MULTI-ELEMENT FINGERPRINTING OF WETLAND SOIL FOR RAPID ASSESSMENT

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ABSTRACT

Wetland functions and conditions are determined by hydrologic, soil physiochemical, and biotic states. Information obtained from soil analysis can convey wetland history due to hydrologic regime, soil chemical changes, past physical disturbance, and past and current nutrient and pollutant levels. In this research, multi-element fingerprinting was used to characterize the element composition of hydric soil. Specifically, fingerprints were used to characterize wetland characteristics across disturbance and hydrological gradients in the Prairie Pothole Region. This research has demonstrated that fingerprinting not only has the power to convey information regarding disturbance, but can be used to predict wetland water source (groundwater discharge, flow-through, and recharge). Furthermore, this research demonstrates how future wetland assessments might be strengthened through the incorporation of multi-element data from hydric soils.

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CHAPTER 1. GENERAL INTRODUCTION

This research project set out to test how multi-element fingerprints were linked to wetland processes occurring in the soil to ultimately develop element indicators of wetland characteristics. The project was based on findings from a 2009 pilot study examining the relationship between multi-element composition of Prairie Pothole wetland soil and plant community disturbance as assessed by the Index of Plant Community Integrity (IPCI). That study showed strong links and led to a much larger study with similar experimental approaches, but across a wider spatial area and larger sample size. As will be presented in this thesis (chapter two), I found that the value of fingerprinting at detecting characteristics present in pothole wetland ecology remained. Once this relationship was affirmed I set out to test how environmental factors such as disturbance by grazing and hydrological regime influenced fingerprints in an attempt to reduce variation of potential indicators.

Multi-element fingerprints were used to detect differences in wetland vegetative communities under a grazed or non-grazed disturbance regime, and were assessed under two experimental stages. The first stage set out to sample 53 potholes throughout North Dakota whose characteristics were assessed in terms of grazed status, anthropogenic activity, electrical conductivity, and other observable (subjective) and measurable characteristics. Specifically related to grazing status, this study found that there were relations. Stage two set out to follow up on these findings during the second year by testing this relationship under more precise experimental conditions established by Streeter grassland research area. This is an area where wetlands were present on sectioned off plots of land, and grazing intensity was controlled for. Data produced showed no viable relation between the soil element composition and grazing intensity. Due to these findings, I opted not to include this material in my thesis. The idea that fingerprints could discern between vegetative communities under the disturbance of grazing was abandoned and the underlying mechanism for why elements were linked to plant community disturbance was reevaluated.

As will be discussed, the ecology of the PPR is underpinned by hydrology. This led me to conduct a study at the Cottonwood Lake Area (CLA) to help understand how fingerprints were linked to hydrological processes. The CLA is an area in which hydrological, biological, and physiochemical characteristics have been well documented and recharge/discharge status previously assigned. As will be presented in chapter three of this thesis, I found that elements are linked. The value in this finding is that it enables the reduction of variation of element linkages to ecological structure and factors responsible for its disturbance. The following discussion will explain underlying assumptions made above, and will serve as a review of literature that will be cited in subsequent chapters and concluding discussion (chapter 4).

Literature Review

Wetland Functions and Defining Characteristics

Wetlands mark the position between dry land and open-water habitats and their functions are centered on hydrology, biogeochemical cycling, and habitat (Cronk and Fennessy, 2001; Mitsch and Gosselink, 2007). They are valued by humans for their ability to mitigate flood waters, recharge groundwater, improve water quality, and produce agricultural and recreational commodities, and thus are important ecosystems to our society (Cronk and Fennessy, 2001). All wetlands exhibit three broad interrelated characteristics, including hydrology (water level, flow, frequency), physiochemical environment (sediments, soil chemistry, water chemistry), and biota (microbes, vegetation, animals), and interrelations are dramatically affected by geomorphologic setting and climate (Mitsch and Gosselink, 2007). For purposes of environmental protection, the United States Natural Resources Conservation Service defined wetlands in the *swampbuster provision* of the Food Security Act as (1) having a predominance of hydric soils; (2) is inundated or saturated by surface or groundwater at a frequency and duration sufficient to support a prevalence of hydrophytic vegetation typically adapted for life in saturated soil conditions; and (3) under normal conditions does support a prevalence of such vegetation (16 CFR 801 (a)(16); 1985). This definition is a good starting point for selecting indicators which may hold the ability to describe the environment at large; however, only indicators that respond to changes in physical, chemical, or biological states are appropriate (Reddy and DeLaune, 2008). Information obtained from soil analyses can convey wetland history due to influences by hydrologic regime, soil chemical changes, past physical disturbances, and past and current nutrient and pollutant levels (Scozzafava, 2009).

Soil can help to describe changes in hydrology. Obviously, water and its permanence, or hydroperiod, is a very important component in defining the wetland environment. Hydroperiod is given by the balance of inflows (precipitation and groundwater recharge) and outflows (evapotranspiration, surface runoff, groundwater discharge) with respect to time, and is governed by landscape and geologic components (Mitch and Goesslink, 2007). Water transports sediments and nutrients and the properties of which could be explained by geomorphology, hydrologic function, or disturbance. When water inputs exceed water outputs for a sufficient amount of time, microbially-mediated depletion of oxygen occurs and anaerobic conditions give way to chemically reduced soil, which influences the mobility of metals (Mitch and Goesslink, 2007). Under normal conditions a thin layer of oxidized soil remains and serves to volatize gasses and sequester phosphorous (van der Valk et al., 1978; Mitch and Goesslink, 2007).

Reduction-oxidation reactions occur in all wetland soils and the occurrence of dark manganous mottles and greenish-grey ferrous features in the lower soil column serves as indicators of waterlogged (hydric) soils (Vepraskas, 1995). Such indicators signify that chemicals such as nitrogen, sulfur, carbon, and phosphorous are being transformed into atmospheric gasses or immobilized in the soil, and is why wetlands are critically important for transforming environmentally sensitive chemicals.

Soil analysis may hold the ability to convey relationships about soil flora. Under saturated conditions upland plants become unable to complete their metabolic requirements and eventually die due to a lack of oxygen reaching the root zone (rhizosphere). Wetlands plants have evolved to such conditions by adapting root and stem tissues, termed aerenchyma tissue, to facilitate gas exchange with oxygenated surface waters and the atmosphere (Cronk and Fennessy, 2001). Oxygen is diffused to the rhizosphere, where part becomes used in metabolism and part becomes leaked into the immediate surrounding soil, a process termed radial oxygen loss (ROL) (Cronk and Fennessy, 2001). Although ROL competes with metabolism for oxygen, it is thought that ROL is an adaptation to toxic conditions associated with the nature of chemically reduced soil (Cronk and Fennessy, 2001). By leaking oxygen to the surrounding rhizosphere, certain toxic metals, gasses, and organic compounds are oxidized. This oxidized layer enables iron and manganese plaques to form, producing the readily observable rust-colored plaque surrounding roots. Other metals such as Al, As, B, Ba, Ca, Cu, K, Li, Mg, Mn, Na, Ni, P, S, Si, Sr, Ti, and Zn have been shown to accumulate in high concentration where these plaques form (Doyle and Otte, 1997; Kissoon et al., 2010; Kissoon et al., 2011; Li et al., 2011). It has also been shown that plants can alter element ratios around their root zones (Yang et al., 2010; Jacob et al., 2011), and elements are differentially affected by the application of fertilizers (Jacob et al., 2011). Additionally, studies have shown that ROL can liberate sulfate, protons, and increased metal mobility through the dissolution of pyritic soils (Yang et al., 2010). The rate at which ROL proceeds depends on factors including if ROL occurs along the length or the tip of the root, oxygen concentration of adjacent soil, morphological characteristics such as root-to-shoot ratio, canopy type and growth form, and the expression of factors depends on plant species (Cronk and Fennessy, 2001). Even in death, plants, through decomposition produces organic acids, including humic and fulvic acids, which enhances dissolution and bioavailability of trace elements (He et al., 2005).

Finally, physical disturbances and nutrient and pollution levels effect change in soil properties. The most common pollutant in the United States is sedimentation (Gleason and Euliss, 1998). Sedimentation is accelerated by physical disturbance to wetland catchments, the effects of which increase organic matter, alters food webs, and impedes the wetlands ability to cycle and sequester environmentally sensitive nutrients (Gleason and Euliss, 1998). Radioactive fallout from 1940s era nuclear testing has also enriched soils in a layer of ^{137}Cs, and has been used as a tracer to provide independent information on erosion and sedimentation rates and patterns (Ritche and McHenry, 1990). Agricultural activities can also enrich soil with heavy metals through fertilizer, pesticides, and combustion of fossil fuel (Alloway, 1995).

A key tenant to make clear is each wetland characteristic is intimately linked and exerts a signature on abiotic components. Whether it is through natural or anthropogenically-mediated disturbances to redoximorphic states, soil/water chemistries resultant from hydrological states, relation between hydroperiod and vegetative biomass and soil organic matter, metals accumulated from rhizosphere plaques, or any of the heavy metal and radioactive chemicals enriched by anthropogenic activity, soil properties should provide crucial detail regarding wetland characteristic states.

A Need for Rapid Assessment

There is a push to develop low cost and easy to implement wetland assessments and this need was brought forth by legislation proposed by section 404 of the Clean Water Act of 1972 (Reiss, 2006). This legislation states that navigable water and those adjacent to are under the jurisdictional authority of the United States and prohibits the dredge or fill of such lands. Through this and the ‘swampbuster’ provision in the Food Security Act of 1985, the federal government has been able to maintain a ‘no net loss’ policy for wetlands. In effect, this policy mandates that wetland function does not reduce, which means if an area occupied by a wetland is to be developed, an equal area must be repurposed as a wetland. This also means that the condition of wetlands across the country must remain or improve, but not degrade. Although the latter policy had good intentions, it was not properly enforced due to limitations in understanding baseline condition. It is only until recent that this issue took the national stage and efforts are underway to establish the first ever baseline conditions of the nation’s wetlands.

The Environmental Protection Agency’s National Wetland Condition Assessment (NWCA) set out to assess wetland condition throughout the United States and integrate many biophysical variables together to indicate stressors of poorly conditioned wetlands (EPA, 2008). This effort encompasses eight regions, of which included the Prairie Pothole Region (PPR) of North Dakota (EPA, 2011). This region is host to an astoundingly abundant glacially-derived wetland landscape that straddles two countries: five U.S. states and three Canadian provinces. In total, the region accounts for 715,000 km^2 of North America’s total land area (Huang et al., 2011). Due to its immense size, assessment of condition presents a technical and logistical challenge. It would therefore be advantageous to develop a rapid assessment tool which could be used to identify poorly conditioned wetlands to be later intensively assessed by the NWCA. To better understand my selection of assessment variables, it will first be helpful to discuss the region and characteristics underpinning wetland ecological condition. This prerequisite discussion will better frame the discussion of biogeochemical linkages and how multi-element fingerprinting may be suited for assessment.

Environmental Framework of the Prairie Pothole Region

The geological landscape shapes the depression landform and contributes to hydrological relationships. These relationships exert a strong influence on biological and chemical components, and the culminated effect on the environment, in turn, exerts signatures on to soils. Disturbances have been shown to also exert signatures and presumably exert influence on naturally-mediated signatures. The following review will describe the PPR in terms of its main components: geology, hydrology, biology, and disturbance.

Geology

The North American PPR is spatially and temporally diverse (LaBaugh et al., 1998) and is most notably characterized by its numerous glacial depressions that speckle the landscape (Bluemle, 2000). Depressions were formed during the last ice age, by Pleistocene glaciation, which molded the landscape into numerous raised hummocks and lowered water filled depressions called Potholes (Bluemle, 2000). This process draped the region in till originating from the Canadian Shield, incorporating bedrock consisting of Precambrian igneous and metamorphic rocks, early Paleozoic sandstones, limestone, and dolomites, and Cretaceous shale and siltstones (Winter, 2003). In North Dakota, Potholes are mostly limited to all but the southwest corner and eastern edge of the state. The southwestern boundary is set apart by the

Missouri River, and progressing eastward, landforms occupied by Potholes include the Coteau Slope, Missouri Coteau, and Glaciated Plains. The eastern extent is delineated by the flat Red River Valley. Depending on the location in the region, thickness of till varies. Till is thinnest on the Coteau Slope and thickest on the Missouri Coteau and Glaciated Plains (Bluemle, 2000). Generally, elevation decreases west to east.

Hydrology

The most important hydrological feature endemic to the region is a lack of an integrated network of drainage where Pothole surface water can flow to riverine or lacustrine systems (Kamp and Hayashi, 2008). This feature enables water to pool in depressions shed from surrounding upland hummocks. Permanence of water is dictated by a complex interplay between the Pothole's relation to groundwater and net inputs/outputs by both seasonal and decadal climatic patterns (LaBaugh et al., 1998; Johnson et al., 2004). The type of catchment a wetland is located in can also influence inflow dynamics. The catchment can be open or closed. Open catchments contain a spill point, which enables water to flow to adjoining wetlands under deluge atmospheric conditions, whereas closed catchments do not (Rover et al., 2011). Wetland water levels are sustained through precipitation and, in some instances, groundwater. Water inputs to a typical Pothole wetland by precipitation include 48% entering through to the wetland surface, 31% from spring snowmelt, and 21% from runoff from the land surface (Shjeflo, 1968). Overall, water balance is negative in that evaporation of surface water exceeds precipitation (Sloan, 1972; Berkas, 1996; LaBaugh et al., 1998); however, this does not mean that all wetlands will dry on a seasonal basis. Water can also be supplied by groundwater if the wetland depression is close to the groundwater level and this relation is termed recharge, discharge, and flow-through relations to the groundwater table (Berkas, 1996).

If the water table sits below the center of the Pothole and slopes up to meet the wetland edge, then the status is recharge (Sloan, 1972). During months when precipitation is highest, water enters the wetland and infiltrates the till, thus functioning to recharge groundwater. Due to their small size relative to others, these wetlands are typically temporary (Arndt and Richardson, 1988; Euliss et al., 2004). Since precipitation is the only input of water, water stays for only a few months a year (Berkas, 1996). Soil chemistry of this type is typically very low in electrical conductivity (0.39-0.60 dS per m) and devoid of calcite and gypsum (Arndt and Richardson, 1988). Alternatively, if the water table sits at or above the center of the depression, and slopes down to meet the wetland edge, the status is discharge (Sloan, 1972). These wetlands are typically larger in size and are classified as semi-permanent or permanent (Arndt and Richardson, 1988; Euliss et al., 2004). Under this scenario groundwater functions to recharge the wetland and extend water permanence to later in the growing season (Berkas, 1996). The surface water chemistry of discharge wetlands is usually composed of a greater concentration of dissolved solutes for two reasons. First, since groundwater moves very slow through the till, water entering the wetland contains a greater concentration of salts than the amount that could have entered through runoff from upland hummocks (Sloan, 1972). Secondly, since output of water only occurs through evaporation, salts from groundwater seepage become concentrated (Sloan, 1972). Soil chemistry of this type is characterized by high electrical conductivity (11.2-25.7 dS per m) and high abundance of calcite and gypsum (Arndt and Richardson, 1988). Due differences in osmotic pressure exerted by the increased concentration of dissolved solids, the biology of these wetlands have had to adapt and evolve to cope with conditions. It has been shown that vegetative communities are segregated along a salinity gradient (Stewart and Kantrud, 1972), and such a gradient is likely in response to wetland hydrological function. There is a third hydrological function, flow-through, and is a union of the previous statuses. Under this scenario, the water table slopes up to one side of a wetland edge, and on the edge of the other side, slopes down (Sloan, 1972). This effectively creates a link between the two statuses and the integrated effects of the three statuses may serve to facilitate local groundwater flow (LaBaugh et al., 1998). The soil chemistry of this type generally displays intermediate electrical conductivities and calcite and gypsum concentrations (Arndt and Richardson, 1988).

Climate is a major factor dictating wetland water permanence. Depending on climatic cycles, the groundwater relation to any wetland, independent of its long-term relation, may experience groundwater flow reversals and sway closer to recharge or discharge (Winter, 2003b; Johnson et al., 2004). This variability can have an effect on biogeochemical weathering and formation of secondary minerals (Arndt and Richardson, 1988; Brady and Weil, 2002).

Biology

Vast differences in wetland function and corresponding water chemistry enables the region to support a high degree of biological diversity (LaBaugh et al., 1998). The type of ecological community that any particular wetland can support depends largely on the location along a water permanence gradient. Within a wetland, this gradient is organized into concentric zones, and, from the deepest central region to the outer most region zones are classified as permanent open-water, deep-marsh, shallow-marsh, wet-meadow, and low-prairie classes (Stewart and Kantrud, 1971). The zone dominating any particular wetland in the region designates its class. For example, wetlands dominated by the wet-meadow zone are classified as temporary, whereas wetlands dominated by the shallow-marsh are classified as seasonal. Additionally, wetlands dominated by the deep-marsh zone are classified as semi-permanent. More information about wetland zones and type of vegetation supported please refer to Stewart and Kantrud (1971, 1972). Each zone and class produces different types of organic matter and support a wide degree of decomposition rates (van der Valk et al., 1978). Invertebrate detrital shredders have been shown to increase decomposition and concentration of organic matter in the soil, which affects nutrient cycling (Schaller et al., 2010). Through decomposition, soil microbial processes produce organic acids which accelerate biogeochemical weathering of minerals at a rate 1000 times faster than the rate at which abiotic processes can proceed (Brady and Weil, 2002). Since these wetland environments lay amidst human settlements and activities, they are often exposed to a wide degree of disturbances, and depending on intensity, can significantly alter plant communities (DeKeyser et al., 2009).

Disturbance

In the era during pre-settlement times, disturbance in the PPR was naturally-mediated and included burning, water level fluctuations, and grazing (Kantrud et al., 1989). Since then the region progressed towards an agriculturally-dominated landscape, which has resulted in an estimated 45% loss in wetland area (Berkas, 1996; Gleason and Euliss, 1998). In North Dakota, agricultural drainage of wetlands poses the greatest threat to wetland resources (Berkas, 1996). Of the most threatened classes of wetlands are the smaller, temporary wetland basins. Wetlands supported by brief water permanence are under greater agricultural pressure because they dry quicker than wetlands supported by prolonged permanence, which increases the threat of agricultural conversion (Bartzen et al., 2010). Agricultural pressures are known to impact wetlands in other less noticeable ways. Such disturbances can take the form of many factors including alteration to hydrology, increased sedimentation, introduction of competitive species, and poor management practices (DeKeyser et al., 2009). These factors are produced by increased activity in the upland, use of agricultural chemicals, and over grazing.

Unifying Concepts and Assessment via Multi-Element Fingerprinting

The U.S. Environmental Protection Agency (EPA) (Jackson et al., 2000 in Reddy and DeLaune, 2008) provides four guidelines for the development of ecosystem indicators and generally require that, (1) the indicator be relevant to the assessment question and to the ecological resource; (2) the methods of sampling and measuring the environmental variables are feasible, appropriate, and efficient; (3) that human error and natural variability is sufficiently understood and documented; and (4) the indicator should convey information on ecological conditions that is meaningful to environmental decision making.

The goal of this thesis is to develop indicators of wetland characteristics using soil properties and my approach to doing so are largely in line with EPA guidelines. Soil is borne from parent material (continental crust) and 99.5% of the total element content is composed of only ten elements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, and P) (He et al., 2005). The remaining, so-called trace elements make up the other 0.5% and typically do not exceed 1000 mg/kg (He et al., 2005). Many of the wetland properties (i.e., reduction-oxidation reactions, salinity, hydrology, pH, organic matter content, disturbance, etc.) affecting wetland ecology also affect the behavior of elements. Analysis of element concentrations should show patterns specific to a wetland ecologic state.

