm datasets became significant with p-values decreasing from 0.27 to 0.01.

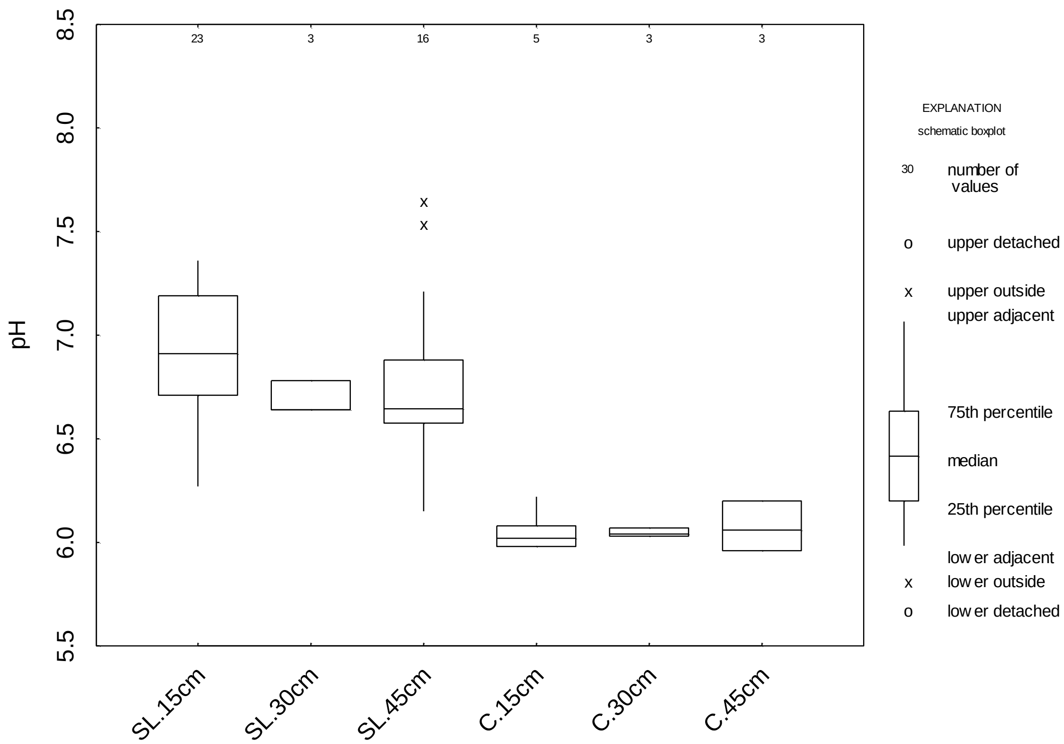

Figure 10: Boxplot of pH showing outliers at 45 cm depth in the Skull Lake WMA data.

A comparison of average Eh across all depths showed no significant difference. However, three samples at 15 cm and two samples at 45 cm were identified as outliers (Figure 9). Removal of these points changed overall average concentrations from 161 mV to 170 mV (Table 6) and reduced standard deviation and mean values for the 15 and 45 cm sample sets (Table 4). This produced a statistically significant difference in mean Eh from 15 to 30 cm and 15 to 45 cm, showing a decreasing downward gradient.

A comparison of all samples indicated that average HS concentrations were higher in the 30 cm sample set than the 15 and 45 cm sample sets. A t-test also indicated the difference in HS concentrations between the 30 cm and both the 15 and 45 cm datasets were significant. The use of a boxplot to identify outliers indicated that all samples above the detection limit in the 15 and 45 cm sample set should be considered outliers. The suspected outliers were ignored because non-detections dominated the data, heavily skewing it towards zero.

Comparison of mean SRP across all depths indicated significantly higher concentrations at 30 cm than both 15 and 45 cm. Identification and removal of two outliers in the 15 cm set (Figure 11) decreased both the mean value and the standard deviation (Table 5). This shows that samples at 45 cm had significantly higher concentrations of SRP compared to samples from 15 cm and that there may be a downward increasing concentration of SRP in the system.

