THE BIOGEOCHEMISTRY OF SOIL AT DEPTH WITHIN THE WETLAND LANDSCAPE OF THE PRAIRIE POTHOLE REGION

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Title

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

The impact of agricultural practices on wetland ecosystems in the Prairie Pothole Region (PPR) has long been recognized but little is understood about impacts on the biogeochemistry of the wetlands at depth. Understanding the relationship of multi-elements within the wetland and surrounding landscape can aid in wetland restoration and provide guidance for wetland management. The objectives of this study were to: 1) identify biogeochemical characteristics of PPR wetlands; 2) identifying differences or similarities in biogeochemical characteristics of the landscape; 3) assess the vertical variation in chemical composition at depth in wetland, wetland and fringe, footslope and backslope soils; and 4) interpret the soil chemistry of undisturbed sites (good quality; prairie vegetation) and disturbed sites (poor quality; cultivated) relative to differences in landscape position locations. A field study was conducted on six disturbed (DW) and 6 undisturbed (UW) wetlands with evaluation of fringe (F), footslope (FS), or backslope (BS) positions. Using redundancy analysis (RDA) with selected environmental variables models of element concentrations at depth in each position were generated. The RDA ordination plots of element concentrations to depth of 1m was constrained by variables sand, silt, clay, depth, bulk density, site, organic matter, electrical conductivity, and pH. Pearson correlation coefficients between soil properties and the five most prominent soil elements differed between landscape positions. Anthropogenic activity likely influenced the subsurface hydrology but differed in physical and chemical properties. These differences appear to be related to the vegetation, levels of soil disturbance of surrounding landscapes and unique chemical and physical characteristics of parent material.

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I truly appreciate all the support from family, advisors, colleagues, and friends. None of this would have happened without their patience and sacrifices that they have made for me to achieve a life goal. I am truly fortunate to have each of you in my life and I am extremely grateful for their support on this very long road of education.

DEDICATION

I dedicate my dissertation work and education career to a strong-willed and loving woman who leads by example, my mother, and to the solid cornerstone in my life who always is steadfast and supportive, my father. Thank you!