Advancements in analytical instrumentation have made great strides in multiple element analysis and have reduced costs to a point that makes it economically feasible to implement at a large scale. One such instrument is Inductively Coupled Mass Spectrometry (ICP-MS) and is used to detect a 62 element suite, producing the so-called multi-element fingerprint, all at once for about $30 a sample (Activation Labs, 2013). Analytical error can be reduced with the use of a reference material of known composition, and is sent alongside the sample to estimate analytical accuracy (Fränzle and Makert, 2002); however, certified labs employ methods to check accuracy, making this practice unnecessary. Natural variation observed in the multi-element fingerprint can then be placed in context of chemical properties (i.e., clay fraction, organic matter, pH, electrical conductivity) measured from the soil sample. Human error can be reduced through rigorous adherence to procedure and use of standard reference materials. The only part of the EPAs guidelines that are unknown as of yet is if multi-element fingerprints have the ability to convey environmental condition (at a landscape spatial extent) in a way that is meaningful to decision makers.

Successful use of multi-element fingerprinting has been reported to provide meaningful information for characterization of soils and plants (Jacob and Otte, 2004) and for identification of sources and sinks of sediments in small watersheds (Tingley et al., 1999; Russell et al., 2001; Wijeyaratne, 2011). Landscape-level multi-element fingerprinting has been conducted for dry land soils throughout the United States by the United States Geological Survey; however, the study was designed as a survey, and not meant to indicate ecological characteristics or condition whatsoever (Grossman et al., 2004). Particular to the PPR, only three studies used the multiple element approach to survey Pothole and river sediments (Martin and Hartman, 1984), examine how sedimentation affects wetland soils (Martin and Hartman, 1986), and to examine how element concentration related to physiographic regions (Martin and Hartman, 1987). Specifically related to elements and indication of condition, only a few studies have been conducted using only a limited suite of elements (Görres and Frenzel, 1997; Cleaveland et al., 2011; Mikak et al., 2011; Mata et al., 2011; Cui et al., 2012).

Here, I propose using multi-element fingerprinting to indicate wetland ecological disturbance and wetland hydrologic function for use in the PPR. The region is an ideal ‘natural laboratory' due to the high density of depressions throughout the landscape, a characteristic which provides a unique opportunity to compare wetlands of similar hydrological, geological, and ecological conditions at a large geographic area. The integrated effect of soil pH, electrical conductivity, loss on ignition, and particle size, and 62 element concentrations should be sufficient to characterize wetland patterns and processes. Element concentrations will be analyzed from the following groups of the periodic table of the elements, (numbers in parentheses indicate the number of elements detected in that group) alkali metals (5/6), alkaline earth metals (5/6), transition metals (20/29), metalloids (6/7), metals (7/7), nonmetals (2/7), lanthanides (14/15), and actinides (3/15). These data will be compared and placed in context to wetland disturbance using the Index of Plant Community Integrity across a state-wide area. Additionally, data will be placed in context to wetland hydrology for wetlands in the Cottonwood Lake Area. The overall expected outcome of this project was to determine the extent to which wetland characteristics are represented in multi-element fingerprints. Under this framework it should be possible to test whether multi-element fingerprinting has the ability to convey useful information to decision makers.

CHAPTER 2. MULTI-ELEMENT FINGERPRINTING OF POTHOLE WETLANDS AS A RAPID ASSESSMENT TOOL IN PREDICTING PLANT COMMUNITY ECOLOGY

Introduction

Criteria used in the development of wetland assessments have included the composition of vegetation (Radomski and Perleberg, 2012), suitability for sustaining wildlife (Lougheed et al., 2001), and the surrounding land use (DeKeyser et al., 2009). Although such assessments provide valuable information about ecological impacts, they do not typically go beyond biotic constituents. The abiotic soil constituents of wetlands provide a wealth of information including geomorphology and water source, two highly important factors underpinning wetland functions (Brinson, 1993). Soil data can describe hydrologic regime, soil chemical changes, past physical disturbances, and past and current nutrient and pollutant levels (Scozzafava, 2009), information which provides an opportunity to improve and build upon existing wetland assessments.

One such area of improvement could utilize soil chemical information measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), a tool which characterizes a suite of element concentration to produce the so-called multi-element fingerprint. Soil chemistry is known to provide information regarding both biotic and abiotic controls exhibited to a wetland environment. For example, the element composition has been used to differentiate wetland environments, including riverine, depression, lacustrine, and riparian types (Jacob et al., 2013; Martin and Hartman, 1984). Wetland soil substrates are classified as mineral or organic and a distinction is given by the relationship of soil organic carbon to clay (Mitch and Gosselink, 2007). The source of wetland water can be approximated by examining the mineralogy of secondary minerals and can also be an indication of geomorphic characteristics (Arndt and Richardson, 1988; Last and Last, 2012). In addition to this detail, soil chemistry can indicate anthropogenic pressures including upland activity and pollutants (Ritchie and McHenry, 1990; Alloway, 1995; Gleason and Euliss, 1998). Furthermore, soil around the rhizosphere of wetland plants form metal plaques, and these plaques have different compositions depending on plant species (Doyle and Otte, 1997; Kissoon et al., 2010; Kissoon et al., 2011; Li et al., 2011). Although wetland biology is a direct reflection of environmental type, hydrology, soils, and geomorphology, there has not been research which utilizes a large suite of elements to study such relationships.

This chapter introduces an approach utilizing multi-element fingerprinting by ICP-MS to characterize wetlands along a disturbance gradient. This was accomplished by determining the multi-element fingerprints of seasonal wetlands within the Prairie Pothole Region (PPR). This region is characterized by high wetland density, which enables the assessment of the relationship between the chemical composition of their soils and their biological quality as defined by the Index of Plant Community Integrity (IPCI) of Hargiss et al., 2008. The IPCI is based on the composition of the vegetation, which is influenced by the surrounding land use. In the IPCI system, each wetland is evaluated based on its vegetation and surrounding land uses and then assigned a numeric value between zero and 100, which then may be categorized as: very poor (0-20), poor (21-40), fair (41-60), good (61-80) or very good condition (81-100). The reasons for investigating the relationship between the multi-element composition of soil and IPCI were that (1) understanding that relationship might enhance our capabilities of meaningful assessment, as well as (2) improve our understanding of ecosystem functioning and services. One of the drawbacks of the IPCI is that it can only be assessed during the growth season, when most plants flower. If a close relationship between the multi-element composition of the soil and IPCI exists, information about the soil chemistry will strengthen the power of the assessment.

The overall hypothesis was that potholes of differing IPCI condition classes would show differences in multi-element contents of their soils. The study involved two sampling periods. The first was in 2009 on 20 wetlands, which aimed to assess if (1) there is enough variation between wetlands of different IPCI categories to make it feasible for this approach to work, and, if so, to (2) assess if differences between wetlands of different IPCI categories showed significant and consistent differences in multi-element composition. Having observed that there were indeed significant differences in multi-element composition of wetlands of different IPCI categories, a second field study in 2011 examined the fingerprints of 23 additional seasonal wetlands throughout North Dakota to (3) verify if significant differences and trends in multi-element composition remained at a wider landscape area.

Materials and Methods

Field Study I, 2009

<u>Study Area</u>

The study area was centrally located along the Missouri Coteau of the North Dakota PPR (Figure 2.1). Wetlands of the PPR were selected due to the high density of depressions throughout the landscape, a characteristic which provides a unique opportunity to compare wetlands of similar hydrological, geological and ecological conditions at a large geographic extent. Agricultural land use dominates the landscape through impacts of grazing, mowing, cultivation, fire, drought, sedimentation, nutrient loading, pesticides, and heavy metals, and these impacts have been shown to significantly influence the species composition of wetland plant communities (DeKeyser et al., 2009; Niemuth et al., 2010). Mean annual temperatures during 1954-2010 for Underwood, ND, a weather station within 20 km of the study site, ranged from -1° C to 12° C (max 11.6° C, min -1.17° C) and mean annual precipitation was 444 mm (High

Plains Regional Climate Center, 2010). The Palmer Drought Severity Index (PDSI) is a meteorological drought index used to assess the severity of dry or wet spells of weather (NOAA, 2007). For North Dakota, the average PDSI for 2009 was 4.31 and in 2011 it was 6.46 (NOAA, 2013). These values indicate extreme deluge (NOAA, 2007).

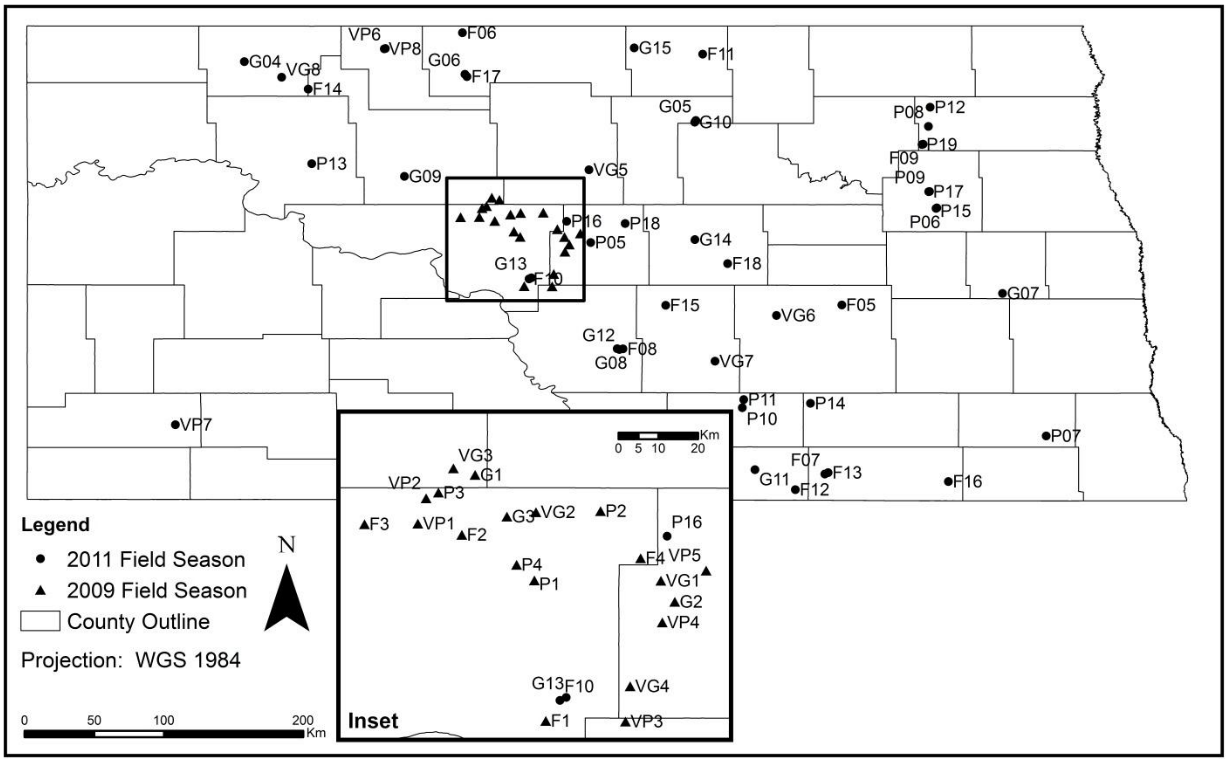


Figure 2.1. The 2009 and 2011 study areas. The 2009 study area was composed of 20 seasonal Prairie Pothole wetland sites in central North Dakota (inset). The 2011 study area was composed of 23 seasonal wetlands sites throughout North Dakota. Sites are denoted by their Index of Plant Community Integrity (IPCI) condition and are very poor (VP), poor (P), fair (F), good (G), and very good (VG) plant communities. The county outline data was courtesy of North Dakota GIS Hub.

Twenty seasonal wetlands, characterized with surface water present early in the growing season but drying out later in the season (Niemuth et al., 2010), and water depths at the centers ranging from 0 to 1 m were included in this study (Fig. 2.1, Table 2.1). Each wetland site was designated by its pre-existing IPCI condition (Hargiss et al., 2008) and given an identifier unique to the wetland under study (Table 2.1). At the time of sampling, multiple factors contributed to plant community condition. For instance, VP5 had been cultivated through the wetland center and had crops surrounding the wetland, whereas VP2 was not cultivated but its upland consisted of canola (*Brassica cultivar)*, a popular crop in North Dakota. Wetland G1 and VP1 had cattle actively accessing the resource and the vegetation was noticeably grazed. Alternatively, wetland F1 and VG4 was located in a relatively pristine prairie grassland environment with little to no noticeable anthropogenic influence. Proximity to road surfaces ranged from 10 m to two kilometers.

Table 2.1. Geographic coordinates and county origin of IPCI-assessed wetlands from field seasons I (n=20 wetlands) and II (n=23 wetlands).

Site	County	Latitude°	Longitude°
VP1†	McLean	47.76762	-101.128
VP2†	McLean	47.82481	-101.109
VP3†	Burleigh	47.32008	-100.658
VP4†	Sheridan	47.54401	-100.575
VP5†	Sheridan	47.66138	-100.476
VP6	Renville	48.85375	-101.734
VP7	Slope	46.42675	-103.09
VP8	Renville	48.85173	-101.741
P01†	McLean	47.63919	-100.864
P02†	McLean	47.79584	-100.714
P03†	McLean	47.83766	-101.081
P04†	McLean	47.67428	-100.904
P05	Ransom	46.35419	-97.4682
P06	Walsh	48.35183	-98.2283
P07	Walsh	48.47516	-98.2176
P08	Sheridan	47.72499	-100.186
F01†	McLean	47.32149	-100.838
F02†	McLean	47.74217	-101.028
F03†	McLean	47.76622	-101.249
F04†	McLean	47.68924	-100.624
F05	Stutsman	47.19987	-98.7878
F06	Bottineau	48.95549	-101.237
F07	Walsh	48.23662	-98.2624
F08	Dickey	46.06065	-98.0993
F09	Bottineau	48.67247	-101.207
F10	Wells	47.4664	-99.5246
G01†	Ward	47.87784	-100.998
G02†	Sheridan	47.59058	-100.546
G03†	McLean	47.78334	-100.926
G04	Bottineau	48.688	-101.22
G05	Steele	47.27393	-97.7497
G06	Burleigh	46.91706	-100.237
G07	Burleigh	46.91274	-100.224
G08	McLean	47.37425	-100.792
G09	Wells	47.62163	-99.7356
VG1†	Sheridan	47.63833	-100.578
VG2†	McLean	47.79321	-100.861
VG3†	Ward	47.89241	-101.047
VG4†	Sheridan	47.39968	-100.647
VG5	McHenry	48.07132	-100.42
VG6	Stutsman	47.1316	-99.2089
VG7	Kidder	46.83646	-99.6064
VG8	Rolette	48.858	-100.128

† Site sampled in field study I, 2009.

Sample Collection and Analysis

Soil sampling occurred over a one week period during July 25-28 2009. Each wetland was sampled along the north-south transect five times at equidistant intervals. The entry and exit sampling points were defined when the water depth was less than 5 cm on the outer edge. If the wetland was dry then best professional judgment was used to determine the diameter. Square soil cores were manually extracted using a spade and only interior soil at a depth of 10 cm was collected. This minimized metal contamination by the spade. Samples were placed in polyethelene freezer bagged and kept on ice until they could be stored in a 3° C refrigerator.

Samples were randomly sorted prior to processing to minimize systematic error. Materials were processed and the chemical composition was stabilized within one day after the last site was sampled. Stabilization entailed drying at 60° C until constant weight, crushed and homogenized using a ceramic mortar and pestle, and sieved through a two millimeter mesh screen. Subsamples were divided for analysis of 1) soil element concentrations, 2) pH, and 3) organic matter content. For subsample one, materials were further sieved through a 63 µm mesh screen and the fraction less than 63 µm (f<63) was retained. Element analysis was performed by Acme Analytical Laboratories by aqua regia digestion and ICP-MS analysis (Ultratrace II method) for 62 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr). Standard certified reference soil was included in the sample set for quality control (NCS DC73384, China National Analysis Center for Iron and Steel 2004), and percent recovery for all elements were 58.4 ±26.5 (mean ±SD) and 0.61,121.73 (min, max). Zn and Ni were within 10% recovery. The pH of subsample two was measured in a 1:2 soil-distilled water mixture with a Symphony pH probe

(14002-860, VWR) and Symphony pH meter (SP70P, VWR). Subsample three was analyzed for percent organic matter, by weight, with loss-on-ignition (LOI) for a 5 g sample at a drying temperature of 105°C for 2 hours and an ignition temperature of 360°C for 2 hours (Sparks 1996).

Field Study II, 2011

Study Area, Sample Collection, and Analysis

The 2011 study area included sites within the 2009 study area and extended across the state of North Dakota, spanning a maximum distance of 600 km (Figure 2.1). These wetlands were selected as part of a larger, separate study which set out to intensify the EPA's National Wetland Condition Assessment by including the IPCI. Their coordinates are listed in Table 2.1. Land use upland to the wetlands studied is consistent with the previous description. A total of 23 seasonally flooded wetlands were sampled from June 13 to July 29 2011 and the methods of sampling and sample processing are the same as 2009 with the exception that samples were refrigerated within one week of collection.

Data Analysis

All computations were processed in Microsoft Excel 2010 (Microsoft Office 2010® © 2010 Microsoft Inc.). Data were log-transformed to normalize for homogeneity of variance across all concentration values. Data were statistically analyzed by ANOVA (general linear model and Tukey's pairwise comparisons) (Minitab® 16 © 2012 Minitab Inc.).

Results

Field Studies I (2009) and II (2011)

In both field studies, Au, Ge, Hf, Lu, Re, Ta, Te, and W concentrations were below their respective detection limit in more than 50% of the samples and were thus excluded from subsequent analysis. Element concentrations below their respective detection limit in less than 50% of the samples had their concentration replaced with the detection limit.

For field study I mean ±standard deviations element composition between IPCI classes VP, P, F, G, and VG is shown in Table 2.2, with pH and LOI as co-variants. Overall, pH decreased from VP to VG, and LOI showed a statistically significant relation to the IPCI, but did not have a distinctive pattern from VP to VG. Since soil properties showed differences between the IPCI, they were included in the statistical analysis as co-variants. The analysis showed that element concentrations and their relation to the IPCI fell within one of four groups. A majority of elements did not significantly differ between the IPCI. Another group of elements did show differences between the IPCI; however, their pattern was not sufficiently consistent to be regarded as a plausible indicator. The remaining elements showed plausible use as an indicator. Of these, several elements showed significantly higher concentrations in VP than VG and were Ag, Al, As, Co, Cs, Ga, K, Mn, Ni, P, and V. Element concentrations higher in VG than VP were Nb, Pb, Sc, Sn, Th, U, and Zr. These 18 observations were encouraging enough to expand the sampling area across North Dakota in 2011.

Table 2.2. Field study I: Mean ± standard deviation of loss-on-ignition (LOI, g 100g^{-1} dry soil), pH, and concentrations of elements that varied significantly between IPCI classes, with associated ANCOVA *p*-values (ns=not significant for *p*-value>0.05). Elements are arranged by relation to the IPCI in alphabetical order. The IPCI conditions are very poor (VP), poor (P) fair (F), good (G), and very good (VG). Means that do not share a letter are significantly different (*p*-value≤0.05).