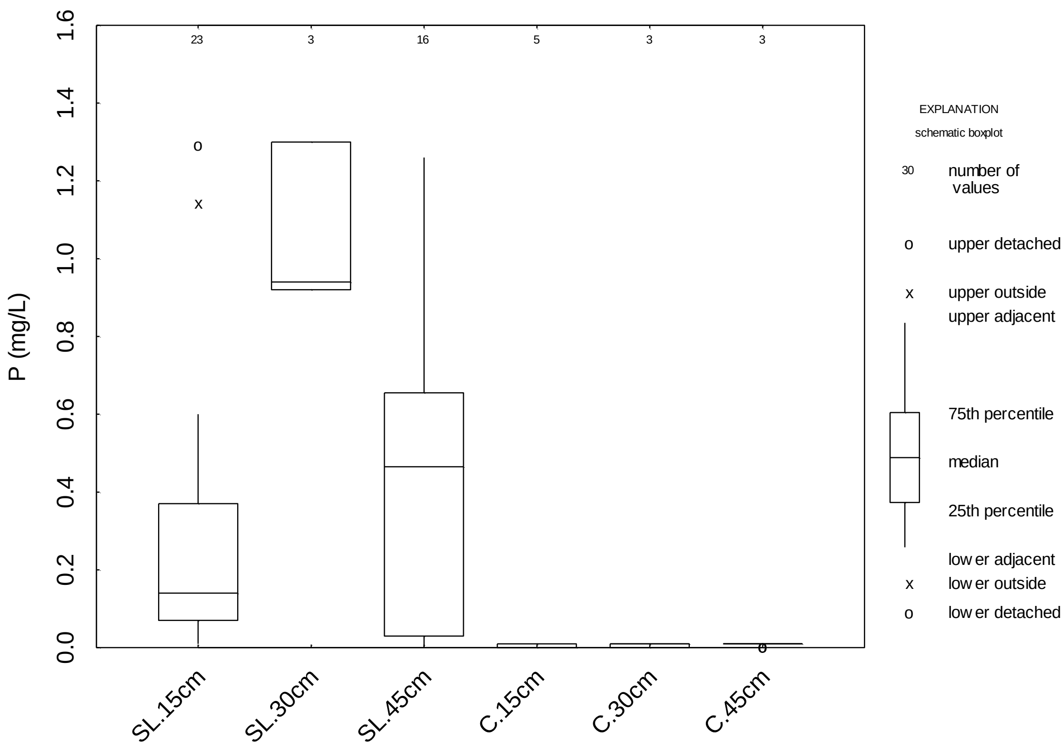

Figure 11: Boxplot of SRP values showing outliers at 15 cm depth in the Skull Lake WMA data.

Turbid samples (highlighted yellow in Appendix 1) were collected at several 45 cm sample sites. These samples were collected from a sand layer underlying the decomposing vegetation. A dark brown residue was left on the filter paper after filtration (Figure 12). This was not seen in other clear samples that were not taken from the sand layer at 45 cm. Samples taken from the sand layer showed very low concentration of P (0.04 mg/L to below detection limit). Samples that were collected from above the sand layer remained clear and showed much higher concentrations of P (0.28 to 1.26 mg/L).

Average nitrite-N values were significantly higher in the 45 cm dataset only in comparison to the 15 cm dataset. One outlier at 0.1 mg/L was identified in the 15 cm dataset, but removal did not change the significance of the comparison. It is notable that

Figure 12: Picture of 0.45 micron filters after filtration. Left filter is from a turbid sample taken from the sand layer at 45 cm and the right filter is from a regular 45 cm sample.

four of the five cloudy samples collected at 45 cm contained the highest amount of nitrite from all samples collected at Skull Lake WMA.

All nitrate samples were consistently below the detection limit across all depths. Only one sample contained 0.1 mg/L nitrate-N of the 45 cm data. This was identified as a suspected outlier, but removal did not affect the final results. It should also be noted that this sample was a cloudy sample containing nitrate, and no SRP.

Mean sulfate concentrations did not vary significantly across all depths in the initial sampling. Only one suspected outlier was identified and removed from the 15 cm dataset, changing the P-value to 0.04, indicating a significantly higher concentration of near surface sulfate at Skull Lake WMA (Table 5).

Concentration versus Ditch Distance

Sample comparisons at 30 cm were inconclusive because of the small sample size at that depth. Using a Pearson correlation, a comparison of the 15 cm pH data to distance from the drainage ditch indicated a strong positive relationship between the two (Figure 13), with an r-value of 0.77 and a p-value of 8.7E-06 (Table 7). A Spearman rank correlation of 0.80 also indicated a strong positive correlation between pH and increasing distance from the ditch. The 45 cm data showed a weak relationship where all sample concentrations remained constant with increasing distance from State Ditch 84 (Figure 13). The 15 and 45 cm Eh data did not indicate any relationship to the distance from State Ditch 84.

Correlation between SRP concentrations and ditch distance for all 15 cm samples was weakly negative (r=-0.48, p-value of 0.010), although a Spearman Rank test indicated a moderately negative correlation between ditch distance and SRP