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LIST OF ABBREVIATIONS

Al .... Aluminum

NH_3 .... Ammonia

NH_4^+ .... Ammonium

Sb .... Antimony

As .... Arsenic

Ba .... Barium

HCO_3 .... Bicarbonate

Bi .... Bismuth

B .... Boron

BD .... Bulk Density

Cd .... Cadmium

Ca .... Calcium

CEC .... Cation Exchange

Ce .... Cerium

Cs .... Cesium

Cr .... Chromium

Co .... Cobalt

Cu .... Copper

DW .... Disturbed Wetlands

Dy .... Dysprosium

EC .... Electrical Conductivity

S^0 .... Elemental Sulfur

EV .... Environmental Variable

EVs .... Environmental Variables

Er .... Erbium

Eu .... Europium

F .... Fair

Fe^{3+} .... Ferric

Fe^{2+} .... Ferrous

Gd .... Gadolinium

Ga .... Gallium

Ge .... Germanium

Au .... Gold

G .... Good

Hf .... Hafnium

Ho .... Holmium

$HPO^{2-}{}_4$ .... Hydrogen Phosphate

H_2S .... Hydrogen Sulfide

IPCI .... Index of Plant Community Integrity

In .... Indium

ICP-MS .... Inductively Coupled Plasma Mass -Spectrometry

IA .... Iowa

Fe .... Iron

La .... Lanthanum

Pb .... Lead

Li .... Lithium

Lu .... Lutetium

Mg .... Magnesium

Mn .... Manganese

Mn^{4+} .... Manganic

Mn^{2+} .... Manganous

Hg .... Mercury

MN .... Minnesota

Mo .... Molybdenum

MT .... Montana

Nd .... Neodymium

Ni .... Nickel

Nb .... Niobium

NO_3^- .... Nitrate

NO .... Nitric Oxide

NO_2^- .... Nitrite

N_2 .... Nitrogen Gas

N_2O .... Nitrous Oxide

ND .... North Dakota

NDSU .... North Dakota State University

OC .... Organic Carbon

OM .... Organic Matter

H_3PO_4 .... Orthophosphoric Acid

$PO^{3-}{}_4$ .... Phosphate

P .... Phosphorus

K .... Potassium

PPR .... Prairie Pothole Region

PPW .... Prairie Pothole Wetlands

PP .... Prairie Potholes

Pr .... Praseodymium

REE .... Rare Earth Elements

Eh .... Redox Potential

Re .... Rhenium

Rb .... Rubidium

Sm .... Samarium

Sc .... Scandium

SeO_4^{2} .... Selenate

SeO_3^{2-} .... Selenite

Se	Selenium
Ag	Silver
Na	Sodium
SD	South Dakota
STDEV	Standard Deviation
Sr	Strontium
SO_4^{2-}	Sulfate
S^{2}	Sulfide
S	Sulfur
Ta	Tantalum
Te	Tellurium
Tb	Terbium
Tl	Thallium
Th	Thorium
Tm	Thulium
Sn	Tin
Ti	Titanium
TN	Total Nitrogen
TOC	Total Organic Carbon
W	Tungsten
UW	Undisturbed Wetlands
U.S.	United States
U	Uranium
NH_2CONH_2	Urea
V	Vanadium
VG	Very Good
VP	Very Poor
Yb	Ytterbium

Y .... Yttrium

Zn .... Zinc

Zr .... Zirconium

1. MULTI-ELEMENT COMPOSITION OF SOIL PROFILES IN PRAIRIE POTHOLES: LITERATURE REVIEW

1.1. Introduction

The Prairie Pothole Region (PPR), located in Montana, North Dakota (ND), South Dakota, Minnesota, Iowa, and extending northward into Canada, contains around 2,602,1625 ha (6,427,350 acres) of the wetlands in the United States (Dahl, 2014). From 1780-1980, 53% of wetland acres vanished across the United States (Dahl, 1990) and in ND the PPR wetlands have been lost from 5,000,000 original acres (2,023,428 hectares) to 2,000,000 current acres (809,371 hectares) (Tiner, 1984). This has been attributed to agricultural land drainage (Tiner, 1984, Martin and Hartman, 1987b, Berkas, 1996). Currently in North Dakota, 85% of the wetlands are protected from anthropogenic conversion (Leitch and Baltezore, 1992) due to the Federal, state, local and tribal agencies impact on implementing the protection and restoration of wetlands.

Wetlands play a vital role in water availability for human use (Gleick, 1993). Major ecosystem services of wetlands include improvement of water quality, recharging existing aquifers, enrichment of biological diversity, governing carbon sequestration, and providing flood control, which reduces soil sedimentation in streams (Woltemade, 2000, Brady and Weil, 2002, Lamers, et al., 2006, Oki and Kanae, 2006, Gleason, et al., 2008, Hussain, et al., 2012).

North Dakota wetlands were impacted by glaciers around 10,000 - 12,000 years ago (Bluemle, 1980, Berkas, 1996). The last glaciers in North Dakota left behind an undulating deposition of glacial till parent material (Bluemle, 1980) where a prairie pothole can be found in the depositional landscape (Sloan, 1970, Berkas, 1996, Tiner, 2003). These wetland systems have undergone vegetation, climate, and organism transformations (Bluemle, 1988). Due to European settlement of the Dakotas after 1861, the PPR was anthropogenically impacted which aids us in understanding prairie pothole wetland history (State Historical Society of North Dakota, 2013). Anthropogenic effects, such as tillage, drainage, grazing, construction, fire, fertilizers and pesticides addition, and influence of development/manufacturing of technological advances, can alter a wetland (Winter, 1988, Leitch and Baltezore, 1992, Euliss and Mushet, 1996, Bethencourt, et al., 1998, Bedford, 1999, Schuster, et al., 2002, DeKeyser, et al., 2003, Mast, et al., 2010, Zhuang and McBride, 2013). This alteration aids in linking wetland disturbance to a timeline. Today, relatively undisturbed prairie pothole wetlands can be found in grazed native grassland landscapes (DeKeyser, et al., 2003, Mita, et al., 2007, Hargiss, et al., 2008, Paradeis, et al., 2010).