							ANCOVA *p*-value		
	Unit	VP	P	F	G	VG	Condition	pH	LOI
n	samples	25	20	20	15	20			
pH		6.48 ±0.81^{b}	6.47 ±0.32^{ab}	5.93 ±0.9^{ab}	6.42 ±0.58^{a}	5.78 ±0.46^{a}	0.002		
LOI	%	6.55 ±2.09^{ab}	8.75 ±2.51^{b}	6.84 ±2.7^{a}	9.28 ±3.89^{b}	8.59 ±4.09^{a}	0.002		
Element concentrations that did not vary between classes									
Ba	μmol·g^{-1}	1.22 ±0.36^{a}	1.23 ±0.18^{a}	1.19 ±0.3^{a}	1.15 ±0.38^{a}	1.26 ±0.15^{a}	ns	0.000	ns
Be	nmol·g^{-1}	81.7 ±11^{a}	79.9 ±13.3^{a}	84.9 ±11.5^{a}	74 ±13^{a}	78.8 ±17.2^{a}	ns	0.034	0.000
Bi	pmol·g^{-1}	750 ±133^{a}	725 ±139^{a}	725 ±93.5^{a}	641 ±91.9^{a}	701 ±125^{a}	ns	ns	0.017
Ca	μmol·g^{-1}	361 ±420^{a}	180 ±46.4^{a}	183 ±167^{a}	185 ±74.3^{a}	148 ±19.4^{a}	ns	0.000	ns
Cd	nmol·g^{-1}	4.43 ±0.83^{a}	4.06 ±0.98^{a}	4.41 ±1.99^{a}	5.04 ±1^{a}	4.69 ±0.57^{a}	ns	ns	ns
Ce	nmol·g^{-1}	257 ±31.6^{a}	259 ±15.5^{a}	270 ±27.9^{a}	242 ±38.2^{a}	263 ±35.5^{a}	ns	0.000	0.000
Cu	nmol·g^{-1}	313 ±45^{a}	315 ±50.4^{a}	306 ±40.7^{a}	322 ±40.8^{a}	334 ±37.7^{a}	ns	0.003	ns
Dy	nmol·g^{-1}	13.4 ±1.77^{a}	12.9 ±1.35^{a}	13.4 ±1.48^{a}	11.9 ±1.62^{a}	12.8 ±2.18^{a}	ns	ns	0.000
Er	nmol·g^{-1}	6.1 ±0.9^{a}	5.86 ±0.72^{a}	6.19 ±0.62^{a}	5.54 ±0.89^{a}	5.83 ±1.02^{a}	ns	ns	0.000
Eu	nmol·g^{-1}	4.26 ±0.63^{a}	4.21 ±0.45^{a}	4.31 ±0.58^{a}	3.82 ±0.57^{a}	4.08 ±0.7^{a}	ns	0.031	0.000
Fe	μmol·g^{-1}	338 ±70.5^{a}	278 ±50^{a}	312 ±67.3^{a}	265 ±60.2^{a}	282 ±74^{a}	ns	ns	0.000
Gd	nmol·g^{-1}	18.6 ±2.44^{a}	18.2 ±1.71^{a}	18.7 ±2.16^{a}	16.3 ±2.09^{a}	17.7 ±2.86^{a}	ns	0.018	0.000
Ho	nmol·g^{-1}	2.45 ±0.41^{a}	2.33 ±0.3^{a}	2.43 ±0.28^{a}	2.18 ±0.38^{a}	2.39 ±0.46^{a}	ns	ns	0.000
In	pmol·g^{-1}	219 ±44.4^{a}	218 ±44.7^{a}	231 ±42.6^{a}	203 ±42.5^{a}	205 ±42.6^{a}	ns	0.027	0.002
Mg	μmol·g^{-1}	224 ±81.6^{a}	178 ±27.1^{a}	200 ±101^{a}	212 ±103^{a}	152 ±30.4^{a}	ns	0.000	ns
Nd	nmol·g^{-1}	114 ±15.5^{a}	114 ±8.61^{a}	119 ±14.5^{a}	106 ±15.2^{a}	116 ±17.9^{a}	ns	0.000	0.000
Pr	nmol·g^{-1}	31.1 ±4.19^{a}	31.2 ±2.2^{a}	32.8 ±3.97^{a}	29 ±4.17^{a}	31.6 ±4.64^{a}	ns	0.000	0.000
Se	nmol·g^{-1}	17.9 ±4.72^{a}	17.8 ±3.55^{a}	18.4 ±4.18^{a}	19.3 ±4.21^{a}	17.7 ±2.55^{a}	ns	0.000	0.005
Sm	nmol·g^{-1}	21.7 ±2.79^{a}	21.4 ±1.82^{a}	22.5 ±2.8^{a}	19.6 ±2.75^{a}	21.7 ±3.49^{a}	ns	0.000	0.000
Ti	nmol·g^{-1}	9.22 ±4.78^{a}	11.1 ±3.12^{a}	12.3 ±5.06^{a}	9.68 ±3.67^{a}	12.2 ±6^{a}	ns	ns	0.000
Tm	pmol·g^{-1}	710 ±242^{a}	681 ±217^{a}	651 ±182^{a}	671 ±208^{a}	710 ±243^{a}	ns	ns	0.010
Y	nmol·g^{-1}	127 ±18.2^{a}	122 ±13.6^{a}	127 ±13.7^{a}	112 ±16.3^{a}	121 ±21.5^{a}	ns	ns	0.000
Yb	nmol·g	4.72 ±0.81^{a}	4.48 ±0.62^{a}	4.68 ±0.62^{a}	4.05 ±0.69^{a}	4.28 ±0.8^{a}	ns	ns	0.000
Element concentrations that significantly differed between classes, without a clear pattern from VP to VG									
B	μmol·g^{-1}	1.42±0.65^{b}	1.01±0.17^{a}	1.07±0.32^{ab}	1.28±0.76^{ab}	1.05±0.30^{ab}	0.021	0.000	ns
Cr	nmol·g^{-1}	525±89.4^{ab}	525±68.3^{a}	532±82.5^{ab}	477±74.4^{ab}	494±69.6^{b}	0.017	0.000	0.000
La	nmol·g^{-1}	131±18.6^{ab}	132±8.52^{b}	137±15^{ab}	122±19.1^{ab}	131±18.2^{a}	0.029	0.000	0.000
Li	μmol·g^{-1}	1.63±0.35^{bc}	1.59±0.37^{b}	1.4±0.28^{abc}	1.36±0.51^{ab}	1.1±0.19^{a}	0.000	0.000	0.001
Mo	nmol·g^{-1}	5.64±1.72^{c}	4.41±1.76^{ab}	3.68±1.56^{ab}	3.52±1.76^{a}	5.37±2.41^{bc}	0.000	ns	0.001
Na	μmol·g^{-1}	19.1±21.7^{ab}	8.9±1.36^{a}	9.63±3.65^{ab}	35.7±37.1^{b}	10.4±2.52^{ab}	0.000	0.000	ns
Rb	nmol·g^{-1}	273±27.6^{ab}	253±24.4^{a}	262±45.2^{a}	295±39.5^{b}	271±45.4^{ab}	0.005	ns	0.000
S	μmol·g^{-1}	75.6±118^{b}	25.5±10.1^{a}	22.4±17^{ab}	82.3±97.8^{b}	32.3±20.8^{b}	0.001	0.000	0.000
Sb	nmol·g^{-1}	2.29±0.78^{b}	2.41±0.79^{b}	1.93±0.54^{b}	1.2±0.18^{a}	1.72±0.49^{b}	0.000	0.038	ns
Sr	μmol·g^{-1}	0.68±0.80^{b}	0.32±0.56^{a}	0.34±0.16^{ab}	0.45±0.21^{ab}	0.37±0.03^{b}	0.001	0.000	ns
Tb	nmol·g^{-1}	2.44±0.33^{ab}	2.49±0.25^{b}	2.52±0.29^{ab}	2.18±0.32^{a}	2.49±0.38^{ab}	0.017	ns	0.000
Tl	nmol·g^{-1}	1.12±0.18^{ab}	1.09±0.15^{b}	1.11±0.13^{ab}	0.95±0.14^{ab}	0.97±0.21^{a}	0.005	ns	0.000
Zn	μmol·g^{-1}	1.22±0.19^{ab}	1.13±0.22^{a}	1.18±0.25^{ab}	1.38±0.3^{b}	1.32±0.2^{ab}	0.026	ns	ns

(continues)

Table 2.2. Field study I (continued).

							ANCOVA *p*-value		
	Unit	VP	P	F	G	VG	Condition	pH	LOI
n	samples	25	20	20	15	20			
pH		6.48±0.81^{b}	6.47±0.32^{ab}	5.93±0.9^{ab}	6.42±0.58^{a}	5.78±0.46^{a}	0.002		
LOI	%	6.55±2.09^{ab}	8.75±2.51^{b}	6.84±2.7^{a}	9.28±3.89^{b}	8.59±4.09^{a}	0.002		
Element concentrations that significantly decreased from VP to VG									
Ag	pmol·g^{-1}	756±150^{b}	705±123^{b}	717±120^{ab}	713±279^{b}	612±97.8^{a}	0.001	0.001	ns
Al	µmol·g^{-1}	695±110^{b}	648±80.9^{b}	674±157^{ab}	593±103^{ab}	596±86^{a}	0.000	0.000	0.000
As	nmol·g^{-1}	103±31.6^{b}	73.5±22.2^{b}	63.2±16^{b}	62.7±23.6^{b}	56.9±9.07^{a}	0.000	ns	ns
Co	nmol·g^{-1}	114±31.1^{c}	89.6±21.2^{bc}	90.4±18.3^{ab}	70.7±17.2^{ab}	72.3±23.6^{a}	0.000	ns	0.001
Cs	nmol·g^{-1}	10.3±0.98^{c}	9.13±1.22^{bc}	9.45±2.81^{ab}	8.81±1.13^{abc}	8.48±1.47^{a}	0.001	0.000	0.001
Ga	nmol·g^{-1}	95.9±16.3^{c}	93.4±10.3^{c}	94.7±17.8^{bc}	76.8±12.9^{ab}	77±10.6^{a}	0.000	0.000	0.005
K	µmol·g^{-1}	97±18.2^{c}	90.7±19.3^{bc}	96±19.6^{bc}	72.3±18.4^{a}	79.5±19.4^{ab}	0.000	ns	ns
Mn	µmol·g^{-1}	10.3±7.46^{b}	3.95±1.41^{a}	3.69±1.2^{a}	3.76±1.77^{a}	3.29±1.11^{a}	0.000	0.003	0.010
Ni	nmol·g^{-1}	356±79.9^{b}	321±72.2^{b}	305±41.6^{ab}	255±46.6^{b}	266±73.7^{a}	0.002	ns	0.004
P	µmol·g^{-1}	30.9±5.6^{b}	23.2±4.28^{a}	28.7±9.65^{ab}	23.7±5.62^{a}	28.3±5.17^{a}	0.000	0.000	0.045
V	µmol·g^{-1}	0.97±0.19^{b}	0.95±0.17^{b}	0.96±0.11^{b}	0.71±0.16^{a}	0.68±0.16^{a}	0.000	ns	0.000
Element concentrations that significantly increased from VP to VG									
Nb	nmol·g^{-1}	6.42±1.41^{a}	7.10±1.28^{ab}	6.78±1.05^{ab}	6.46±1.08^{ab}	7.32±8.79^{b}	0.037	ns	ns
Pb	nmol·g^{-1}	60.7±10.2^{a}	61.4±8.93^{a}	57.6±7.16^{a}	54.8±5.8^{a}	72.1±11.6^{b}	0.000	ns	ns
Sc	nmol·g^{-1}	60.8±29.6^{a}	67.2±14.1^{b}	71.4±19.4^{ab}	59.9±17.1^{ab}	68±20.9^{b}	0.001	0.020	0.000
Sn	nmol·g^{-1}	5.61±0.87^{a}	5.29±0.57^{a}	5.51±0.83^{a}	5.21±0.76^{a}	8.66±4.75^{b}	0.000	ns	ns
Th	nmol·g^{-1}	9.22±4.78^{a}	11.1±3.12^{b}	12.3±5.06^{b}	9.68±3.67^{ab}	12.2±6^{b}	0.000	0.009	0.000
U	nmol·g^{-1}	8.82±10.7^{a}	8.78±12.6^{a}	6.72±5.25^{a}	39.3±52.2^{b}	29±15.5^{b}	0.000	0.003	0.000
Zr	nmol·g^{-1}	43.5±21.5^{a}	51.5±18.3^{ab}	52.1±24.5^{ab}	50.8±24.6^{ab}	56.9±27.4^{b}	0.001	0.000	0.020

Field study II mean ±standard deviation element concentration of each IPCI class VP, P, F, G, and VG is shown in Table 2.3. Soil properties (pH, LOI) showed significant differences between classes, and were included in statistical analysis as co-variants. Soil pH was higher in poorer sites compared to fairer sites. Soil LOI was high in VG and low in G-F-P-VP IPCI classes. As was the case in field study I, elements fell within one of four groups. Interesting elements included those concentrations that increased from VP to VG, and this group accounted for the majority. The minority groups were element concentrations which decreased from VP to VG and were B, Ca, Se, and Sr.

Table 2.3. Field study II: Element concentration mean ± standard deviation and associated ANOVA *p*-value (ns=not significant for *p*-value>0.05) for IPCI wetland soils. Elements are arranged by relation to the IPCI in alphabetical order. The IPCI conditions are very poor (VP), poor (P), fair (F), good (G), and very good (VG). Means that do not share a letter are significantly different (*p*-value≤0.05).

							ANCOVA *p*-value		
Class	Unit	VP	P	F	G	VG	Class	pH	LOI
	n	15	20	30	30	20			
pH		6.94 ±0.75^{a}	7.69 ±0.35^{bc}	7.36 ±0.98^{abc}	7.1 ±0.91^{ab}	7.77 ±0.2^{c}	0.002		
LOI	%	4.42 ±1^{a}	5.62 ±1.56^{a}	5.97 ±4.06^{a}	5.47 ±2.56^{a}	12.4 ±5.51^{b}	0.000		
Element concentrations that did not vary between classes									
Ag	pmol·g^{-1}	665 ±390^{a}	623 ±245^{a}	651 ±312^{a}	673 ±359^{a}	738 ±369^{a}	ns	ns	ns
Mn	µmol·g^{-1}	9.96 ±2.88^{a}	13.8 ±3.54^{a}	18.9 ±16.8^{a}	15.9 ±11.4^{a}	16.8 ±10.1^{a}	ns	0.000	0.001
Mo	nmol·g^{-1}	9.57 ±8.64^{a}	4.79 ±3.92^{a}	5.89 ±4.49^{a}	7.45 ±6.71^{a}	4.7 ±3.55^{a}	ns	ns	ns
Ni	nmol·g^{-1}	463 ±136^{a}	388 ±46.3^{a}	360 ±83.8^{a}	419 ±145^{a}	315 ±94.5^{a}	ns	ns	0.000
Pb	nmol·g^{-1}	111 ±46.1^{a}	86.2 ±21^{a}	86.6 ±27.9^{a}	90.4 ±21.6^{a}	61.7 ±21.3^{a}	ns	0.037	0.004
Se	nmol·g^{-1}	8.61 ±5.07^{a}	10.2 ±4.01^{a}	9.46 ±5.07^{a}	9.33 ±3.7^{a}	17.4 ±7.52^{a}	ns	ns	0.003
Sn	nmol·g^{-1}	103 ±94.1^{a}	62.8 ±46.1^{a}	77.2 ±70.5^{a}	53.3 ±47.6^{a}	40.3 ±48.5^{a}	ns	ns	ns
Element concentrations that significantly differed between classes, without a clear pattern from VP to VG									
Al	µmol·g^{-1}	705 ±127^{b}	496 ±67.6^{ab}	485 ±163^{a}	587 ±91.8^{b}	346 ±143^{ab}	0.001	0.000	0.000
As	nmol·g^{-1}	86.2 ±40.7^{b}	43.3 ±9.23^{a}	54.8 ±22.3^{ab}	66.4 ±51.3^{ab}	48.1 ±24.6^{ab}	0.013	ns	0.000
Be	nmol·g^{-1}	90.2 ±19.6^{b}	72.7 ±9.16^{b}	65.1 ±23.1^{a}	77.7 ±12^{b}	44.4 ±21.3^{ab}	0.002	0.000	0.000
Bi	pmol·g^{-1}	935 ±305^{b}	658 ±53.5^{b}	635 ±207^{a}	758 ±117^{b}	459 ±148^{ab}	0.002	0.000	0.000
Cd	nmol·g^{-1}	4.25 ±1.21^{ab}	3.9 ±0.36^{b}	3.54 ±0.96^{a}	3.48 ±0.76^{a}	2.75 ±0.83^{ab}	0.009	0.000	0.000
Ce	nmol·g^{-1}	327 ±21.5^{ab}	270 ±47.1^{b}	272 ±95.8^{a}	288 ±35.2^{ab}	153 ±67.8^{ab}	0.020	0.000	0.000
Co	nmol·g^{-1}	153 ±27.2^{b}	126 ±20.2^{ab}	118 ±39.5^{a}	126 ±41.2^{ab}	82 ±32.7^{ab}	0.024	ns	0.000
Cr	nmol·g^{-1}	674 ±123^{b}	526 ±55.5^{ab}	505 ±146^{a}	601 ±126^{b}	378 ±132^{ab}	0.008	0.005	0.000
Cs	nmol·g^{-1}	11.5 ±1.31^{b}	8.17 ±1.32^{ab}	8.67 ±3.17^{a}	9.58 ±1.38^{b}	6.53 ±2.24^{b}	0.001	0.001	0.000
Cu	nmol·g^{-1}	327 ±92.6^{b}	251 ±30.4^{ab}	248 ±78.5^{a}	285 ±35.2^{b}	192 ±69.2^{ab}	0.009	ns	0.000
Dy	nmol·g^{-1}	16.8 ±2.59^{ab}	13.5 ±1.99^{b}	13.4 ±4.46^{a}	14.4 ±1.69^{ab}	8.46 ±3.78^{ab}	0.021	0.000	0.000
Er	nmol·g^{-1}	7.93 ±1.14^{ab}	6.4 ±0.93^{b}	6.28 ±2.12^{a}	6.88 ±0.91^{ab}	4.01 ±1.78^{ab}	0.011	0.000	0.000
Ga	nmol·g^{-1}	74.2 ±12.7^{ab}	50.5 ±8.1^{b}	48.7 ±23.4^{a}	60.8 ±10.5^{b}	30.2 ±17.5^{b}	0.000	0.000	0.000
Gd	nmol·g^{-1}	23.9 ±2.96^{ab}	19.2 ±3.21^{b}	19 ±6.49^{a}	20.3 ±2.52^{ab}	11.3 ±5.12^{ab}	0.016	0.000	0.000
Ho	nmol·g^{-1}	3.07 ±0.48^{ab}	2.55 ±0.37^{b}	2.45 ±0.86^{a}	2.61 ±0.32^{ab}	1.55 ±0.72^{ab}	0.009	0.000	0.000
K	µmol·g^{-1}	102 ±17.7^{b}	76.5 ±18.9^{ab}	78.2 ±32.9^{a}	90.3 ±10.9^{b}	51 ±11.7^{ab}	0.002	0.000	0.000
La	nmol·g^{-1}	163 ±11.6^{ab}	136 ±24.4^{b}	136 ±47.9^{a}	146 ±18.6^{ab}	77.4 ±34.8^{ab}	0.018	0.000	0.000
Mg	µmol·g^{-1}	240 ±54.8^{ab}	368 ±167^{b}	237 ±123^{a}	303 ±223^{ab}	632 ±319^{c}	0.000	0.000	ns
Na	µmol·g^{-1}	18.1 ±14.9^{b}	12.8 ±4.37^{a}	25.5 ±33.2^{ab}	13.3 ±15.3^{a}	26.8 ±11.9^{ab}	0.004	0.000	ns
Nd	nmol·g^{-1}	146 ±13.4^{ab}	119 ±21.6^{b}	119 ±42.4^{a}	126 ±14.3^{ab}	67.7 ±31.3^{ab}	0.017	0.000	0.000
Pr	nmol·g^{-1}	41.4 ±3.64^{ab}	33.9 ±6.11^{b}	34 ±12^{a}	36.1 ±4.38^{ab}	19.4 ±8.85^{ab}	0.022	0.000	0.000
Rb	nmol·g^{-1}	328 ±38.9^{ab}	279 ±33.1^{b}	257 ±102^{a}	313 ±41.7^{b}	206 ±65.3^{b}	0.000	0.000	0.000
Sb	nmol·g^{-1}	1.71 ±0.98^{ab}	1.3 ±0.34^{a}	1.36 ±0.54^{a}	1.48 ±0.77^{a}	1.69 ±0.54^{b}	0.017	ns	0.003
Sc	nmol·g^{-1}	86.3 ±22.5^{b}	47 ±16.1^{b}	47.2 ±24.7^{a}	64.7 ±20.5^{b}	17.2 ±13.7^{ab}	0.000	0.005	0.000
Sm	nmol·g^{-1}	27.4 ±3.07^{ab}	21.9 ±3.88^{b}	21.9 ±7.69^{a}	23.3 ±2.6^{ab}	12.6 ±5.73^{ab}	0.010	0.000	0.000
Tb	nmol·g^{-1}	3.15 ±0.53^{ab}	2.58 ±0.4^{b}	2.54 ±0.9^{a}	2.75 ±0.35^{ab}	1.57 ±0.72^{ab}	0.013	0.000	0.000
Tm	pmol·g^{-1}	1140 ±153^{b}	858 ±302^{a}	908 ±300^{a}	967 ±290^{ab}	622 ±132^{ab}	0.029	ns	0.000
U	nmol·g^{-1}	9.63 ±7.39^{ab}	5.76 ±2.69^{a}	7.83 ±4.68^{ab}	7.88 ±3.01^{ab}	9.56 ±4.58^{b}	0.039	ns	ns
Y	nmol·g^{-1}	159 ±25.4^{ab}	129 ±19.9^{b}	127 ±41.6^{a}	138 ±17^{ab}	83.6 ±36.9^{ab}	0.031	0.000	0.000
Yb	nmol·g^{-1}	5.78 ±0.9^{ab}	4.85 ±0.74^{b}	4.62 ±1.53^{a}	5.16 ±0.73^{ab}	3.03 ±1.32^{ab}	0.013	0.002	0.000
Zn	µmol·g^{-1}	1.48 ±0.27^{b}	1.29 ±0.11^{b}	1.16 ±0.32^{a}	1.34 ±0.17^{b}	0.99 ±0.3^{ab}	0.002	0.000	0.000

(continues)

Table 2.3. Field study II (continued).