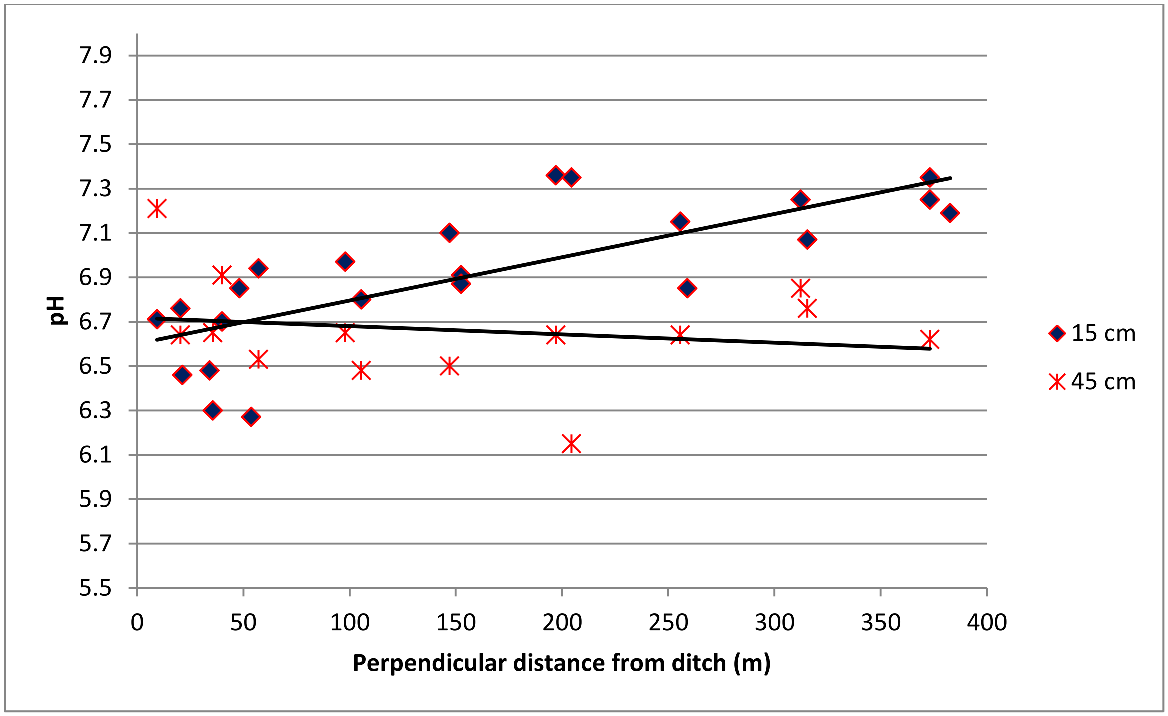

Figure 13: Distance (m) from State Ditch 84 versus pH comparison for 15 and 45 cm samples at Skull Lake WMA. Linear regression trend-lines were used to indicate differences in pH as distance from the ditch increased.

Table 7: Pearson correlation r-values, r^2 (coefficient of determination), and p-values; Spearman Rank ρ-values for 5 geochemical concentrations compared to distance from State Ditch 84 at 15 cm and 45 cm in Skull Lake WMA.

	Pearson r-value		**Pearson r^2**		**Pearson p-value**		**Spearman ρ**	
	15 cm	45 cm	15 cm	45 cm	15 cm	45 cm	15 cm	45 cm
pH	0.77	-0.11	0.59	0.01	8.7E-06	0.34	0.80	-0.19
Eh	0.27	-0.18	0.07	0.03	0.11	0.25	-0.02	0.06
HS	-0.43	-0.37	0.18	0.14	0.02	0.08	-0.18	0.11
SRP	-0.48	-0.29	0.23	0.08	0.01	0.14	-0.53	-0.14
NO_2-N	-0.68	0.25	0.46	0.06	1.8E-04	0.18	-0.65	0.26
NO_3-N	0.07	-0.02	0.00	0.00	0.38	0.47	0.43	-0.02

concentration (ρ=-0.53) (Table 7). Further examination revealed some connection between SRP concentrations and distance from the ditch. Low concentrations of near-surface SRP occurred near the ditches and at the end of the sample transects. This relationship is most readily seen approximately 160 m from the main ditch (at the secondary ditch) (Figure 6), where a sharp rise and fall in SRP concentration with increasing distance from the secondary ditch can be seen (Figure 14). Higher concentrations of SRP were also present between the two ditches, but did not show the same statistical significance. The 45 cm data set revealed no correlation between SRP concentrations and distance from the ditch. Moderate negative correlation between the ditch and nitrite-N was also shown with an r-value of -0.68, a p-value of 1.8E-04, and a ρ of -0.65 in shallow groundwater samples (15 cm) (Table 7).