1.2. Classification

Wetland classification varies depending on observation of wetland types. Each wetland has its own characteristics (hydrology, landscapes, biocriteria, vegetation) making it difficult to fit to uniform government guidelines (Leitch and Baltezore, 1992, Brinson, 1993b, DeKeyser, et al., 2003, Hargiss, et al., 2008, DeKeyser, et al., 2009). Stewart and Kantrud (1971) identified seven major classes of wetlands with five subclasses. In the PPR, wetlands are typically identified as temporary, seasonal, or semi-permanent with a hydrology classification of recharge, throughflow, or discharge (Stewart and Kantrud, 1971). A closed hydrological system generally describes a wetland in the PPR (Dahl, 2014). Wetland functions can be categorized through biogeochemistry, hydrology, vegetation, and environment (Brinson, 1993b).

Wetlands are studied and characterized by different classifications such as hydrology, vegetation, and salinity. Several land use studies/models have identified wetlands that vary from one another based on vegetation, hydrology, topsoil, sediment, and human influence (Brinson, 1993a, Holmgren, et al., 1993, Hupp, et al., 1993, Euliss and Mushet, 1996, Gwin, et al., 1999, Winter, 2000, Voldseth, et al., 2007, Euliss, et al., 2010, Euliss and Mushet, 2011, Gleason, et al., 2011). Analysis of soil element content is a potential technique to distinguish between wetlands with different levels of disturbance in the PPR (Martin and Hartman, 1987a, Bedford, 1999, Beck and Sneddon, 2000, Wilson, et al., 2008, Mikac, et al., 2011, Zhuang and McBride, 2013).

Adjacent landscapes impact wetlands. From 1997-2009, the PPR emergent wetlands declined by 39% due to anthropogenic impact on the surrounding landscape (Dahl, 2014). Landscape position and soil properties such as organic matter (OM), bulk density, texture, and pH were found to be continuous variables tied together within the system (Malo, et al., 1974). Mita et al. (2007) and Gwin et al. (1999) showed that wetlands associated with grassland or disturbed/croplands landscapes were different from each other. Freeland et al. (1999) found cultivated landscape topsoil accumulation in wetlands with a thicker A-horizon and higher phosphorus (P) concentration levels when compared to wetlands with grassland landscape. Wetlands associated with grassland landscape had higher total nitrogen (TN) in the topsoil vs. a wetland associated to a cultivated landscape (Martin and Hartman, 1987b). Soil texture was found to have variable amounts of sand, silt, and clay at depth in the wetlands associated with either grassland or cropland landscapes (Martin and Hartman, 1987b, Freeland, et al., 1999, Jolley, et al., 2010). Bulk density and pH were found to be higher in a disturbed wetland soil (Jolley, et al., 2010) as well as higher salt and sodium (Na) soil conditions than in an undisturbed wetland (Parkin, 1993).

A wetland soil is different from a dryland/upland (toeslope/footslope/backslope/summit location) soil due to having higher amounts of available organic carbon (OC) and water, which generate chemical and physical transformations (reduction, translocation, and oxidation/reduction). Understanding soil landscape, hydrology, biology, and transformations can aid in understanding the biogeochemical and physical behavior of element concentrations within soil. Soil that is saturated with water over a period shows in soil oxygen depletion which creates an anaerobic environment, hence, changes in the biogeochemical processes and hydric soil formation (Vepraskas and Faulkner, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008b, Vasilas, et al., 2010, Davranche, et al., 2011). A hydric soil is generally characterized as a soil saturated for a period during the year creating anaerobic conditions and supports some hydrophytic vegetation (Mausbach and Parker, 2001, Mitsch and Gosselink, 2007, Vasilas, et al., 2010). Hydric soils go through chemical depletions, additions, and transformations creating similar soil classifying characteristics and indicators (Vasilas, et al., 2010). With oxygen depletion, electron acceptors other than oxygen, for example nitrate (NO_3^-), manganic (Mn^{4+}), ferric (Fe^{3+}), sulfate (SO_4^2) and bicarbonate (HCO_3) ions, are used by resident microbes for respiration (Vepraskas and Faulkner, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a, Davranche, et al., 2011).