							ANCOVA *p*-value		
Class	Unit	VP	P	F	G	VG	Class	pH	LOI
	n	15	20	30	30	20			
pH		6.94 ±0.75^{a}	7.69 ±0.35^{bc}	7.36 ±0.98^{abc}	7.1 ±0.91^{ab}	7.77 ±0.2^{c}	0.002		
LOI	%	4.42 ±1^{a}	5.62 ±1.56^{a}	5.97 ±4.06^{a}	5.47 ±2.56^{a}	12.4 ±5.51^{b}	0.000		
Element concentrations that significantly decreased from VP to VG									
Ba	μmol·g^{-1}	1.58 ±0.31^{b}	1.49 ±0.26^{b}	1.75 ±1.01^{b}	1.51 ±0.32^{b}	1.18 ±0.44^{a}	0.000	0.046	0.006
Eu	nmol·g^{-1}	5.31 ±0.91^{c}	3.98 ±0.72^{abc}	4.04 ±1.31^{ab}	4.37 ±0.56^{bc}	2.43 ±1.19^{a}	0.001	ns	0.000
Fe	μmol·g^{-1}	383 ±90^{b}	291 ±34.9^{ab}	293 ±75.6^{a}	329 ±79^{ab}	215 ±81.1^{a}	0.003	ns	0.000
In	pmol·g^{-1}	267 ±77^{c}	209 ±43.8^{ab}	203 ±41.8^{ab}	221 ±49.8^{bc}	183 ±26.8^{a}	0.000	ns	ns
Nb	nmol·g^{-1}	7.03 ±2.22^{b}	5.49 ±2.06^{b}	5.35 ±2.73^{b}	5.24 ±1.78^{b}	2.69 ±1.93^{a}	0.000	ns	ns
Th	nmol·g^{-1}	20.4 ±4.19^{c}	8.92 ±3.52^{b}	11.3 ±6.37^{b}	13 ±5.76^{b}	3.12 ±1.82^{a}	0.000	ns	0.000
Ti	μmol·g^{-1}	8.91 ±0.96^{c}	5.95 ±1.7^{abc}	6.54 ±2.5^{ab}	6.89 ±1.47^{bc}	3.13 ±1.59^{a}	0.000	0.044	0.000
Tl	nmol·g^{-1}	1.01 ±0.11^{b}	7.49 ±0.93^{b}	8.30 ±0.31^{b}	9.41 ±0.31^{b}	5.72 ±0.23^{a}	0.000	ns	ns
V	μmol·g^{-1}	0.97 ±0.08^{b}	0.87 ±0.13^{b}	0.79 ±0.26^{ab}	0.89 ±0.24^{b}	0.67 ±0.28^{a}	0.001	ns	ns
Zr	nmol·g^{-1}	47.5 ±14.1^{c}	28.6 ±7.24^{bc}	28.5 ±13^{ab}	40.2 ±23.4^{bc}	14.4 ±8.1^{a}	0.000	0.014	0.002
Element concentrations that significantly increased from VP to VG									
B	μmol·g^{-1}	3.45 ±0.44^{a}	4.43 ±0.62^{a}	3.99 ±0.62^{a}	3.84 ±0.76^{a}	7.58 ±1.54^{b}	0.000	0.000	0.001
Ca	μmol·g^{-1}	147 ±30.2^{a}	695 ±541^{ab}	982 ±1460^{b}	450 ±500^{ab}	2360 ±1010^{b}	0.035	0.000	0.000
Li	μmol·g^{-1}	1.95 ±0.32^{a}	1.73 ±0.31^{a}	1.71 ±0.68^{a}	1.9 ±0.82^{a}	2.79 ±1.04^{b}	0.000	0.000	0.000
P	μmol·g^{-1}	24.3 ±12^{a}	26.7 ±5.68^{bc}	24.5 ±6.7^{ab}	25.4 ±8.39^{a}	28.5 ±5.86^{c}	0.000	0.000	ns
S	μmol·g^{-1}	21.7 ±18.1^{a}	26 ±8.7^{a}	28.9 ±20.4^{a}	24.1 ±17.2^{a}	88.5 ±47.3^{b}	0.002	0.007	0.000
Sr	μmol·g^{-1}	0.54 ±0.17^{a}	0.81 ±0.3^{a}	0.9 ±0.78^{a}	0.76 ±0.86^{a}	4.94 ±2.58^{b}	0.000	0.000	0.000

Comparison of Field Seasons

Since recovery of standard reference materials was low a different way of validating our data sets was sought. Element concentrations obtained from the study (field study I & II) were compared with data from the United States Geological Survey's National Geochemical Survey (USGS-NGS) (Grossman et al., 2004). These data included 23 USGS-NGS points within 7 km of 18 fingerprinted wetlands. Average concentrations of a majority of the 27 elements for all points were within similar ranges (R^2=0.94) (Figure 2.2). Elements crossing the xy-intercept (<10% difference) were Pb, Cu, and Mn. Dry land soils had substantially higher abundances (>100% difference) for V, Sr, Ga, Sc, Ba, Al, Th, K, Ti, Nb, and Na. Wetland soils showed slightly higher abundances (>10% difference) for P and Zn. Elements are ordered from least different to most different. Overall, the USGS-NGS reported higher concentrations than those reported in this study.

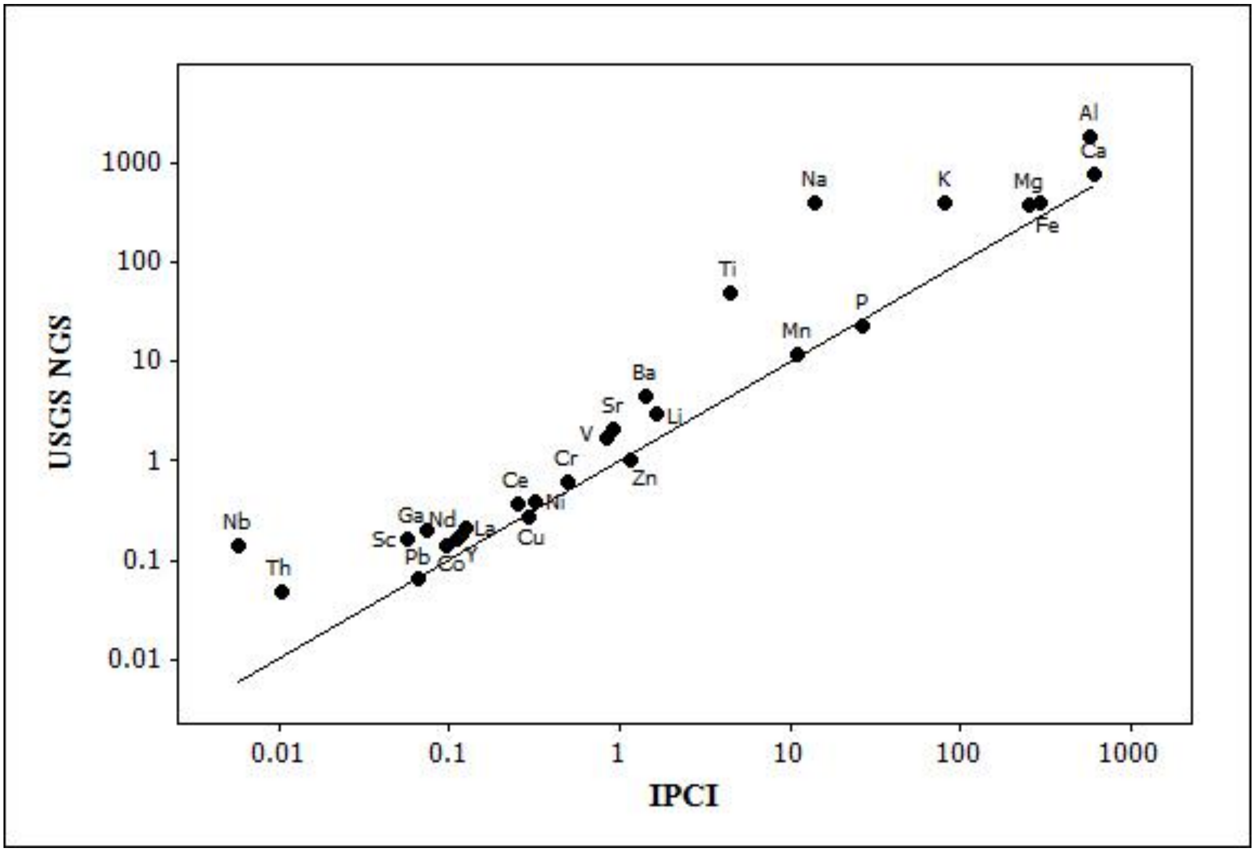


Figure 2.2. The relationship between element concentrations measured in IPCI-sampled wetland (field seasons I and II) and dry land environments (measured by the USGS-NGS). The scale is expressed as the logarithm of the concentration in $\mu\text{mol}\cdot\text{g}^{-1}$. A regression fit ($R^2$=0.94) was included to show relative element abundance and indicates 1:1 relationship between IPCI and USGS NGS.

Soil properties did not show similarities between field studies. This may indicate that soil properties are highly variable and require more detailed study in future studies. When using field study II to verify field study I, data showed V as the only robust similarity between studies, as shown by a general decreasing trend from VP to VG. Field study I showed that the pattern formed two statistical groups: VP-P-F and G-VG (*p*-value=0.000, Table 2.2, Figure 2.3). Field study II showed that the pattern was roughly the same (*p*-value=0.001, Table 2.3, Figure 2.3), with the exception that Tukey’s comparisons were not consistent for F and G classes. Other elements showed a general pattern with the IPCI, but the significance of the relation was either not significant (*p*-value>0.05) or the relation significantly differed between classes, without a clear pattern from VP to VG.

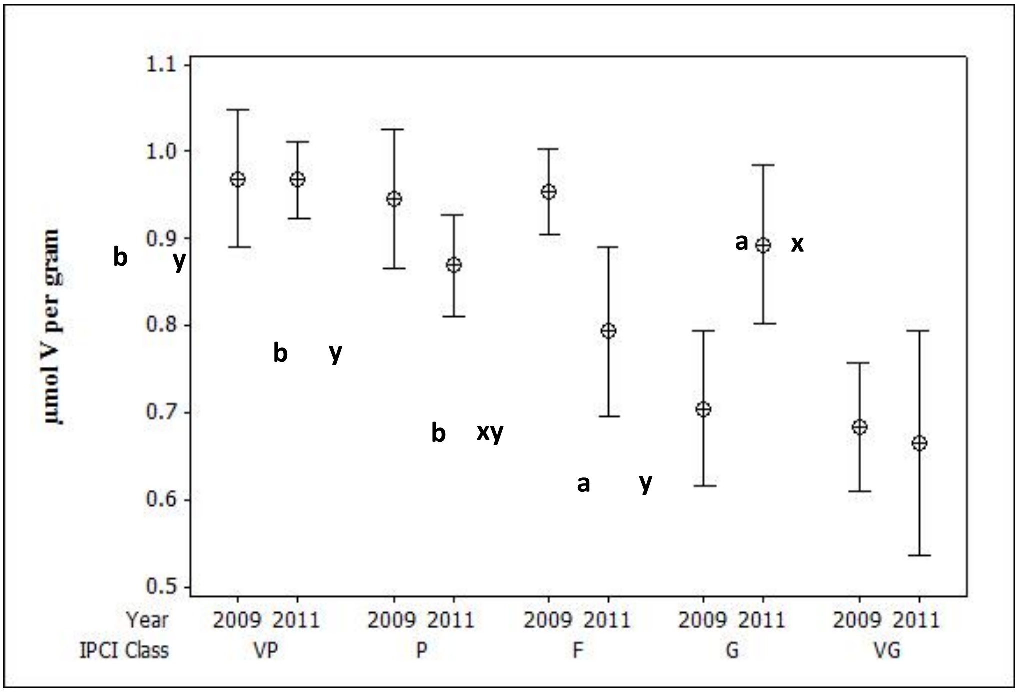


Figure 2.3. Chart compares V in the soil for field study I (2009) and II (2011) between the IPCI vegetative classes very poor (VP), poor (P), fair (F), m good (G), and very good (VG). Means that do not share a letter are significantly different (*p*-value≤0.05).

Although not sharing a strong general pattern seen with V, other elements show plausible response to differences in vegetative community integrity. Elements showing a general decreasing trend from VP to VG between studies are Al, As, Co, Fe, K, and Tl. No elements showed a general increasing trend. A comparison of sets also shows general opposing trends and elements include Ca, B, Nb, and U. In an attempt to make more robust statistical conclusions and strengthen trends, the two data sets were combined.

Combining Field Season I and II Data Sets

The combined table shows a dramatic increase in elements showing general patterns (Table 2.4). Soil LOI showed co-variance, so it was included in the statistical analysis, and was significantly higher in VG class. Soil pH did not show differences and was not included as a co-variant in the statistical analysis. Element concentrations that did not vary between class, or whose concentrations significantly differed between classes with no clear relation to the IPCI accounted for a minority of the elements. Element concentrations accounting for the majority decreased significantly from VP to VG. Additionally, the table shows that the relationship with V remains and its concentration generally decreases from VP to VG, forming VP-P and F-G-VG significant groups (Figure 2.4). V and Ca are inversely related and weakly correlated (r=-0.326). Only four element concentrations (B, Ca, Sr, U) increased from VP to VG (Table 2.4).

Table 2.4. Field study I and II combined: Element concentration mean ± standard deviation and associated ANOVA *p*-value (ns=not significant for *p*-value>0.05) for IPCI wetland soils. Elements are arranged by relation to the ICPI in alphabetical order. The IPCI conditions are very poor (VP), poor (P), fair (F), good (G), and very good (VG). Means that do not share a letter are significantly different (*p*-value≤0.05).

							ANOVA	ANCOVA
	Unit	VP	P	F	G	VG	Class	LOI
	n	40	40	50	45	40		
pH	-	6.65 ±0.81^{a}	7.1 ±0.7^{a}	6.85 ±1.17^{a}	6.91 ±0.88^{a}	6.77 ±1.07^{a}	ns	
LOI	%	5.75 ±2.04^{a}	7.18 ±2.6^{a}	6.32 ±3.57^{a}	6.74 ±3.53^{a}	10.5 ±5.16^{b}	0.000	
Element concentrations that did not vary between classes								
Ag	pmol·g^{-1}	722 ±266^{a}	664 ±196^{a}	678 ±253^{a}	686 ±332^{a}	675 ±274^{a}	ns	0.019
Ba	µmol·g^{-1}	1.36 ±0.38^{a}	1.36 ±0.25^{a}	1.53 ±0.85^{a}	1.39 ±0.37^{a}	1.22 ±0.32^{a}	ns	ns
In	pmol·g^{-1}	237 ±62.3^{a}	213 ±43.9^{a}	214 ±43.8^{a}	215 ±47.7^{a}	194 ±36.8^{a}	ns	0.001
Mn	µmol·g^{-1}	10.1 ±6.1^{a}	8.89 ±5.66^{a}	12.8 ±15^{a}	11.8 ±10.9^{a}	10 ±9.85^{a}	ns	0.031
Mo	nmol·g^{-1}	7.11 ±5.69^{a}	4.6 ±3^{a}	5.01 ±3.75^{a}	6.14 ±5.84^{a}	5.03 ±3.01^{a}	ns	ns
Na	µmol·g^{-1}	18.7 ±19.2^{a}	10.8 ±3.75^{a}	19.1 ±26.8^{a}	20.8 ±26.6^{a}	18.6 ±11.9^{a}	ns	ns
P	µmol·g^{-1}	28.4 ±9.02^{a}	25 ±5.27^{a}	26.2 ±8.18^{a}	24.9 ±7.56^{a}	28.4 ±5.46^{a}	ns	0.000
Pb	nmol·g^{-1}	79.7 ±38^{a}	73.8 ±20.3^{a}	75 ±26.2^{a}	78.6 ±24.6^{a}	66.9 ±17.8^{a}	ns	0.000
S	µmol·g^{-1}	55.4 ±96.6^{a}	25.7 ±9.28^{a}	26.3 ±19.2^{a}	43.5 ±63.3^{a}	60.4 ±45.9^{a}	ns	0.000
Se	nmol·g^{-1}	14.4 ±6.62^{a}	14 ±5.37^{a}	13 ±6.44^{a}	12.6 ±6.08^{a}	17.5 ±5.54^{a}	ns	0.000
Sn	nmol·g^{-1}	42 ±73.8^{a}	34 ±43.4^{a}	48.5 ±64.8^{a}	37.3 ±44.9^{a}	24.5 ±37.6^{a}	ns	0.000
Th	nmol·g^{-1}	13.4 ±7.11^{a}	9.99 ±3.46^{a}	11.7 ±5.84^{a}	11.9 ±5.35^{a}	7.67 ±6.36^{a}	ns	0.000
Tm	pmol·g^{-1}	873 ±299^{a}	770 ±275^{a}	805 ±287^{a}	868 ±299^{a}	666 ±198^{a}	ns	0.000
Zr	nmol·g^{-1}	45 ±19.1^{a}	40 ±18^{a}	38 ±21.6^{a}	43.7 ±24.1^{a}	35.6 ±29.4^{a}	ns	0.002
Element concentrations that significantly differed between classes, without a clear pattern from VP to VG								
Ce	nmol·g^{-1}	283 ±44.1^{ab}	264 ±35.1^{b}	271 ±75.7^{ab}	272 ±41.8^{b}	208 ±77.4^{a}	0.004	0.000
Cs	nmol·g^{-1}	10.8 ±1.25^{c}	8.65 ±1.35^{abc}	8.98 ±3.02^{a}	9.32 ±1.34^{bc}	7.5 ±2.12^{ab}	0.000	0.000
Cu	nmol·g^{-1}	318 ±66.1^{b}	283 ±52.3^{ab}	271 ±71.7^{a}	297 ±40.6^{ab}	263 ±90.4^{ab}	0.010	0.001
Ga	nmol·g^{-1}	87.8 ±18.3^{b}	71.9 ±23.6^{b}	67.1 ±31.1^{a}	66.2 ±13.6^{b}	53.6 ±27.7^{ab}	0.001	0.000
Ho	nmol·g^{-1}	2.68 ±0.53^{b}	2.44 ±0.35^{b}	2.44 ±0.69^{a}	2.47 ±0.4^{ab}	1.97 ±0.74^{ab}	0.005	0.000
Li	µmol·g^{-1}	1.75 ±0.37^{ab}	1.66 ±0.34^{ab}	1.59 ±0.57^{a}	1.72 ±0.77^{ab}	1.94 ±1.13^{b}	0.025	0.000
Mg	µmol·g^{-1}	230 ±72.3^{ab}	273 ±153^{ab}	222 ±115^{a}	273 ±195^{ab}	392 ±330^{b}	0.028	ns
Nd	nmol·g^{-1}	126 ±21.2^{ab}	117 ±16.4^{b}	119 ±33.8^{ab}	119 ±17.3^{ab}	91.9 ±35.1^{a}	0.004	0.000
Ni	nmol·g^{-1}	396 ±116^{b}	355 ±68.8^{ab}	338 ±74.6^{a}	364 ±144^{ab}	290 ±87.3^{ab}	0.016	0.000
Pr	nmol·g^{-1}	35 ±6.39^{ab}	32.5 ±4.74^{b}	33.5 ±9.58^{ab}	33.7 ±5.44^{ab}	25.5 ±9.31^{a}	0.005	0.000
Rb	nmol·g^{-1}	293 ±41.6^{b}	266 ±31.6^{b}	259 ±83.7^{a}	307 ±41.5^{b}	239 ±64.6^{ab}	0.000	0.000
Tb	nmol·g^{-1}	2.71 ±0.54^{ab}	2.53 ±0.33^{b}	2.53 ±0.71^{a}	2.56 ±0.43^{ab}	2.03 ±0.73^{ab}	0.009	0.000
Zn	µmol·g^{-1}	1.32 ±0.26^{b}	1.21 ±0.19^{ab}	1.17 ±0.29^{a}	1.35 ±0.22^{b}	1.15 ±0.3^{ab}	0.002	0.000

(continues)

Table 2.4. Field study I and II combined (continued).