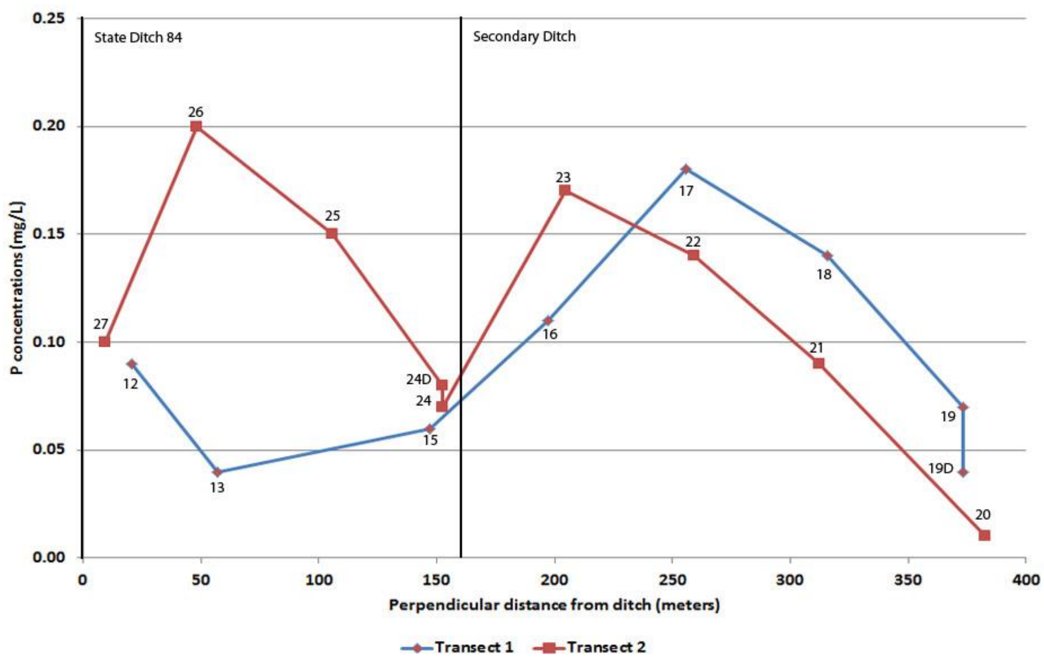

Figure 14: Correlation between PO_4 and perpendicular distance from the ditch at a depth of 15 cm after removal of outliers, Skull Lake WMA, 9/21/2011. The secondary valley at 150 m corresponds with a secondary non-functioning ditch connected to the first one. Numbers correspond to sample numbers in Appendix 1.

Skull Lake/Caribou WMAs

Average pH was 0.75 higher at the Skull Lake WMA sample sites than at the Caribou WMA sample sites, but both sites had circumneutral pH. Average Eh at Skull Lake and Caribou was 170 mV and 36 mV respectively, indicating higher potential for oxidation in the Skull Lake WMA soils. Small amounts of HS were seen in the initial

Skull Lake WMA sample plot, but more sampling did not detect HS at either site. SRP concentrations varied widely at Skull Lake WMA with a site average of 0.40 mg/L while concentrations were at or below the detection limit (0.01 mg/L) in Caribou WMA. Nitrite-N and nitrate-N concentrations were negligible at both sites. Low concentrations of sulfate were detected at Skull Lake WMA and variable higher concentrations were detected at depth in the Caribou WMA sample plot with a site average of 9.0 mg/L. Measurements of pH, Eh, and SRP were significantly higher (p-value greater than 0.05) at Skull Lake WMA than Caribou WMA.

CHAPTER V

DISCUSSION

Comparative sampling between the largely undisturbed sedge meadows of Caribou WMA and the degraded cattail marsh of Skull Lake WMA helped determine differences in nutrient distribution between the two sites. The effect that State Ditch 84 has had on Skull Lake WMA was determined through correlation of nutrient profiles with distance from the ditch. This will help indicate what factors may have led to wetland degradation at Skull Lake WMA and influence decisions towards the possibility of ecological restoration.

Caribou and Skull Lake WMAs Comparison

Although mean pH was significantly different between Caribou and Skull Lake WMAs, both sites were within the neutral range (circumneutral) (Tiner, 1997). Soil pH less than 5.5 is considered acidic and greater than 7.5, basic (Wright et al., 2009). Soil acidity has been shown to decrease the bioavailability of P through the dissolution of Al and Fe, and subsequent precipitation of Al-P and Fe-P compounds. A decrease in P availability is also prevalent in basic soils due to excessive Ca precipitating with P (Reddy, et al., 1999; Richardson & Vepraskas, 2001; Mitsch & Gosselink, 2007; Wright et al., 2009). Neutral soils such as those found throughout the study area are the most conducive to P availability.

Average oxidation-reduction potential of pore water at Caribou WMA was lower than at Skull Lake WMA. Differences in Eh between the two sites may possibly be due to better development of aerenchyma in cattails and leakage of oxygen from the rhizosphere into the surrounding saturated subsurface (Brix et al., 1992), although differences in temperature or pH may also cause differences (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008). Cattail leaves may be able to provide enough oxygen to the rhizosphere for a radius of a few feet to be affected by leakage, even after senescence (Sojda & Solberg, 1993). Although increased Eh has an overall negative effect on nutrient uptake, when coupled with high P availability, it has been shown to benefit *Typha* over native species and has been linked to the expansion of *Typha* in the Everglades (Delaune, et al., 1999; Li, et al., 2009).

Hydrogen sulfide was not detected in Caribou WMA but small amounts were detected in initial sampling at Skull Lake WMA. This is not completely unusual in wetlands with slow decomposition rates (MCBS, 2009d). Low concentrations of sulfate detected at Skull Lake WMA showed no variability unlike samples from Caribou WMA (Table 5). Adaptations (aerenchyma) to low Eh ecosystems allow cattails to do well, enabling them to detoxify H_2S to non-toxic sulfate in the oxidized rhizosphere. Typha may be more tolerant of excessive sulfate and the subsequent reduced form of sulfide in anoxic aquatic environments because of its ability to provide oxygen to the roots (Li, et al., 2009). High amounts of sulfate have been linked to increases in P concentrations due to high mineralization rates; interference of sulfide with iron-phosphate binding, forming iron sulfides instead and releasing more P to the environment (Smolders & Roelofs, 1993; Lamers et al., 1998). Increased sulfate can also lead to increased sulfide toxicity to the roots of aquatic plants (Smolders & Roelofs, 1995), resulting in decreased uptake of P in plant biomass and increased P availability in the ecosystem (Lamers et al., 1998).