1.3. Manganese and Iron

Manganese (Mn) is an essential micronutrient needed by plants and microbes and plays a role in ecosystem multi-element chemistry concentration. It is influenced by pH and redox potential (Eh) which affects the microbial conversion of manganese ions such as the manganese (Mn^{4+}) and manganous (Mn^{2+}) forms. Microbes effect these transformations under anaerobic conditions. The Mn forms can be water soluble, microbe available, or maybe express as the black color present in the soil. The insoluble oxide form is found in disturbed cropland. Manganese is taken up as Mn^{2+} within plants (Black, 1993, Craft, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a, Vasilas, et al., 2010, Davranche, et al., 2011). A cropland study that compared soil samples collected over a hundred years period, identified that topsoil Mn concentrations significantly decreased perhaps due to removal of harvested crop components (Zhuang and McBride, 2013).

Plants and microbes need iron (Fe), a micronutrient. Within the ecosystems, iron influences many element concentrations and is impacted by soil factors such as pH and Eh. In a wetland, depending on moisture and oxygen availability, it is in either the ferrous (Fe^{2+}) or ferric (Fe^{3+}) form. At a lower pH and Eh in water saturated soil, microbes reduced less soluble Fe^{3+} to more soluble Fe^{2+} and can be expressed visibly as red oxidized (Fe^{3+}) or reduced (Fe^{2+}) gleyed soil zones. As a wetland goes through wet and dry cycles, Fe easily goes back and forth between Fe^{3+} and Fe^{2+}forms in different concentrations. Ferric ion is usually insoluble while $Fe^{2+}$is more soluble and readily moves within the soil profile. In disturbed cropland systems, Fe is usually in Fe^{3+} form and must be converted to Fe^{2+} form by plants or microorganisms for their use (Black, 1993, Craft, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a, Vasilas, et al., 2010, Davranche, et al., 2011).

Often linked together in element cycles are Fe and Mn. The chemistry of these two elements is influenced by pH, Eh, and different soil conditions (Collins and Buol, 1970, Feijtel, et al., 1988, Grybos, et al., 2009). These two elements can influence other element cycles in different ecosystems by either binding or releasing element concentrations, such as Zn and As that co-precipitate with or absorb onto their oxides, within the environment (Feijtel, et al., 1988, Holmgren, et al., 1993, Grybos, et al., 2007, Wang, et al., 2011b). In Louisiana marsh sediments, Mn and Fe of disturbed and undisturbed sites varied with higher levels reported in the disturbed sites due to different vegetation (Beck and Sneddon, 2000). A soil study done under anaerobic conditions in the lab found concentrations of Mn and Fe to increase while NO_3^- decreased (Grybos, et al., 2007, Grybos, et al., 2009). With Mn and Fe cycles under anaerobic conditions, phosphorus was linked to their association (Nilsen and Delaney, 2005) and sulfur (S) and Fe influenced each other's cycles (Boomer and Bedford, 2008). Cropland associated with coal mining found that Fe and Mn have been identifed to contribute to the toxicity of the soil and are impacted by S oxidation (Bhuiyan, et al., 2010).

1.4. Sulfur

Within different ecosystems, wetland or dryland, sulfur can undergo transformations through differing biochemical processes. Sulfur is naturally occurring within the soil parent material and shallow groundwater and can occur as accumulated salts such as gypsum (Bluemle, 1980). Sulfur availability is dependent on microorganisms and soil OM. It is altered by pH, Eh, Fe and Mn and goes through oxidation and reduction cycles. In addition, sulfur can influence zinc (Zn) and copper (Cu) availability along with other trace element concentrations (Craft, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a, Vasilas, et al., 2010, Davranche, et al., 2011) like mercury (Hg) (Cowdery and Brigham, 2011, Demers, et al., 2013) and cadmium (Cd) (Jacob, et al., 2013). Under anaerobic conditions in saturated soil, microbes influence S by reducing it from SO_4^{2-} to sulfide (S^{2}), generating the rotten egg smelling hydrogen sulfide (H_2S) gas. In drier aerobic systems, it is transformed from organic S to SO_4^{2-} or converted to elemental sulfur form, S^0. However, S^0 doesn't persist very long before it is converted to SO_4^{2-} (Craft, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a, Vasilas, et al., 2010, Davranche, et al., 2011). A long-term agricultural field study showed S in the topsoil decreased over 100 years while the levels in the subsoil increased during the same period. This could be attributed to S migration through leaching, tillage, and reduced atmospheric sulfur emission from a coal power plant closure (Zhuang and McBride, 2013). An increase or a decrease in sulfur concentrations may aid in identifying a wetlands soil timeline.