							ANOVA	ANCOVA
	Unit	VP	P	F	G	VG	Class	LOI
	n	40	40	50	45	40		
pH	-	6.65 ±0.81^{a}	7.1 ±0.7^{a}	6.85 ±1.17^{a}	6.91 ±0.88^{a}	6.77 ±1.07^{a}	ns	
LOI	%	5.75 ±2.04^{a}	7.18 ±2.6^{a}	6.32 ±3.57^{a}	6.74 ±3.53^{a}	10.5 ±5.16^{b}	0.000	
Element concentrations that significantly decreased from VP to VG								
Al	µmol·g^{-1}	699 ±115^{b}	572 ±106^{ab}	561 ±185^{a}	589 ±94.6^{ab}	471 ±172^{a}	0.000	0.000
As	nmol·g^{-1}	96.8 ±35.8^{b}	58.4 ±22.7^{a}	58.1 ±20.3^{a}	65.2 ±43.8^{a}	52.5 ±18.8^{a}	0.000	0.001
Be	nmol·g^{-1}	84.9 ±15.2^{c}	76.3 ±11.8^{bc}	73 ±21.5^{ab}	76.4 ±12.3^{abc}	61.6 ±25.9^{a}	0.001	0.000
Bi	pmol·g^{-1}	819 ±229^{b}	691 ±109^{ab}	671 ±175^{a}	719 ±121^{ab}	580 ±182^{a}	0.000	0.000
Cd	nmol·g^{-1}	4.36 ±0.98^{b}	3.98 ±0.73^{ab}	3.89 ±1.5^{ab}	4 ±1.12^{ab}	3.72 ±1.21^{a}	0.041	ns
Co	nmol·g^{-1}	129 ±35^{c}	108 ±27.4^{bc}	107 ±35.2^{ab}	108 ±43.7^{ab}	77.2 ±28.6^{a}	0.000	0.000
Cr	nmol·g^{-1}	581 ±125^{c}	526 ±61.4^{abc}	516 ±125^{ab}	559 ±125^{bc}	436 ±120^{a}	0.001	0.000
Dy	nmol·g^{-1}	14.6 ±2.67^{b}	13.2 ±1.71^{b}	13.4 ±3.55^{ab}	13.6 ±2.02^{ab}	10.6 ±3.75^{a}	0.002	0.000
Er	nmol·g^{-1}	6.79 ±1.33^{b}	6.13 ±0.86^{b}	6.24 ±1.68^{ab}	6.43 ±1.1^{ab}	4.92 ±1.7^{a}	0.003	0.000
Eu	nmol·g^{-1}	4.66 ±0.9^{c}	4.1 ±0.61^{bc}	4.15 ±1.08^{ab}	4.18 ±0.61^{bc}	3.26 ±1.27^{a}	0.001	0.000
Fe	µmol·g^{-1}	355 ±80.4^{b}	284 ±43.1^{a}	301 ±72.3^{a}	307 ±78.7^{ab}	248 ±83.8^{a}	0.000	0.000
Gd	nmol·g^{-1}	20.6 ±3.7^{b}	18.7 ±2.59^{b}	18.9 ±5.17^{ab}	19 ±3.04^{b}	14.5 ±5.24^{a}	0.001	0.000
K	µmol·g^{-1}	99 ±18^{b}	83.6 ±20.2^{ab}	85.3 ±29.5^{a}	84.3 ±16.1^{ab}	65.3 ±21.4^{a}	0.001	0.000
La	nmol·g^{-1}	143 ±22.4^{b}	134 ±18.2^{b}	137 ±38^{ab}	138 ±21.8^{b}	104 ±38.5^{a}	0.002	0.000
Nb	nmol·g^{-1}	6.65 ±1.76^{b}	6.3 ±1.88^{b}	5.92 ±2.31^{ab}	5.64 ±1.67^{ab}	5.01 ±2.77^{a}	0.001	ns
Sb	nmol·g^{-1}	2.08 ±0.89^{b}	1.85 ±0.82^{bc}	1.59 ±0.6^{bc}	1.38 ±0.65^{ab}	1.7 ±0.51^{a}	0.000	ns
Sc	nmol·g^{-1}	70.3 ±29.6^{b}	57.1 ±18.1^{b}	56.9 ±25.5^{b}	63.1 ±19.3^{b}	42.6 ±31.1^{a}	0.000	ns
Sm	nmol·g^{-1}	23.8 ±4^{b}	21.6 ±3^{b}	22.1 ±6.17^{ab}	22.1 ±3.14^{ab}	17.2 ±6.58^{a}	0.003	0.000
Ti	µmol·g^{-1}	6.27 ±2.41^{b}	5.12 ±1.57^{ab}	5.56 ±2.37^{ab}	5.8 ±2.04^{b}	3.6 ±1.42^{a}	0.006	0.000
Tl	pmol·g^{-1}	1080 ±164^{b}	920 ±214^{ab}	942 ±285^{a}	943 ±263^{ab}	769 ±297^{a}	0.008	0.000
V	µmol·g^{-1}	0.97 ±0.16^{b}	0.91 ±0.15^{b}	0.86 ±0.23^{a}	0.83 ±0.23^{ab}	0.68 ±0.22^{a}	0.000	0.000
Y	nmol·g^{-1}	139 ±26^{b}	126 ±17.1^{b}	127 ±33.1^{ab}	130 ±20.8^{ab}	102 ±35.2^{a}	0.003	0.000
Yb	nmol·g^{-1}	5.11 ±0.98^{b}	4.67 ±0.7^{b}	4.65 ±1.24^{ab}	4.79 ±0.89^{b}	3.66 ±1.25^{a}	0.001	0.000
Element concentrations that significantly increased from VP to VG								
B	µmol·g^{-1}	2.18 ±1.15^{a}	2.72 ±1.79^{ab}	2.82 ±1.53^{ab}	2.99 ±1.44^{ab}	4.32 ±3.48^{b}	0.034	0.010
Ca	µmol·g^{-1}	281 ±346^{a}	438 ±460^{ab}	662 ±1200^{ab}	362 ±427^{ab}	1250 ±1320^{b}	0.017	0.005
Sr	µmol·g^{-1}	0.65 ±0.37^{a}	0.56 ±0.33^{a}	0.68 ±0.67^{a}	0.66 ±0.73^{a}	2.65 ±2.93^{b}	0.000	0.043
U	nmol·g^{-1}	9.13 ±9.49^{a}	7.27 ±9.15^{a}	7.39 ±4.9^{b}	18.4 ±33.1^{b}	19.3 ±15^{b}	0.000	0.003

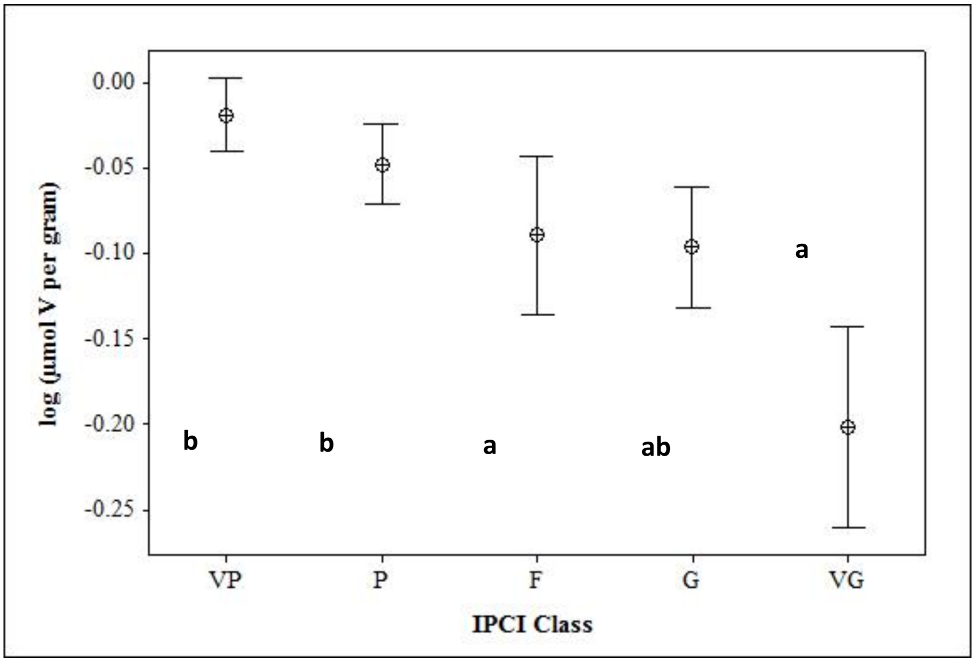


Figure 2.4. 95% confidence interval for the combined data set (field study I and II) for logarithmic value of V with respect to very poor (VP), poor (P), fair (F), good (G), and very good (VG) IPCI classes. Means that do not share a letter are significantly different (*p*-value=0.000).

Discussion

Analytical Recovery

The element analysis were carried out by an accredited lab, and in addition to their reference materials, we submitted our own reference materials. This practice is meant to ensure that concentrations measured accurately represented the concentrations in the soil. Since our recovery was lower than we would have liked we decided to compare our data to that of USGS published data examining the surface geochemistry of North Dakota dry land soils. Our comparison revealed surprisingly similar relations despite the differences in datasets and presents for the first time geochemical differences in wet- and dryland soils. It is expected that some variation between the two datasets is due to differences in methods. In addition, the soils sampled in the USGS study were non-hydric, dryland (as opposed to wetland) soils, while the soils in our study were taken from wetlands. The biogeochemistry (Mitsch & Gosselink, 2007; Kissoon et al., 2010; Jacob et al., 2011; Kissoon et al., 2011) of wetlands is different from dryland soils and thus lead to differences in element concentrations. But across the landscape sampled in this study the ranges in element concentrations are similar between our dataset and that of the USGS.

Confidence in the IPCI

Before discussing the positive and negative relations between element concentration and IPCI condition, it may be helpful to consider how temporal variability effects vegetative expression of IPCI condition and how this factors into our definition of a potential link. Euliss and Mushet (2011) examined four year temporal variability in relation to IPCI condition at the United States Geological Survey Cottonwood Lake Area near Jamestown, ND. They showed that as the IPCI condition of a pothole wetland increased from fair to very good the range of conditions detected among years decreased. Since very poor and poor conditioned wetlands were for the most part not detected in their study, it is suspected that the range of temporal variability decreases with decreasing condition. The thought here is that poorer wetlands receiving very poor and poor distinction have been impacted in ways that limit the variable expression of vegetative indices that may otherwise be expressed by wetlands of fairer condition. If this is truly the case then the confidence in an IPCI assessment at consistently detecting wetland condition over a time span is greater for wetlands assessed at the extreme ends of the IPCI condition spectrum. Since our sites did not receive temporal replication, we cannot be certain that condition will not change if the IPCI was performed on the same sites at a different point in time, especially of fairer wetlands. Considering this, when identifying potential links by comparing between field seasons it may not be so important for stepwise trends to consistently differ from class to class, or even over spatial and temporal scales, rather a consistent difference between the condition extremes exist. Wetlands receiving poorer conditions are primarily in areas where anthropogenic activity is present. Whether it is grazing, haying, or cultivation, all processes disturb the landscape and underlying soil, and should exert a signature observable by multi-element fingerprinting.

Multi-Element Links

In addressing issues raised above, a criterion used in the selection of elements showing plausible use in wetland assessment was if element groupings or patterns increased or decreased from very poor to very good. Overall, it was found that V was consistently observed irrespective of geographic scale. The source of V in the environment is derived from igneous rock (Edwards et al., 1995). Glacial activity transported massive quantities of granite and gneiss (igneous rocks) from outcrops in Saskatchewan, Manitoba, and Ontario, Canada, where it was deposited in the present day Prairie Pothole Region (Bluemle, 2000). Although we did not characterize oxidation states, V^{5+} oxide is considered to be the soluble form in soils (Edwards et al., 1995). Once the element is mobile it can be transported in the till through ground water flow, where it precipitates out of solution when encountering reducing agents, such as organic matter, or antagonisms with other elements, such as Ca (Edwards et al., 1995; LaBaugh et al., 1998). Cycling of V may be related to these factors, and is confirmed by patterns observed for LOI and Ca. An alternate explanation for its occurrence is through artificial enrichment by combustion of fossil fuels (Edwards et al., 1995; Pourret et al., 2012).

The whole of this research shows that elements show patterns consistent with impacted and less impacted wetland ecosystems. Although, strictly speaking the IPCI examines wetland integrity at the vegetative level, the index represents a tool that objectively approximates wetland impact at extremes: highly impacted and lesser impacted. Differences in element patterns between studies could be due to a number of things related to wetland geomorphology or other site specific characteristics, but broadly it is likely related to the range of sampled area as well as differences in physiographic regions. Field study I was approximately 100 km wide and nested entirely in the Missouri Coteau physiographic region. This region is topographically high and displays hilly (8°-15° slope angles) wetland catchments (Clayton et al., 1980; Bluemle, 2000). Field study II was approximately 600 km wide and was distributed along multiple physiographic regions, of which the majority of sites were nested on Missouri Escarpment, a region that is topographically low and displays gently undulated collapsed, gently sloped (1°-2° slope angles) wetland catchments (Clayton et al., 1980; Bluemle, 2000). Such settings support differences in biotic assemblages which can result due to differences in water chemistry evolved from underlying glacial depositions, differences in regional groundwater flow and resultant water balance (Kantrud et al., 1989; Winter, 2003), as well as differences in climate (Kantrud et al., 1989). Naturally, it would be expected that elements would show different patterns and variability under a sampling regime which compared one region with many.

It is important here to stress the notion that V (or any of the other elements presented) may somehow decrease (or increase) vegetative community indices (and resulting IPCI condition) cannot be made at this time. Cause and effect relationships cannot be established since our data reflect a survey of community-wide structural patterns related to element concentration. Due to this constraint, it would be incorrect to establish values with which to characterize condition based on any of the element trends presented. To establish such cause and effect relationships, future research must examine ecological response to physical determinants in a controlled setting, such as sedimentation and hydrological characteristics and their signature on multi-element fingerprints. Nevertheless, this research demonstrated that the vegetative structure is linked to the element concentrations in the soil. These findings provide previously unavailable prescience for further multi-element inquiries.

Considerations for Future Multi-Element Research

Although we found several elements which show plausible function for use in future rapid assessment tools, there is still very much to be understood before a rapid assessment tool is developed. Multi-element fingerprinting provides a snapshot of the wetland chemical environment at a highly specific point in time and space and does not necessarily represent an environmental constant. This is a caveat worth noting because the majority of ecological studies which take the landscape setting into consideration have made the assumption that conditions do not change (Euliss et al., 2004; Renschler et al., 2007). Future studies which probe the relationship between biotic community structure and multi-element fingerprints must address such spatial and temporal uncertainties as well as the influence of land use, climate, and hydrologic setting. In addressing biologic assessment uncertainties associated with climate and hydrologic setting, Euliss et al., 2004 proposed a wetland continuum model which placed the hydrologic relation to atmospheric conditions (drought to deluge) and hydrologic relation to groundwater (recharge to discharge) on two axis to predict the ‘biological expression’ of a pothole wetland at any position on the plot. This is a crucial detail when undertaking future element fingerprinting, as certain elements show differential mobility under different environmental conditions (Acosta et al., 2011; Jacob et al., 2011; Schaller et al., 2010). As such, variability of ‘biologic expression’ would undoubtedly increase fingerprint variability, possibly rendering them ineffective at distinguishing among environmental conditions. It would therefore be useful to conduct fingerprinting of a series of wetlands in the context of the wetland continuum model in order to capture element variation associated with varying levels of ‘biological expression’.

Conclusions

The results of this study demonstrate the potential of multi-element fingerprinting of wetlands soils at detecting broad plant community structural conditions as established by the Index of Plant Community Integrity (IPCI). The concentration of V showed a decrease from very poor to very good and this link was independent of two geographic scales. This may be explained by the presence of higher organic matter in very good wetlands, an antagonism with Ca, or due to fossil fuel combustion. Since cause and effect relationships were not assessed in this study, it would be incorrect to establish concentration ranges for characterizing IPCI condition. More research is needed to examine IPCI variability and element variability in the context of the landscape to fully scrutinize this approach.

CHAPTER 3. LINKS BETWEEN PRAIRIE WETLAND MULTI-ELEMENT SOIL COMPOSITION AND HYDROLGY OF A SMALL WETLAND COMPLEX

Introduction

The biological diversity of the Prairie Pothole Region (PPR) of North America is underpinned by differences in hydrochemistry and conditions that exist along a gradient from fresh to saline (Arndt and Richardson, 1988; Swanson et al., 2003). This gradient is formally categorized in terms of water balance as displaying recharge or discharge relationships to groundwater (Berkas, 1996; Swanson et al., 2003). Chemical and biological states of a single wetland through time are not static, and fluctuate with decadal climatic cycles (LaBaugh et al., 1998; Johnson et al., 2004). As such, certain concerns with variability arise when describing wetland ecological condition at a single point in time. Ecological communities respond to change in water permanence and balance, and establishment of a baseline condition during a particular field season may not be the best representation of long-term ecological trends (Euliss and Mushet, 2011). To circumvent concerns, Euliss et al. (2004) described how geomorphic setting and climatic variability could be integrated into a concept where biological studies are placed within the context of two axes: (1) the hydrologic relation of wetland water level to atmospheric water inputs (drought to deluge) and (2) hydrologic relation of wetland water level to groundwater (recharge to discharge). In practice, quantification of wetland position on either axis is cumbersome since, to date, no system of characterization exists for all wetland states (i.e. inundation and desiccation). Standard quantification of relations is expensive and invasive because groundwater well monitoring is required. It would therefore be advantageous to develop a rapid assessment tool which could be used to characterize a wetland at any position on the axes for any wetland in the region. Quantification of atmospheric relations to groundwater was not done in this study, but methods currently being developed place remotely sensed wetland water levels in context to the Palmer Drought Severity Index (Huang et al., 2011; Rover et al., 2011). It has been shown that recharge-discharge relationships remarkably differ in terms of soil chemical properties (dissolved solutes, sulfate concentrations, secondary mineral composition), and that the relation exists along a gradient (Arndt and Richardson, 1988; Euliss et al., 2004). It seems that characterization of soil chemical relationships is most appropriate in terms of quantitative assessment (Arndt and Richardson, 1988). Despite the value of this type of assessment, there has been no follow up on how such a characterization might be implemented.