Concentrations of sulfate were well below levels found to affect wetland macrophyte growth. The inability to detect any hydrogen sulfide at Caribou WMA across all sample depths coupled with evidence of increasing sulfate concentrations with increasing depth indicates an environment that is not sufficiently anoxic to reduce sulfate to sulfide. Average Eh concentrations of 36 mV also support this conclusion because sulfate is known to start reducing around -100 mV (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008).

A significantly higher concentration of bioavailable P was found at Skull Lake WMA than at Caribou WMA. Detectable concentrations of SRP ($\geq$0.01 mg/L) at depth (30 and 45 cm) in Caribou WMA may suggest this depth is beyond the root zone of the Carex, allowing accumulation in a low nutrient system. Concentrations of SRP at Skull Lake WMA were much higher, but followed a similar pattern of increasing concentration with depth, up to a certain point. All SRP concentrations for all depths were significantly higher than samples from Caribou. Average concentrations increased as depth increased to 30 cm and decreased at 45 cm. Several samples within the 45 cm series were pushed into fine sand underlying the wetland sediments and had low concentrations of P (undetectable to 0.04 mg/L). These samples were turbid and left behind a brown film when filtered through a 0.45 micron filter paper (Figure 11). This may be evidence of biological activity or possible chemical binding in and near the subsurface sands, reducing bioavailable P (Reddy et al., 1999; Oates, 2008).

Nitrite was at or below the detection limit for Caribou and Skull Lake WMA samples. This may indicate that denitrification and nitrification are happening readily near the surface, but N may not be available at depth because it has been assimilated by plants and is no longer available (Mitsch & Gosselink, 2000; Reddy & DeLaune, 2008). Low concentrations of nitrite-N were detected primarily in turbid samples that were collected within the sand layer underlying the surface soils. The presence of nitrite in the sands may indicate microbial activity, either denitrifying or nitrifying.

Nitrate was almost completely undetectable at both sites. NO_3 is readily used by macrophytes, but in an anoxic environment with an Eh below 250 mV, this can readily be reduced to less usable forms of N such as NO_2^-, NH_4^+, and the more volatile N_2, or N_2O, which can escape into the atmosphere. This makes N one of the most limiting wetland nutrients (Mitsch & Gosselink, 2000). Lack of nitrate at Skull Lake WMA may be due to denitrification but is most likely due to immediate plant uptake since P is not the limiting nutrient within the system. Concentrations of SRP, nitrite-N, and nitrate-N ranging from below the detection limit to the detection limit indicate that Caribou WMA is a low nutrient ecosystem.

Horizontal Distribution

A positive correlation between distance from the ditch and pH in shallow pore water samples indicates a connection between groundwater and shallow subsurface water near the ditch, affected by the in-flow of surface water (Figure 12). This may also show a direct link between groundwater flow in the sands underlying the wetlands and the ditch.

SRP concentration versus distance correlation in shallow pore water samples differs slightly. If transect data are plotted separately as east and west, a better concentration correlation becomes evident. At approximately 150 m from State Ditch 84, both transects start to follow a similar pattern of increasing then decreasing concentrations, where 160 m corresponds with a secondary non-functioning ditch connected to the main one (Figures 6 & 13). During high flow periods, the side ditch may provide the surrounding area with fresh P influx and deposition. As distance continually increases from both ditches, SRP concentrations are seen to continually decrease, indicating a negative relationship between distance and SRP concentration.

A negative correlation between State Ditch 84 and nitrite in shallow pore water samples is also evident. Samples within 100 meters of the ditch were shown to have low concentrations of NO_2, and all samples past 100 meters had undetectable NO_2 concentrations. This may indicate that the ditch is acting as a conduit for nitrite, although it is difficult to tell because concentrations are low.

Factors Responsible for Ecosystem Changes at Skull Lake WMA

Hydrology at Skull Lake WMA has been entirely altered since initial human contact. Ditching and draining efforts, then flooding with the addition of an impoundment have changed both the extent of the wetland as well as plant species distribution over time in comparison to Caribou WMA. Water impoundment increases water depth and residence time, drowning out shorter macrophytes and stressing those with poorly developed aerenchyma. The spread of taller *Typha* species may also shade out shorter, native *Carex* species.