1.5. Phosphorus

Another element required by vegetation and mesofauna in both dryland and wetland ecosystems is phosphorus. The difference between the cycles of this nutrient and the cycles of N, S, and C is that it relies mainly on a sedimentary and some biological cycling. The P concentraton within the soil system is dependent on the season and water availaility (Winter and Woo, 1990, Woltemade, 2000). There is no major chemical form of gaseous P and thus, it cannot be lost from the system as a gas (van der Valk, et al., 1978, Craft, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a).

Phosphorus varies in forms and movement. In both systems, it is either in soluble or insoluble forms depending on pH, texture, Fe, Eh, calcium (Ca), aluminum (Al), magnesium (Mg), OM, and environmental impacts such as algae levels (van der Valk, et al., 1978, Craft, 2001, Brady and Weil, 2002, Nilsen and Delaney, 2005, Mitsch and Gosselink, 2007, Reddy, 2008a). Orthophosphates ($H_2PO^-_4$, HPO^{2-}_4, PO^{3-}_4) are the main forms of phosphorus found in the environment that easily move into the soil and/or water fraction (van der Valk, et al., 1978, Vepraskas and Faulkner, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Reddy, 2008a). Transported phosphorus can occur in sediment of overland flow or landscape runoff as dissolved orthophosphate (van der Valk, et al., 1978, Woltemade, 2000, Craft, 2001, Brady and Weil, 2002, Mitsch and Gosselink, 2007, Boomer and Bedford, 2008, Reddy, 2008a). A study at the North Dakota Cottonwood Lake Research Area found that wetlands surrounded by cropland landscape had higher concentrations of P in the topsoil vs a wetland linked to a grassland landscape (Freeland, et al., 1999). A cropland study compared samples, collected a hundred years apart, and found that P in the topsoil had increased over the years due to fertilizer and lime additions, and bioturbation (Zhuang and McBride, 2013). Phosphate fertilizers are of concern because they contain metals such as uranium (U) (Hamamo, et al., 1995), arsenic (As), molybdenum (Mo), selenium (Se), tungsten (W) (Charter, et al., 1995) cadmium (Cd), lanthanum (La), cerium (Ce), hafnium (Hf), europium (Eu), ytterbium (Yb), and samarium (Sm) which could subsequently end up in the wetlands (Nicholson, et al., 1994, Mortvedt, 1996, Abdel-Haleem, et al., 2001). Phosphorus changes in soil (sediment) can be another aid in identifying the wetland timeline history.

1.6. Analysis of Elements

Multi-element analysis can be an effective tool in studying soil chemistry. With advances in technology, multi-element analysis enables us to examine detailed wetland chemistry in an efficient manner. Either inductively coupled plasma atomic emission spectroscopy or inductively coupled plasma-mass spectrometry (ICP-MS) can analyze multiple metal and other element concentrations at one time (Entwistle and Abrahams, 1997, Beck and Sneddon, 2000).

1.7. History, Landscapes, and Wetlands

Freeland et al. (1999) stated that wetlands can show the past as well as present landscape practices in a soil timeline. A similar type of historical timeline is seen in marsh and estuarine sediments of Maryland (Khan and Brush, 1994). Wetlands have the potential to become sinks for many elements due to their depositional position in the landscape (Brinson, 1993a). By studying, the past and present biogeochemistry of soil profiles in wetlands and landscapes, the approaches for the development of wetland restoration can be improved (Brinson, 1993a).

A few historical events have created large enough impacts to be useful in dating soil profiles. Since 1861, tillage practices have been an influence that affects the movement of soil within the North Dakota landscape (State Historical Society of North Dakota, 2013). Gleason and Euliss (1998) identified wetlands surrounded by a tilled landscape have increased soil erosion from the upland and sediment deposition into the wetland when compared to wetlands surrounded by grassland. The upper landscape that contains grasses reducing water impact from runoff and catches sediment (Dahl, 2014). Another historical event is that during the Dust Bowl era (1931-1939), severe wind erosion from the Great Plains resulted in mass movement of fine soil particles deposited in different United States' areas (Baumhardt, 2003).