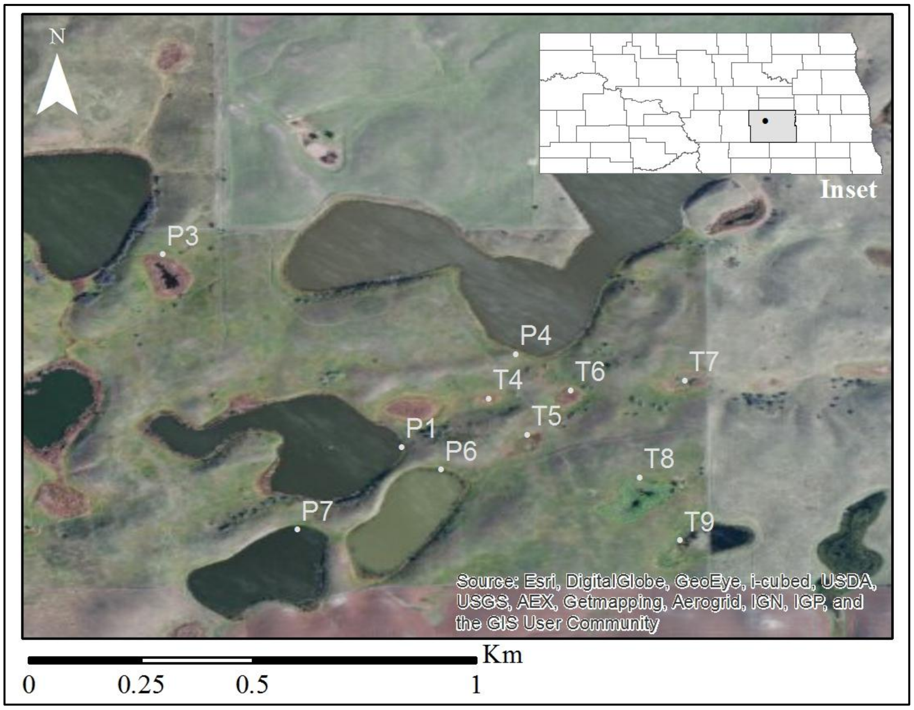
The relationship a pothole has with the water table dictates hydrological relationships and soil chemical composition. When a wetland is topographically low on the landscape, the water table sits above the bottom of the wetland, enabling groundwater to freely enter, thus functioning to discharge groundwater (Heagle et al., 2013). The water chemistry of this relation is composed of a greater concentration of dissolved solutes for two reasons. First, since groundwater moves slowly through the till, water entering the wetland contains a greater concentration of salts than the amount that could have entered through runoff from upland hummocks (Sloan, 1972). Secondly, since output of water only occurs through evaporation, salts from groundwater seepage become concentrated (Sloan, 1972). When the wetland is at a topographically high position on the landscape the water table rests at or below the bottom of the wetland, preventing groundwater from entering, and the wetland functions to recharge groundwater (Heagle et al., 2011). The soil chemistry of this type of wetland is fresh (Arndt and Richardson, 1988). Since fresh water percolates through the soil column to the water table, water will leach the soil of its water soluble minerals, and this is reflected by the absence of calcite and gypsum (Arndt and Richardson, 1988). The third status is flow-through and characterizes wetlands occupying the position between topographic highs and lows (Euliss et al., 2004). This status can simultaneously function to recharge and discharge groundwater, but depending on meteorological deluge or drought conditions, wetlands can serve to largely recharge or discharge water. Since these processes exert a remarkable influence on soil chemistry, multi-element fingerprinting was utilized. This is a chemical approach which utilizes inductively coupled plasma mass spectrometry (ICP-MS) to characterize the concentrations of 60+ elements of the periodic table. Sampling can be done simply and quickly and analysis should provide previously unknown insight to wetland hydrological relationships. This may ultimately help the development of a method whereby rapid, cost-effective assessment is possible.

In the study presented here the aim was to detect how multi-element soil chemistry was linked to groundwater discharge or recharge relationships for a Prairie Pothole wetland complex in south central North Dakota. Based on the enriching nature of discharge wetlands, it was hypothesized that the aqueous soluble group one (Li, Na, K, Rb, Cs) and two (Be, Mg, Ca, Sr, Ba) elements of the periodic table of elements would show higher concentrations in discharge and reduced concentrations in recharge wetlands. This paper also aimed to show the link between other less-studied elements and groundwater relation. Findings will evaluate the applicability of multi-element fingerprinting for use as a rapid assessment technique in characterizing a wetlands position along a groundwater hydrology gradient from recharge to flow-through to discharge.

Materials and Methods

Study Area

The wetland complex was situated in the Cottonwood Lake Study Area (CLA) and was located on the Missouri Coteau in Stutsman County, North Dakota (Figure 3.1). The geology of the region is made up of thick glacial till that was draped over the Pleistocene landscape during the last glaciation, which resulted in soil high in silt and clay intermixed with bolder-sized rocks (Winter, 2003). The CLA was selected because it was an area of relatively high wetland density where biological, hydrological, and physiochemical research had been intensively conducted since the mid-1960s (Winter, 2003). Information regarding groundwater level and flow direction for wetlands in this study can be found in Winter, 2003.



Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community

Figure 3.1. A map of the locations of sampled sites in the Cottonwood Lake Study Area in Stutsman County, North Dakota (inset). Points indicate the northern, southern, or eastern point of entry. Wetland hydroperiod is denoted by ‘P’ for permanent and ‘T’ for temporary.

A total of 16 wetlands are within the CLA, of which 11 were selected for analysis in this paper (Table 3.1, Figure 3.1). These wetlands were previously identified by permanent and temporary wetland status and are so-named by the prefix ‘P’ or ‘T’ followed by wetland number. The hydrological relations to groundwater were identified based on the table provided by Euliss and Mushet (2011) and a subset of the 16 was selected based on maximizing spatial differences and selecting wetlands with wet surface water conditions. Wetland locations and hydrological characteristics are presented in Table 3.1. The Palmer Drought Severity Index (PDSI) is a meteorological drought index used to assess the severity of dry or wet spells of weather (NOAA, 2007). The CLA was located in North Dakota climate region five in the PDSI system, and average PDSI for 2012 was -1.35 (NOAA, 2013). This value indicates incipient drought (NOAA, 2007). Due to this, five wetlands (three flow-through and two recharge) were dry in the wetland center. The wetland soil element composition is expected to be different under dry conditions due to differences in redoximorphic potentials (Kissoon et al., 2011).

Table 3.1. The entry location, hydrological function, and condition of sampled wetland sites.

SiteID	Latitude	Longitude	Function	Condition
P1	47.09832	-99.0973	Discharge	wet
P4	47.10019	-99.095	Discharge	wet
P6	47.09787	-99.0965	Discharge	wet
P7	47.09666	-99.0994	Discharge	wet
P3	47.10219	-99.1021	Flow-through	wet
T4	47.09928	-99.0956	Flow-through	dry
T6	47.09946	-99.0939	Flow-through	dry
T7	47.09966	-99.0916	Flow-through	dry
T5	47.098	-99.095	Recharge	wet
T8	47.0975	-99.0924	Recharge	dry
T9	47.09677	-99.092	Recharge	dry

Sample Collection and Analysis

Samples were collected under incipient drought conditions on 16 July 2012. Sampling design for each of the 11 wetlands consisted of collecting five replicate soil samples at equidistant intervals along the north-south or east-west near-center transect. The first sampling location was identified when the water level reached a depth of 5 cm. Best professional judgment was used if the wetland was dry. Square soil plugs were extracted 10 cm below the water-soil interface using a steel spade. An interior soil sample was taken from the bottom of the plug so to reduce the risk of metal contamination from the spade. Soils were taken using an inverted polyethylene freezer bag and immediately sealed until they could be put on ice. Upon completion of fieldwork, soils were refrigerated (4° C) until they could be processed for analysis. If the water level was too deep for sampling, sampling was done along a parabola, with the apex (sample 3) taken at a depth no greater than 1 m. The entry and exit points (samples 1 and 5) were approximately 5 m apart. This alternate method was used for all permanent wetlands and attempted to replicate conditions along the hydroperiod gradient.

Prior to analysis samples were randomized to minimize systematic error, transferred to paper bags to minimize contamination from dust, and dried in a 60° C oven until constant weight. A ceramic mortar and pestle was used to crush and homogenize the bulk material. The sample was passed through a 2 mm mesh sieve and three subsamples were taken for analysis of multi-element composition, pH and EC, and loss on ignition (LOI). Material for multi-element analysis was passed through a 62 micron mesh sieve. Multi-element analysis was performed by Activation Laboratories by aqua regia digestion and ICP-MS analysis (Ultratrace II method) for 62 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr). The pH and EC of subsample two was measured in a 1:2 soil-distilled water mixture with a Symphony pH probe (14002-860, VWR) and Symphony pH meter (SP70P, VWR), and an Symphony EC probe (11388-376, VWR) and Symphony EC meter (SP90M5). Subsample three was analyzed for percent organic matter, by weight, with loss-on-ignition (LOI) for a 5 g sample at a drying temperature of 105°C for 2 hours and an ignition temperature of 360°C for 2 hours (Sparks, 1996).

Statistical Analysis

All computations were processed in Microsoft Excel 2010. Data for statistical analysis were log-transformed to normalize for homogeneity of variance across all concentration values. Statistical analysis included ANOVA (general linear model and Tukey's pairwise comparisons) and correlation analysis with Minitab statistical software (Minitab® 16 © 2012 Minitab Inc.). Strong correlations were noted if the correlation coefficient, r, was between 0.6 and 1. Decision trees (DT) were built using Weka 3 (Hall et al., 2009), a suite of machine learning software. This tool aided selection of element indicators. Data used to construct DT were untransformed. Trees were produced under the training set J48 tree classifier.

Results and Discussion

Data Pre-Process

The concentration of Au, Ge, Hf, In, Lu, Re, Ta, Te, and W were below their respective detection limit in more than 50% of the samples and was thus excluded from analysis. Element concentrations that were below their respective detection limit in less than 50% of the samples had their concentration replaced with the detection limit.

Description of Data

Element concentrations were broadly related to discharge, flow-through, and recharge hydrologic relations to groundwater (i.e., concentrations differing between discharge, flow-through, and recharge) in four ways: (1) differ with increasing pattern, (2) differ with decreasing pattern, (3) differ with no pattern, and (4) do not differ (Table 3.2). Proton (e.g., low pH) and LOI was highest in recharge and soil EC was highest in discharge and flow-through. Elements generally increasing from discharge to recharge were Al, Be, Cd, Sc, Cu, Ga, K, and P. Elements generally decreasing from discharge to recharge were As, B, Ca, Co, Fe, Li, Mg, Mn, Na, Nb, Ni, S, Sb, Sr, Th, Ti, and Zr. These element data form the basis of the remaining paper.

Element Selection and Implementation for Assessment – Manual Approach

When identifying potential elements for assessment it is ideal to examine element patterns which show strong relationships with respect to hydrological relations. This can be done manually by selecting elements especially high or low, and Table 3.2 shows that Mg was especially high in discharge and K was especially high in recharge. Because these data distinguish between hydrological gradient extremes, their potential for assessment is strong. A plot of Mg and K with respect to groundwater relation confirms this and shows clustering of observations, with clusters falling along a recharge, flow-through, and discharge gradient (Figure 3.2). Of the two-element relations tested, the relationship between Mg and K was the most clean and possessed the tightest distribution.

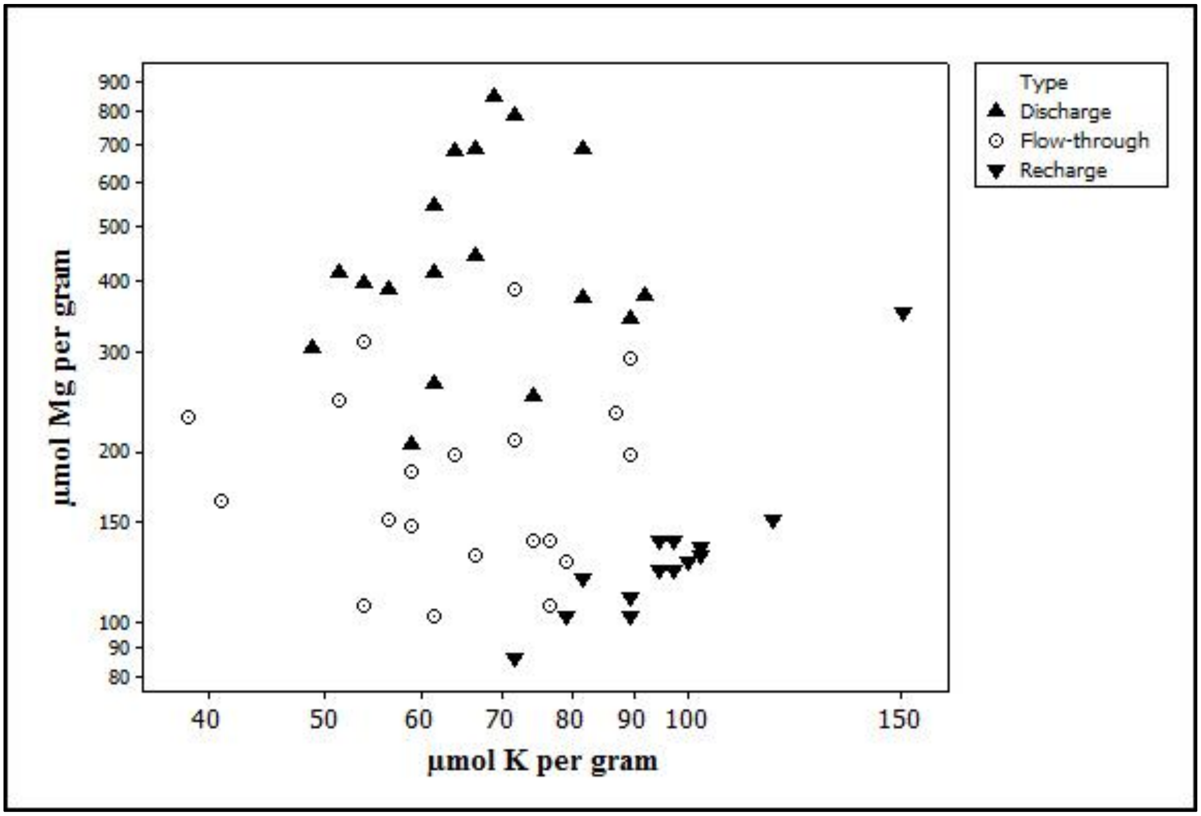


Figure 3.2. Concentrations of Mg and K in hydric soil with respect to hydrological relation to groundwater shows discharge and recharge distributions form distinct groups, with flow-through occupying an intermediate position. Values are represented in log scale.

Further, the relationship between Mg and K could be expressed as a ratio. Presenting data in this form is an ideal way of expressing multi-element relationships. This form is used by many bio- and geochemical disciplines, including identification of limiting ecological conditions (Li et al., 2013), discerning anthropogenic and natural pollution sources (Soler et al., 2002), understanding geological processes (Munroe et al., 2007) and tracing river sediments (Wijeyaratne, 2011). In this case, the ratio between Mg and K with respect to hydrological relations shows similar and better defined regions. The ratio is low and compact in recharge and high and disbursed in discharge, with flow-through showing intermediate value and dispersion (Figure 3.3).

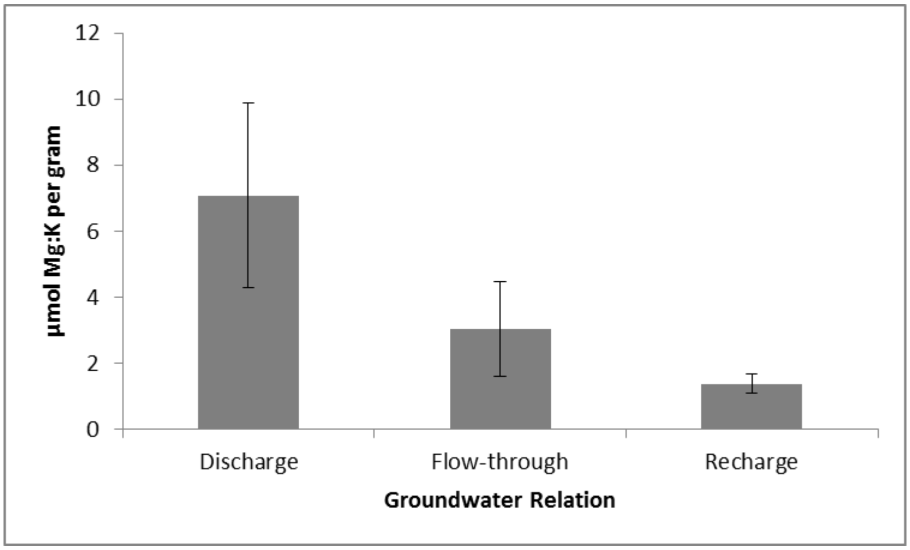


Figure 3.3. Mg:K box plot distributed between groundwater relations: discharge, flow-through, and recharge.

Element Selection and Implementation for Assessment – Semi-Automated Approach

Although two element ratios possess the ability to discern between groundwater relations, Figure 3.2 showing this relation is not well defined and may be difficult to assign discharge-recharge regions intrinsic to the plot. Incorporating additional elements should strengthen discharge-recharge regions in the plot. It is difficult, however, to identify elements which show this potential. To aid in selection the machine learning program Weka was utilized to produce decision trees. Decision trees define thresholds (element concentration in this case) to guide the user to ascertain a particular environmental condition (Džeroski, 2001; Zimmer et al., 2009; Kampichler et al., 2010). Accuracy is assigned as a percentage of samples correctly predicted by the tree. In this case, data used to construct the tree included all elements showing general relationships to groundwater presented in Table 3.2. Ti was excluded from the data set due to non-continuous concentrations (See Ti in Figure 3.4). The resulting tree (Figure 3.5) narrowed the data to five elements and shows that relationships with Na, K, Cs, Cd, and As could be used to predict 100% of the samples (n=53) collected at CLA.

Table 3.2. Prairie Pothole groundwater hydrological discharge, flow-through, and rechage relations to element concentration (agerage ±SD) and statistical significance for 11 wetlands at the Cottonwood Lake Area located in Stutsman county, North Dakota. Trends are gouped by elements (1) generally increasing and (2) generally decreasing from discharge to recharge, (3) showing significance (*p*-value≤0.05) without a trend from discharge to recharge, and (4) showing no significnace (*p*-value>0.05).