There is evidence linking the decrease of P availability with increasing distance from the drainage ditch in shallow sub-surface waters. This relationship disappears at depth. This means the existence of the ditch does have a direct impact on the existence and concentration of P found within the wetlands. Since State Ditch 84 flowing through Skull Lake WMA is a conduit for field runoff, P may be deposited during flooding. Prior to impoundment construction, P may have been relatively free to flow through the wetland. Phosphorus accumulation over time may be a result of stagnation within the impoundment, allowing P enriched water to deposit particles from the water column (Reddy et al., 1999). Reactive P is also most available in waters with neutral pH (Wright, et al., 2009), so the risk of Skull Lake and Caribou WMAs becoming eutrophic wetlands is increased.

Links between changing hydrology (increased flooding, water depth, and/or residence time) and nutrient enrichment (especially available P concentrations) have been correlated to the expansion of *Typha* in native wetlands (Newman et al., 1998; Galatowitsch et al., 1999; Woo & Zedler, 2002; Richardson et al., 2008). The effects of altered hydrology on plant communities have been shown to be exacerbated by nutrient availability and vice versa (White, 1994). With evidence of altered hydrology at Skull Lake WMA, similar conclusions can be drawn.

Native plant species in Caribou WMA are well adapted to low nutrient conditions which would be insufficient for survival of invasive species. Introduction of invasive species (*Typha*, *Phalaris*) to a stressed ecosystem (changing hydrology, increasing nutrient load) would lead to establishment and eventual dominance by aggressive non-native species. It is well known that *Typha* in particular is well developed to take advantage of such situations (Galatowitsch et al., 1999).

Restoration Potential

Chemical management through application of a variety of herbicides has shown to be successful in killing invasive wetland plants, but may not affect seed viability. Unfortunately, the chemicals used are non-specific and only ones readily degradable in water are allowed for use in aquatic environments (MNDNR, 2013b). The high cost of herbicides will probably be the most prohibitive to this technique (Apfelbaum, 1985; Sojda & Solberg, 1993).

Physical management through mowing, crushing, disking, or grazing may be easier and cheaper to accomplish. These methods are used to destroy or damage the aerenchyma and/or rhizomes, disrupting the ability to move oxygen to the roots and carbohydrate storage, weakening the plant during the growing season (Linde et al., 1976; Apfelbaum, 1985; Ball, 1990).

Prescribed fire has not been shown to control cattails by itself, but may decrease plant vigor if done regularly (Apfelbaum, 1985). Burning can usually only be done in late fall and winter. Fires are generally not hot enough to damage the rhizomes of cattail, but those that are carry a risk of damaging the soil, seed bank, and possibly lowering the base level of a wetland in extreme cases (Sojda & Solberg, 1993).

Water level control can be one of the most useful tools in controlling cattail growth. Continual water level management in the spring, keeping the surface a few centimeters to meters above new shoots can weaken plants during this critical time (Apfelbaum, 1985). Extremely high water levels (>1.2 meters) have been shown to stress plants sufficiently to kill them after a few years. High water levels have also been shown to encourage muskrat populations, which can severely diminish cattails over a few years (Beule, 1979; Ball, 1990).

Both chemical and physical management in conjunction with water level control have been shown to work best during summer and fall when plants are storing carbohydrates for the winter. Prescribed fire in the fall with controlled water levels kept above growing shoots in the spring has also been successful (Sojda & Solberg, 1993).

Keeping water levels above any burned or cut surface is important in cattail control because it breaks the pathway for oxygen to move through the aerenchyma to the rhizomes. This forces anaerobic processing of carbohydrates stored in the rhizomes, depleting plant stores, eventually killing the plant (Linde, et al., 1976). All of these management practices work best and sometimes only when implemented multiple times a year over two to three years (Apfelbaum, 1985; Sojda & Solberg, 1993).

Due to the size of Skull Lake WMAs wetlands (15.4 km^2), chemical management may be cost prohibitive. Most physical management practices such as mowing, crushing, or disking may also pose a problem because of the large area and the amount of soil saturation. Grazing may be a plausible solution, but several issues should be kept in mind: animal control, further invasive propagation, and increased nutrient turnover. Although prescribed fire or water level management may not produce significant results separately, a combination of the two may be most feasible at Skull Lake WMA. The presence of the impoundment and water control structure would enable wetland flooding shortly after burning and may decrease cattail populations over multiple years.

Even with successful implementation of these management practices and removal of cattails, a viable seed bank may not be present. The amounts of bioavailable P in the soils may allow for quick recovery of invasive species if not constantly monitored and managed after the initial removal effort. If ecological restoration is not a viable solution, functional wetland management or restoration to improve downstream water quality may be an alternative solution.

CHAPTER VI

CONCLUSIONS

The results of this study support the initial hypothesis that nutrient distribution between Skull Lake and Caribou WMAs is significantly different. Vertical nutrient profiles from 15 to 45 cm showed little change in wetland pore waters at Caribou WMA. Low nitrogen and phosphate availability and an abundance of plants adapted to such ecosystems indicate that the wetland is nutrient limited. Skull Lake vertical profiles indicated pH and Eh decreased with increasing depth as SRP and NO_2 concentrations increased with increasing depth.

Several significant differences in nutrient profiles between Caribou WMA and Skull Lake WMA are apparent. Measurements of pH, Eh, bioavailable P, and in initial samples, HS are significantly higher in Skull Lake WMA than in Caribou WMA. Higher concentrations of NO_2 near the surface are evident at Caribou WMA in comparison to Skull Lake. High concentrations of bioavailable P and ecosystem dominance by aggressive non-native plant species with high nutrient requirements (*Typha, Phalaris*) at Skull Lake WMA indicate ecosystem eutrophication. Lack of available nitrate and nitrite may indicate a system limited by nitrogen.

Correlations between distance from the ditch and nutrient concentrations were inconclusive except for pH, SRP, and NO_3 at shallow depths (15 cm). An increase from 6.46 to 7.35 over 350 m showed a significant increase in pH with increasing distance indicating increased acidity associated with the ditch. Changes in P concentration were less apparent, but indicate increasing concentrations in P with increasing distance from the ditches, near the surface. This suggests that shallow groundwater may be supplying P to the ditch and exporting it out of the system during the fall. The opposite may be true during spring runoff, after storm events, and after field fertilization upstream. A negative correlation between nitrite and distance indicates that the ditch may be moving nitrite into the ecosystem surrounding the ditch.

Changes in ecosystem and species distributions over time, from largely unaltered (Caribou WMA) to degraded (Skull Lake WMA), have occurred through a series of human induced factors. The introduction of ditching and draining for agricultural purposes increased runoff discharge through Skull Lake WMA. Impoundment of State Ditch 84 within Skull Lake WMA changed the hydrology of the surrounding wetlands, increasing water depth, residence time, and wetland extent, and stressing a previously nutrient poor ecosystem. Pooling and reduced velocities of water entering Skull Lake WMA allowed for accumulation of P. Expansion of invasive species in Skull Lake WMA was inevitable. State Ditch 84 continues to be a conduit for runoff, directly affecting pH and P concentrations within Skull Lake WMA.

Complete reversal of these effects is unlikely, but some measure of *Typha* control and restoration may be possible over time. Management through mowing, disking, or burning coupled with continuous water level management to keep plant shoots submerged well into the growing season should be effective over several years. Seed bank viability as well as high concentrations of bioavailable P would curtail complete restoration. If restoration is undertaken, continued monitoring and management will be paramount to determining success. If full ecological restoration does not seem feasible, then functional restoration or management of Skull Lake WMA may be a better option.

APPENDIX

Appendix A

Collection dates, coordinates, accuracy, depth, and constituent measurements for all water samples taken at Caribou and Skull Lake WMAs

ID	Date	Type	X	Y	Z	WMA	pH	Eh (mV)	HS (a)	PO_4 (b)	NO_2-N (a)	NO_3-N (a)	SO_4 (c)
									(mg/L)				
12	9/21/11	R	669272	5424304	15	S	6.76	198	LOD	0.09	LOD	ND	
13	9/21/11	R	669257	5424339	15	S	6.94	189	LOD	0.04	ND	**LOD	
14	9/21/11	R	669236	5424381	15	S	6.97	194	LOD	0.40	LOD	ND	
15	9/21/11	R	669227	5424431	15	S	7.10	196	LOD	0.06	ND	ND	
16	9/21/11	R	669214	5424482	15	S	7.36	182	LOD	0.11	ND	ND	
17	9/21/11	R	669196	5424542	15	S	7.15	201	LOD	0.18	ND	ND	
18	9/21/11	R	669173	5424604	15	S	7.07	187	LOD	0.14	ND	**LOD	
19	9/21/11	R	669150	5424657	15	S	7.25	182	LOD	0.07	ND	ND	
20	9/21/11	R	669085	5424667	15	S	7.19	184	LOD	0.01	ND	ND	
21	9/21/11	R	669111	5424596	15	S	7.25	184	LOD	0.09	ND	ND	
22	9/21/11	R	669129	5424543	15	S	6.85	183	LOD	0.14	ND	ND	
23	9/21/11	R	669150	5424491	15	S	7.35	179	LOD	0.17	ND	ND	
24	9/21/11	R	669170	5424437	15	S	6.91	187	LOD	0.07	ND	ND	
25	9/21/11	R	669186	5424391	15	S	6.80	188	LOD	0.15	ND	ND	
26	9/21/11	R	669210	5424334	15	S	6.85	195	LOD	0.20	LOD	ND	
27	9/21/11	R	669227	5424293	15	S	6.71	208	LOD	0.10	LOD	ND	
12	10/28/11	R	669272	5424304	45	S	6.64	**245	LOD	0.36	LOD	ND	
13	10/28/11	R	669257	5424339	45	S	6.53	**231	LOD	1.14	LOD	LOD	
14	10/28/11	R	669236	5424381	45	S	6.65	113	LOD	0.68	0.1	ND	
15	10/28/11	R	669227	5424431	45	S	6.50	171	LOD	0.55	0.1	ND	
*16	10/28/11	R	669214	5424482	45	S	6.64	156	LOD	0.02	0.1	0.1	
*17	10/28/11	R	669196	5424542	45	S	6.64	152	LOD	LOD	**0.2	LOD	
18	10/28/11	R	669173	5424604	45	S	6.76	168	LOD	0.63	LOD	ND	
19	10/28/11	R	669150	5424657	45	S	6.62	124	LOD	0.38	ND	ND	
*21	10/28/11	R	669111	5424596	45	S	6.85	166	LOD	0.04	0.16	ND	
23	10/28/11	R	669150	5424491	45	S	6.15	163	LOD	1.00	LOD	ND	
25	10/28/11	R	669186	5424391	45	S	6.48	169	LOD	0.58	0.1	ND	
27	10/28/11	R	669227	5424293	45	S	7.21	145	LOD	0.60	LOD	LOD	
*17	10/28/11	D	669196	5424542	45	S	**7.66	167	LOD	LOD	0.1	LOD	
19	9/21/11	D	669150	5424657	15	S	7.35	182	LOD	0.04	ND	ND	
24	9/21/11	D	669170	5424437	15	S	6.87	190	LOD	0.08	ND	ND	
15	9/21/11	FB	669227	5424431	0	S	N/A	N/A	LOD	LOD	ND	ND	
23	10/28/11	FB	669150	5424491	0	S	N/A	N/A	LOD	LOD	ND	ND	
22	9/21/11	FB	669129	5424543	0	S	N/A	N/A	LOD	LOD	ND	ND	
29	6/8/10	R	678797	5427757	30	C	6.03	10	LOD	0.01	0.1	ND	3
29	6/8/10	R	678797	5427757	45	C	6.06	21	LOD	0.01	LOD	LOD	9