Element	Unit	Discharge	Flow-through	Recharge	Type
		----------------------	average ±SD	----------------------	*p*-value
pH		7.3 ±0.36	6.41 ±0.87	5.58 ±0.55	0.000
LOI	%	8.04 ±4.65	14.2 ±7.32	13.2 ±5.3	0.001
EC	µS·cm^{-1}	205 ±158	372 ±361	47.5 ±47.9	0.000
Elements generally increasing from discharge to recharge					
Al	µmol·g^{-1}	454 ±106	563 ±71.6	613 ±122	0.000
Be	pmol·g^{-1}	54.9 ±13.4	67.1 ±12.2	68.1 ±16.7	0.006
Cd	pmol·g^{-1}	2.63 ±0.7	3.27 ±0.68	3.47 ±1.18	0.017
Cs	pmol·g^{-1}	6.91 ±1.78	9.35 ±1.05	9.6 ±1.67	0.000
Cu	pmol·g^{-1}	230 ±48.3	306 ±43.6	280 ±32.7	0.000
Ga	pmol·g^{-1}	47.3 ±11.9	59.2 ±11.6	61.7 ±12.4	0.001
K	µmol·g^{-1}	67.2 ±12.6	66 ±14.9	96.5 ±18.9	0.000
P	µmol·g^{-1}	24.1 ±3.32	28.9 ±9.11	36.4 ±9.79	0.001
Elements generally decreasing from discharge to recharge					
As	pmol·g^{-1}	73.9 ±29	41.2 ±17	28.4 ±9.47	0.000
B	µmol·g^{-1}	2.42 ±1.34	1.48 ±0.99	1.02 ±0.43	0.000
Ca	µmol·g^{-1}	850 ±712	290 ±266	125 ±27.1	0.000
Co	pmol·g^{-1}	109 ±25.2	73.6 ±25.6	62.1 ±28.5	0.000
Fe	µmol·g^{-1}	289 ±65.9	254 ±65.9	232 ±77	0.041
Li	µmol·g^{-1}	1.7 ±0.38	1.28 ±0.42	1.04 ±0.44	0.000
Mg	µmol·g^{-1}	468 ±193	191 ±75.8	137 ±62.6	0.000
Mn	µmol·g^{-1}	10.6 ±5.56	4.63 ±3.57	3.55 ±2.29	0.000
Na	µmol·g^{-1}	21.1 ±4.55	17.6 ±11	9.37 ±2.03	0.000
Nb	pmol·g^{-1}	6.28 ±1.74	5.81 ±2.02	4.66 ±1.5	0.028
Ni	pmol·g^{-1}	389 ±95.8	324 ±88.1	278 ±89.7	0.002
S	µmol·g^{-1}	114 ±85.6	59 ±51.7	20.1 ±5.76	0.000
Sb	pmol·g^{-1}	1.8 ±0.96	0.96 ±0.46	0.73 ±0.26	0.000
Sr	pmol·g^{-1}	767 ±411	545 ±303	290 ±96.2	0.000
Th	pmol·g^{-1}	8.24 ±3.14	9.24 ±6.25	5.11 ±4.96	0.010
Ti	µmol·g^{-1}	5.69 ±1.2	4.8 ±1.37	4.32 ±2.01	0.018
Zr	pmol·g^{-1}	31.2 ±11.2	36.8 ±31.9	10.9 ±14.6	0.000

(continues)

Table 3.2. Prairie Pothole groundwater hydrological discharge, flow-through, and recharge relations to element concentrations (continued).

Element	Unit	Discharge	Flow-through	Recharge	Type
		------------------------ average ±SD ------------------------			*p*-value
pH		7.3 ±0.36	6.41 ±0.87	5.58 ±0.55	0.000
LOI	%	8.04 ±4.65	14.2 ±7.32	13.2 ±5.3	0.001
EC	µS·cm^{-1}	205 ±158	372 ±361	47.5 ±47.9	0.000
Elements showing differences with no pattern from discharge to recharge					
Rb	pmol·g^{-1}	253 ±72.9	316 ±79.2	259 ±55.5	0.016
U	pmol·g^{-1}	5.32 ±1.75	22.4 ±22	4.76 ±0.97	0.000
Zn	µmol·g^{-1}	0.97 ±0.22	1.38 ±0.46	1.14 ±0.25	0.002
Elements showing no differences from discharge to recharge					
Ag	nmol·g^{-1}	684 ±267	731 ±265	676 ±182	ns
Ba	µmol·g^{-1}	1.02 ±0.36	1.16 ±0.33	1.25 ±0.14	ns
Bi	nmol·g^{-1}	556 ±187	514 ±176	514 ±168	ns
Ce	pmol·g^{-1}	193 ±38.8	211 ±36.2	223 ±44.5	ns
Cr	pmol·g^{-1}	491 ±115	532 ±90.8	511 ±117	ns
Dy	pmol·g^{-1}	11.5 ±2.39	12.2 ±1.71	12.4 ±2.4	ns
Er	pmol·g^{-1}	5.25 ±1.08	5.5 ±0.92	5.46 ±1.01	ns
Eu	pmol·g^{-1}	3.51 ±0.75	3.78 ±0.6	3.99 ±0.72	ns
Gd	pmol·g^{-1}	15.6 ±3.12	16.4 ±2.35	17.7 ±3.36	ns
Ho	pmol·g^{-1}	2.05 ±0.42	2.18 ±0.41	2.22 ±0.44	ns
La	pmol·g^{-1}	101 ±20.2	109 ±16.7	116 ±22	ns
Mo	pmol·g^{-1}	7.74 ±4.58	9.59 ±5.58	6 ±2.81	ns
Nd	pmol·g^{-1}	83.3 ±16.8	90.2 ±16.8	94.2 ±18.8	ns
Pb	pmol·g^{-1}	53.2 ±16.1	48.1 ±12.3	50.9 ±9.51	ns
Pr	pmol·g^{-1}	23.3 ±4.61	25.2 ±4.28	26.4 ±5.14	ns
Sc	pmol·g^{-1}	57.2 ±19.5	60.3 ±23.7	45.2 ±28.8	ns
Se	pmol·g^{-1}	7.6 ±6.46	15.3 ±12.7	12.8 ±9.49	ns
Sm	pmol·g^{-1}	15.9 ±3.19	16.9 ±2.87	17.9 ±3.67	ns
Sn	pmol·g^{-1}	3.28 ±0.73	3.76 ±0.91	3.78 ±1	ns
Tb	pmol·g^{-1}	2.06 ±0.47	2.17 ±0.32	2.35 ±0.5	ns
Tl	nmol·g^{-1}	873 ±240	837 ±174	802 ±156	ns
Tm	nmol·g^{-1}	691 ±227	651 ±182	671 ±208	ns
V	pmol·g^{-1}	931 ±291	810 ±134	797 ±189	ns
Y	pmol·g^{-1}	115 ±26.9	119 ±17.8	119 ±23.1	ns
Yb	pmol·g^{-1}	3.72 ±0.85	3.87 ±0.88	3.66 ±0.94	ns

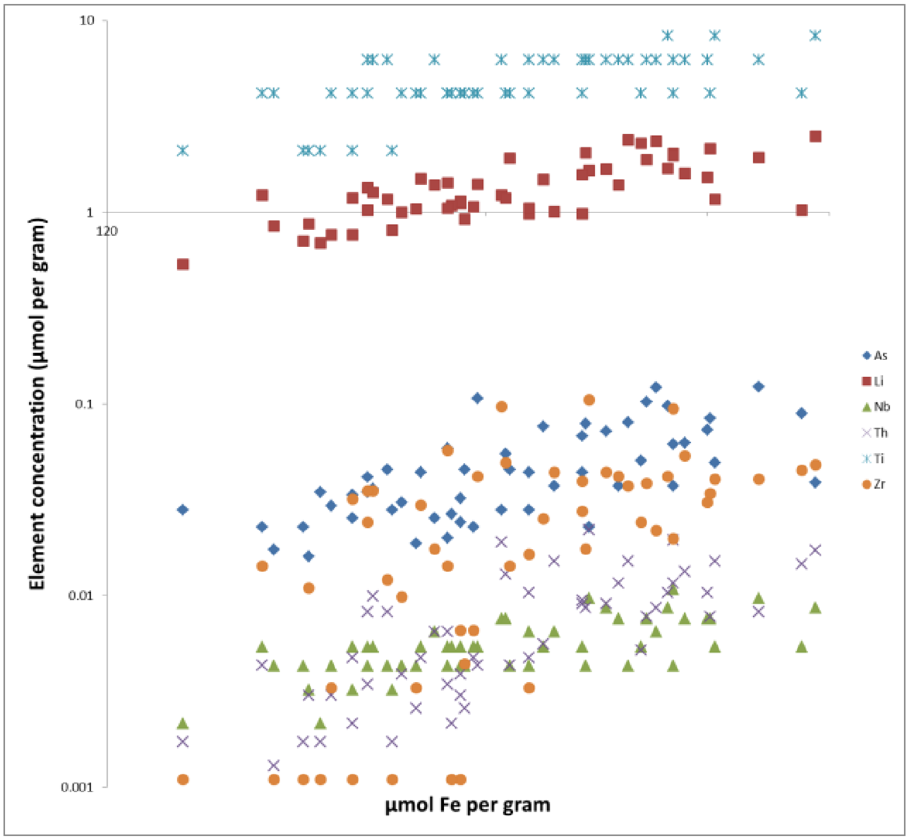


Figure 3.4. The correlation between concentrations of Fe and As, Li, Nb, Th, Ti, and Zr (µmol·g^{-1})

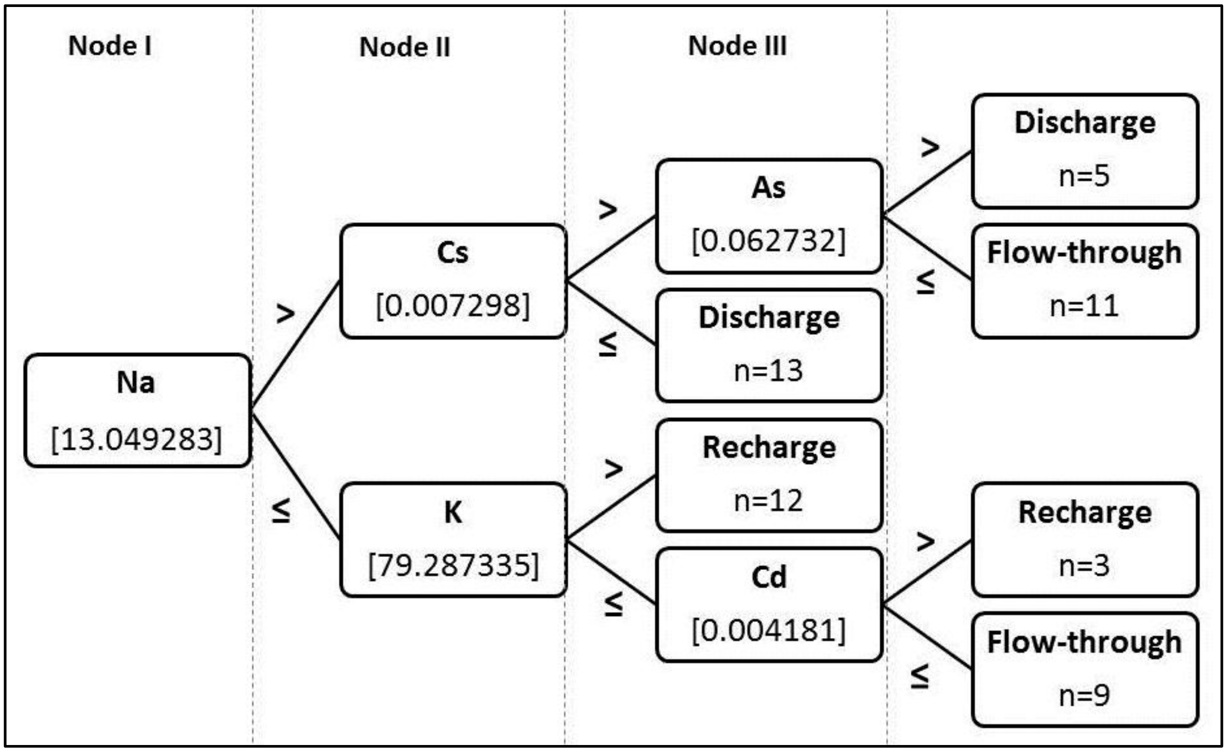


Figure 3.5. Elements found by Weka data mining software (cluster-J48) for prediction of wetland hydrological relation to groundwater. This decision tree used the concentration of Na, K, Cd, Cs, and As to predict 100% of the sample set (n=53).

Elements selected by the tree can then be represented in a two dimensional plot by relativizing elements to the left (Na, K, and Cd) and right (Na, Cs, and As) sides of the tree. Elements selected were relativized with respect to their position (greater than and less than or equal) on the tree. The left side of the tree was relativized in the form: (Na/K)/Cd; the right, in the form: As/(Cs/Na). This method produced the plot shown in Figure 3.6 and shows highly clustered regions for recharge and discharge groundwater relations, with flow-through transcending the intermediate region. Placing new data in this form may be superior to the plot presented in Figure 3.2 because discharge and recharge regions cluster in a way that is highly distinct, yet of similar density and dispersion. It should be noted that element thresholds were not integrated in the plot, and hence do not represent the DT in its true form.

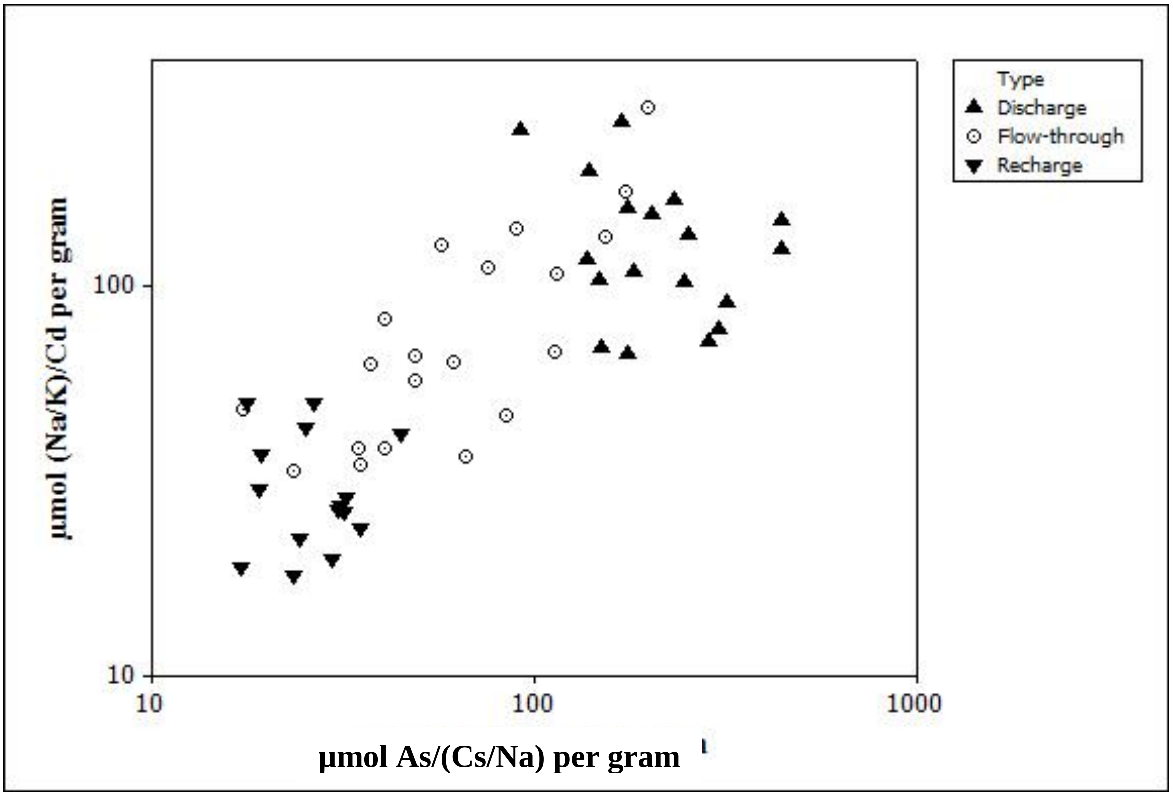


Figure 3.6. The ratio of Na, K, and Cd (Units: ($\frac{\mu\text{mol Na}}{\mu\text{mol Cd} \cdot \mu\text{mol K}}$)$\cdot$g^{-1} dw) as a function of the ratio of As, Cs, and Na (Units: µmol As$\cdot$($\frac{\mu\text{mol Cs}}{\mu\text{mol Na}}$)$^{-1}\cdot$g^{-1} dw), for discharge, flow-through, and recharge wetlands.

Representing decision tree relationships in terms of a ratio, as was demonstrated in Figure 4, cannot be accomplished under relationships guided by the DT. Decision trees make predictions by reducing data sets into simplified groups. Since Na is initially utilized to break apart data (Node I, Figure 3.5), it is crucial to include the element in the ratio. However, dividing the left and right forms together cancels Na, thus rendering the ratio ineffective. Due to this constraint a ratio was not produced.

Indicators in Context to Wetland Hydrology

My hypothesis that alkaline metals (groups 1 and 2) would be enriched in discharge was only partially correct. Metals belonging to the alkaline groups such as Ca, Li, Mg, Na, and Sr were high in discharge but metals of the same groups Be, Cs, and K was high in recharge. Element concentrations high in discharge and low in recharge could be explained by enrichment and depletion of products from the disassociation of minerals occurring in the till. Pyrite (FeS_2) and gypsum ($CaSO_4$), minerals present in the till of the prairie pothole region and of the CLA, undergo disassociation in the presence of oxygenated water to produce sulfate salts, iron oxyhydroxides, and protons (acid) (Goldhaber et al., 2011). In recharge, oxygenated rainwater infiltrating the till could be causing the disassociation reaction whereby the water soluble reaction products are flushed from the soil profile. Through groundwater flow and transport of solutes to the lowest point in the landscape, the evaporative function of discharge wetlands assimilate and concentrate reaction products in overlying waters (Swanson et al., 2003) and soils (Arndt and Richardson, 1988). Soil chemical properties support this interpretation since soil pH and EC was low in recharge and high in discharge. Although pyrite and gypsum was not quantified in this study, the mineral occurrence in discharge wetland systems (Winter, 2003; Goldhaber et al., 2011) could help explain why high levels of Fe and Ca, relative to recharge, was observed. Elements which strongly correlate with Fe are the siderophilic elements Co (r=0.835), Mn (0.602) and Ni (0.714). Other elements showing the same general pattern may be explained by the strength of correlation with Fe which include As (r=0.675), Li (0.729), Nb (0.676), Th (0.745), Ti (0.637), and Zr (0.622) (Figure 3.4). These elements were selected on the basis of being within the correlation region observed for the siderophilic elements. It is harder to explain the occurrence of the remaining elements (B, Mg, Na, Sb, and Sr) given the data set, but their variation is likely explained by the assimilation mechanism.

Element patterns observed for recharge are less easily explained; however, soil properties could aid interpretation. High soil LOI was observed for recharge wetlands. Elements whose concentrations generally increased from discharge to recharge and correlate strongly with soil LOI could be an indication that organic matter in the soil is influencing element variation, but the only element showing a strong relation was Cd (r=0.68) and elements showing the next two strongest relations were P (0.416) and Cu (0.4) (Figure 3.7).

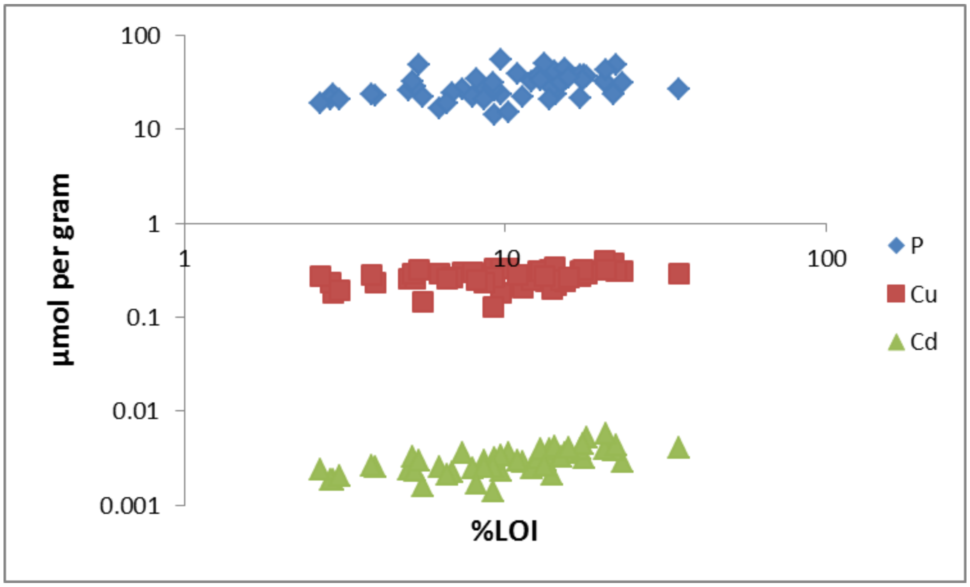


Figure 3.7. The correlation between %LOI and P, Cu, and Cd (µmol·g^{-1}). Concentrations are presented in log scale.