29	6/8/10	R	678797	5427757	15	C	5.98	**48	LOD	LOD	LOD	ND	LOD
29	6/8/10	FB	678797	5427757	0	C	N/A	N/A	LOD	LOD	ND	ND	ND
31	6/8/10	R	678787	5427795	30	C	6.04	23	LOD	LOD	LOD	ND	1
31	6/8/10	R	678787	5427795	15	C	6.02	**12	LOD	LOD	LOD	ND	LOD
32	6/8/10	R	678773	5427771	45	C	6.20	13	LOD	0.01	LOD	ND	14
32	6/8/10	R	678773	5427771	15	C	5.98	36	LOD	0.01	LOD	ND	2
30	6/8/10	R	678812	5427779	45	C	5.96	56	LOD	0.01	LOD	LOD	51
30	6/8/10	R	678812	5427779	15	C	6.22	39	LOD	0.01	LOD	ND	LOD
2	7/8/10	R	669279	5424260	30	S	6.64	**140	0.1	1.30	LOD	ND	2
2	7/8/10	R	669279	5424260	15	S	6.46	133	0.1	**1.15	LOD	ND	2
3	7/8/10	R	669279	5424246	30	S	6.78	156	0.1	0.94	LOD	ND	2
3	7/8/10	R	669279	5424246	45	S	6.65	137	0.1	0.28	LOD	ND	LOD
3	7/8/10	R	669279	5424246	15	S	6.30	164	**0.3	**1.30	LOD	ND	1
3	7/8/10	FB	669279	5424246	0	S	N/A	N/A	LOD	LOD	LOD	ND	ND
4	7/8/10	R	669275	5424227	30	S	6.64	159	0.1	0.92	ND	ND	2
4	7/8/10	R	669275	5424227	15	S	6.27	**141	**0.3	0.60	LOD	ND	**11
5	7/8/10	R	669299	5424242	45	S	6.91	146	0.1	1.26	0.1	ND	2
5	7/8/10	R	669299	5424242	15	S	6.70	162	0.1	0.37	LOD	ND	2
*6	7/8/10	R	669258	5424245	45	S	**7.55	125	LOD	LOD	ND	LOD	2
6	7/8/10	R	669258	5424245	15	S	6.48	**140	0.1	0.43	ND	ND	2
33	6/8/10	R	678792	5427776	30	C	6.07	85	LOD	0.01	LOD	LOD	10
33	6/8/10	R	678792	5427776	15	C	6.08	40	LOD	LOD	LOD	ND	**7

* Yellow highlighting indicates samples taken from a sand layer near 45 cm. Some statistical analysis was done with the removal of these datapoints.
**Red lettering indicates samples considered outliers as calculated by 1.5*IQR +/- 75/25 percentile respectively.

R indicates a regular sample

D indicates a duplicate sample.

FB indicates where a field blank was taken

S indicates Skull Lake WMA

C indicates Caribou WMA

ND (no detect) indicates no detection of the constituent

LOD (limit of detection) indicates samples with concentrations below the detection limit threshold of the particular constituent

(a) LOD for HS, NO_2, and NO_3 are 0.1 mg/L

(b) LOD for PO_4 is 0.01 mg/L

(c) LOD for SO_4 is 1.0 mg/L

Z coordinates are in cm

Uncertainty for all waypoints is +/- 3 meters as calculated by a Garmin etrex Vista HCx handheld GPS unit.

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