All other elements correlated weakly with LOI. It is apparent there are other factors which influence the variation of Al, Be, Cs Ga, and K. The radioactive isotope ^{137}Cs is used to indicate erosion because it does not become mobile in soil unless physically disturbed (Ritchie and McHenry, 1990). It is unlikely ICP-MS is picking up on the isotope, as it accounts for a small constituent of total Cs abundance; however, the mechanism of ^{137}Cs enrichment may be true for all Cs in soil, and may explain the high concentrations observed in recharge wetlands. The USGS study area where this study took place was converted from pasture land in the 1960s and is considered undisturbed (Euliss and Mushet, 2011). However, if it is shown that CLA recharge wetlands are more eroded than discharge, Cs could possibly hold assessment value. Taking the above as true, Cs could be used to explain the variation of other elements. Cs correlates strongly with Al (r=0.769) and less strongly with K (0.538) (Figure 3.8). Al and K are part of clay minerals (Jepson and Rowse, 1975) and it is possible, along with Cs, that they have been enriched by erosional processes. Since the basin area of recharge wetlands is generally smaller than discharge basins, erosional processes may be intensified, however, more research is needed to confirm this. As for the remaining elements, it is unclear what is driving the variation of Be and Ga.

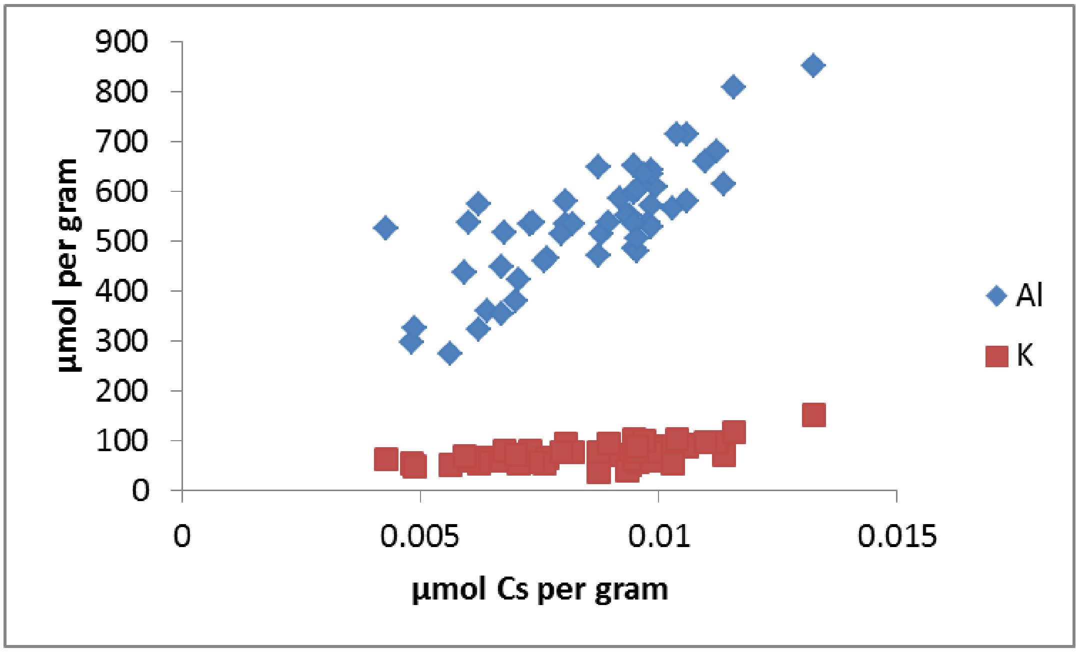


Figure 3.8. The correlation between Cs and Al and K (µmol·g^{-1}).

The element composition responding to hydrological relation is probably driven by soil mineralogy. Heagel et al., (2013) described how minerals are enriched in the till of saline wetlands and how this enrichment buffers water salinity, preventing hypersaline conditions in the PPR of Canada. The authors point to a wet-dry cycle whereby enrichment of mineral salts in the till is driven by evaporation occurring at the water edge. Although the authors did not discuss sub-saline systems, it is suspected that this mechanism of enrichment holds true. The logic behind this is that the relatively stable water levels of saline wetlands will enable the water edge to concentrate and store minerals, while fluctuating water levels of less saline wetlands will distribute minerals along the fluctuation zone, contributing to a less concentrated store of minerals. This concept can be easily applied to wetland relation to groundwater. Discharge wetlands tend to maintain their water levels throughout the year, whereas recharge wetlands tend to dry midway through the growing season (LaBaugh et al., 1998).

Although the element relatavizations used to build Figure 3.6 appear highly complex, approximate mechanisms for element patterns, as explained above, provide some insight to their distribution on the plot. Node I uses an element high in discharge (Na) to split the set, and nodes II and III uses elements high in recharge (II: Cs and K; III: As and Cd) to complete the tree (Figure 3.6). Of these elements, only Na was found to be associated with minerals found in the PPR, minerals which include bradleyite, burkeite, gaylussite, hanksite, nahcolite, natron, pirssonite, trona, and tychite (Last and Last, 2012). These minerals are all authigenic and/or endogenic in nature. Authigenic minerals are those which precipitate from pore solutions or from the chemical alteration of a pre-existing solid, and endogenic minerals are those which precipitate from the water column by inorganic or biological processes (Last and Last, 2012).

Given all the above, future studies should examine mineralogical composition of soil to better elucidate mechanisms driving element composition.

It is important to stress that this study was performed under incipient drought conditions, where four of the 11 wetlands studied were dry at the time of sampling. It should also be stressed that these data reflect a very small area of one square mile (2.59 Km^2), and that these wetlands are part of a larger hydrological system. Keeping these considerations in mind, this research shows that there are multi-element patterns consistent with the recharge-discharge relationship a wetland has with groundwater. Processes and interactions described above are ubiquitous throughout the region and therefore should be readily observable at greater scales. It should be noted that the hydrology of greater-scale systems can be complex, and landscape-level groundwater flow systems should be considered. Also important is the dynamic nature of overland spill points connecting adjoining wetlands. This variable has the potential to complicate larger studies and should also be considered. If these findings are consistent at greater scales, and remain after climatic variability is accounted for, the methods described for rapid assessment should hold value to those who examine prairie wetland ecological trends as well as provide a way to overcome concerns reported by the scientific community.

Conclusion

Multi-element methods have been used to describe and place the groundwater hydrological relationships recharge, flow-through, and discharge in the context of soil chemical composition. This paper demonstrates how ratios and decisions trees could be used to summarize multi-element data to characterize wetlands along a hydrologic gradient: recharge, flow-through, and discharge. This ability is highly important in describing pothole wetland function because, next to anthropogenic activity, because wetland biology responds to water permanence and water and soil chemistry, hydrology is the main factor driving ecological structure and associated ecosystem services. This is a pilot-scale study and requires more research. Hydrological relationships may change temporally and spatially and future sampling schemes should control for this. Despite these limitations, this study further demonstrates the value of multiple element analysis for assessment.

CHAPTER 4. GENERAL DISCUSSION

The overall goal of this research was to develop chemical element indicators of wetland characteristics using a method called multi-element fingerprinting. This was accomplished by quantifying element concentrations in hydric soils of glacially-derived depression wetlands and relating them to previously established characteristics. The intention was to improve on how biological information is collected and interpreted in the Prairie Pothole Region (PPR). Data produced also serves as an initial benchmark for studying hydric soil multi-element relationships outside of the PPR. Since this was an initial investigation into the relation of elements to characteristics, it was only logical to apply fingerprinting methods to the most regionally important factors. My literature review found that the most important factor influencing the ecology of the region was anthropogenically-mediated disturbance of structure and performance of the soil column. Apart from the numerous processes contributing to this disturbance, the next greatest factor influencing ecological communities was if water inputs were precipitation- or groundwater-dominated in origin. Wetland water levels dominated by precipitation inputs are termed recharge, whereas wetlands dominated by groundwater are termed discharge. In light of these findings, in addition to fingerprinting a wide variety of wetlands along the Index of Plant Community Integrity (IPCI) disturbance gradient (Chapter 2), I decided to include a study on how a wetland’s water source was represented in fingerprints (Chapter 3). Under such experimental framework, it was possible to address one of the EPA’s guidelines, a guideline which stated that the development of an ecosystem indicator should convey information on ecological conditions that is meaningful to environmental decision making (Jackson et al., 2000 in Reddy and DeLaune, 2008). The following generalized discussion will support how the multi-element fingerprinting approach can aid in the development of more rigorous and accurate analysis and understanding of pothole and other similar depression wetlands. This discussion will loosely address the following questions: (1) what can fingerprinting tell us about the IPCI; (2) how might the hydrological function of a wetland affect IPCI classification; (3) what might fingerprinting tell us about discrete classification of dynamic environmental states; (4) is there a place for fingerprinting in future biological studies; (5) how might the methods of multi-element fingerprinting be improved; and (6) does the multi-element fingerprinting approach provide meaningful information to decision makers?

Disturbance, the IPCI, and Hydrologic Function

Before addressing questions outlined above it is prudent to explain how the IPCI disturbance gradient and hydrological functions with respect to water source (recharge or discharge groundwater) are related. The foundation of the IPCI was built upon the influence of anthropogenic activity, or lack thereof, on vegetative states of prairie wetlands. The classification structure developed resulted in two systems and differentiation between them was based on water regime (outlined by Steward and Kantrud (1972)): (a) temporary and seasonal, and (b) semi-permanent and permanent. Classification systems are differentiated due to greater disturbance pressures on temporary and seasonal wetlands (Hargiss, 2005). However, the fundamental basis on how wetland integrity is assessed is rooted in water regime, processes dictated by a relationship between evaporation/precipitation (water permanence) and water source. The classification system used in Chapter 2 utilized the seasonal IPCI system, and, given the above, it could be thought of as targeting recharge to recharge-like wetlands (Hargiss, 2005). If selection of the correct IPCI system depends on discrete classes of water regime then it would be expected that all wetlands within the seasonal IPCI system display recharge to recharge-like characteristics. Multi-element fingerprinting may help to evaluate the accuracy of this assumption.

The relationship between a wetland's water source was evaluated in Chapter three and a method was developed to characterize recharge, flow-through, and discharge hydrology using five elements: As, Cd, Cs, K, and Na. Although speculated upon, it was largely unknown why these elements are important for defining function. Irrespective of this, the five element characterization was applied to the IPCI element data presented in Chapter 2. The resulting plot comparing distributions is presented in Figure 4.1. There are a few very important findings shown. First, the five element characterization derived from a small (260 ha) wetland complex (black •), when applied to the IPCI data across a broader state-wide area, shows the same relative distribution (grey +). A certain, but unknown level of variation is expected due to increased geographic area; however, many points appear to display signatures associated with discharge relations to groundwater, a relation that reflects the semi-permanent water regime (Euliss et al., 2004). Not surprisingly, the majority of IPCI wetlands sampled display signatures associated with recharge, a hydrological function related to the so-called seasonal wetlands (Euliss et al., 2004). Furthermore, this dense clustering of IPCI observations near the recharge data region could be interpreted as a confirmation that the IPCI is targeting the regime the tool was designed for. Observations outside of this region appear to display discharge signatures, a hydrology synonymous with groundwater fed semi-permanent regimes. This may indicate that biological studies which make distinctions based on wetland water regime, as outlined by Stewart and Kantrud (1971, 1972) may not be correct. This finding underscores the importance of placing wetlands within the context of the physical environment and demonstrates how fingerprinting may be used to do so.

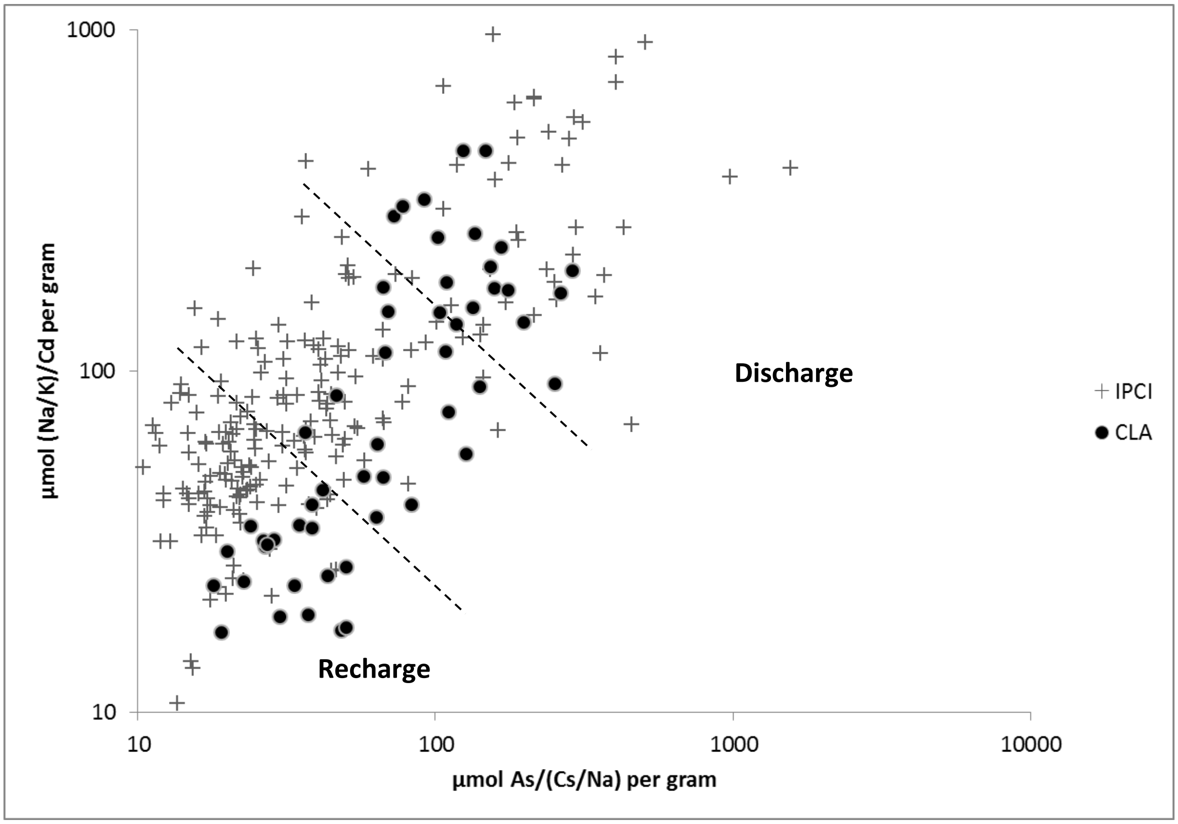


Figure 4.1. The five element relation to characterizes recharge, flow-though, and discharge relationships to groundwater for the Cottonwood Lake Area (CLA), a small wetland complex in central North Dakota. The recharge, flow-through, and discharge regions (dashed lines) are denoted according to the plot (Figure 3.6) shown in chapter 3. The same five element relationship was applied to IPCI-assessed fingerprints (IPCI) sampled across the state-wide area. The CLA relation to groundwater should be used to interpret the IPCI relation.

Future Research

It is too early to implement any findings to support wetland management. Further development of the multi-element approach must be undertaken and verified by the scientific community. It is critically important for future studies to characterize factors contributing to chemical variation. The following discussion will highlight the most notable factors and offer suggestions to improve the success of future studies.

Figure 4.1 provides some indication of fingerprint sensitivity with respect to water source. In Chapter 2, I showed how several elements are linked to the IPCI. It may be possible to identify stronger links as well as increase the number of disturbance indicators if the five-element relationship were transformed in a way that enabled it to be included as a statistical covariant. Unfortunately, Chapter 3 explained the technical difficulty with such a transformation. It is unclear how to manage this issue.

Wetland disturbance is a major factor influencing chemical variation. Chapter 2 showed that multiple elements were related to a disturbance gradient. Given this finding, future studies should probe relations to individual mechanisms of disturbance. Mechanisms of disturbance include sedimentation, climatic variability, grazing, road dust, and draining. Since sedimentation is the most prominent disturbance in North Dakota, and is a suspected mechanism for element patterns observed, isolating this source of variation would undoubtedly increase the power of the approach. Sedimentation can be detected by quantifying ^{137}Cs or through an examination of the soil profile (Ritche and McHenry, 1990).

Grazing was thought to influence multi-element patterns because cattle select for certain plant communities (Patton et al., 2007) expressed in a wetland. Wetland plant species differentially control element variation through redoximorphic states surrounding their rhizospheres (see page 5 for information). If these mechanisms held true then element signatures should be readily observed for ungrazed and various intensities of grazing pressures. Unfortunately, isolating the effect under two separate experimental approaches failed to produce meaningful agreement. Although grazing is a disturbance throughout the region, my unreported findings showed that signatures are not strong enough, if present at all. Pursuing further research of this nature is not recommended unless a more direct and established physical environmental mechanism is proposed. Mechanisms could include disruption of nutrient sequestration due to trampling of wetland perimeters, or mass transfer and enrichment of nutrients through dung.

Experimental designs may incorporate bulk soil density and a more detailed accounting of cattle using the resource.

As a note on sample replication, there is question of what constitutes an effective sample size. Hydrological research at the Cottonwood Lake Area (CLA) showed that the recharge and discharge groundwater input and output regions varied from season to season, a consequence of groundwater flow and climatic variability (Winter, 2003). Other research shows that soil electrical conductivity measurements varied spatially within a saline wetland (Heagle et al., 2013). Given that prairie wetlands accumulate minerals in soil over time (Last and Last, 2012), future studies utilizing fingerprinting should take note on the extent of element variability within wetlands with respect to hydrological function. With that said, it was possible to extract meaningful information regarding impact and hydrology from fingerprints of soils collected along the center transect at equidistant intervals. This underscores the importance of understanding how climate and variations in groundwater flow influence fingerprints.

If multi-element fingerprinting is to gain acceptance in the wetland science and management communities element data must be examined or relatable to common and standard measurements used. This will not only further facilitate communication, but will permit a more effective scrutiny of the approach overall. Common measurements include characterization of soil particles (i.e., soil texture) (Mitch and Gosselink, 2007), 1N HCl acid test for the presence of soil carbonates, soil color charts (Munsell®, EarthColors®), and NRCS field indicators (Schoeneberger et al., 2012). A helpful sample design consideration may include use of porewater samplers to measure water chemistry. This will help to quantify the soluble, transportable fraction with the bulk soil chemical fraction. Other research avenues could incorporate analysis of soil mineralogy. Soil minerals are undoubtedly responsible for much of the variation in fingerprints. Found in association with minerals, the elements Al, K, Na, Ca, etc. may hold valuable information. However, because of mineral ubiquity in the region, patterns could be obscured.

General Conclusions

This thesis set out to understand how element soil chemistry is represented across hydrological and disturbance gradients in glacially-derived depression wetlands of the North Dakota Prairie Pothole Region. Specifically, it was found that element variation is strongly influenced by wetland hydrology. As such, it is recommended that future biological studies integrate more of the physical processes underpinning ecological expression. A main finding of this work was that fingerprints can be used to characterize these physical processes. If future studies reaffirm findings presented, the multi-element approach not only has to potential increase the accuracy of biological assessments, but also to unveil meaningful information about wetland soils and overlying processes.

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