Since the beginning of the industrial revolution, studies have shown that element concentrations in soils have changed (Mast, et al., 2010). For instance in wetland soils, Callaway et al. (1998) identified past inputs of metals due to pollution in Northern Europe (i.e. England, Netherlands, and Poland). Similarly lead (Pb), Hg, and polychlorinated dibenzo-*p*-dioxin concentrations in high elevation lake sediments can be related to historical events such as Pb additives in gasoline and synthesis of chlorinated chemicals (Yang and Rose, 2003, Perry, et al., 2005, Mast, et al., 2010). With atmospheric testing of atomic weapons between 1954-1965, cesium (Cs) was deposited onto the soil across large areas of North America (Rose, et al., 1997, Hodgson, et al., 2001) and has often been used as a bench mark in studies of soil erosion (Ritchie and McHenry, 1990). Recent industrial production in electronics used lanthanides and rare earth elements which are now potentially leading to pollution (Bethencourt, et al., 1998). A study conducted in Maryland marsh sediment, reported that since 1900's a dramatic increase in sediment soil content of P, N, and total organic carbon (TOC) has occurred as well as, a significant increase in concentrations of Cu, Zn, and Pb since 1950 (Khan and Brush, 1994). All these events through human history aids in developing a historic wetland timeline with multi-element concentrations, multi-element fingerprinting.

Wetlands are linked to the surrounding landscape (Paradeis, et al., 2010), which in turn affect their ecosystem functions and services (Simenstad, et al., 2006, Mitsch, et al., 2012). Landscape influences hydrology, sediment, deposition, (Ruhe, 1969, Bedford, 1996), soil development (Vasilas, et al., 2010), and element concentration movement into and within wetlands (Glazovskaya, 1968, Gustavsson, et al., 2001) tying the wetland to the landscape. Wet (hydric) soils are influenced by water movement within the landscape (Vasilas, et al., 2010). However, there is still limited understanding of different ecosystem functions that may occur in natural, restored, or created wetlands (Mitsch, et al., 2012) and our understanding of the relationship between wetland ecosystems and the surrounding landscape is limited with the linkages needing to be better defined (Bedford and Preston, 1988). This connection can be observed through the transition of the biogeochemical functions of wetlands through sediment deposition and nutrient movement (Bowden, 1987, Brinson, 1993a). The landscape influences soil development, structure, vegetation, organisms, and function within the entire ecosystem (Glazovskaya, 1968, Feigum, 2000, Cook and Hauer, 2007). By studying the geochemistry in the landscape, it helps us understand how the elements move within a landscape and understand the relationship among and between various element components (Glazovskaya, 1968). As an example, a study of the behavior of Hg, C, N, and S in wetland with a forest landscape found that concentrations of Hg were greater in the upland forest than in the wetlands and that concentrations of Hg were positively correlated with C and N (Demers, et al., 2013).

Anthropogenic activities affect wetland ecosystems functioning. There is a demonstrated difference between native grassland, cultivated land, and wetland landscapes (Martin and Hartman, 1987b, Gwin, et al., 1999, Mita, et al., 2007). Drainage of a wetland alters the hydrological characteristics of landscapes (Euliss and Mushet, 1996). Once the landscape or wetland is altered, transport mechanisms for deposition and sedimentation impact the wetland functions (Martin and Hartman, 1987b). Tillage is a widely used agricultural practice and has major effects on soil erosion, and influences fertilizer and pesticide movement, (Euliss and Mushet, 1996), soil texture changes (Martin and Hartman, 1987b), water runoff within the landscape (Winter, 2001), wetland drainage (Euliss and Mushet, 1996, Dahl, 2014), and wet/dry cycles of soil. Installing tile drainage in wetlands alters the wetland functions (Galatowitsch and Valk, 1996, Dahl, 2014). In addition, the type of wetland (flowthrough, discharge, recharge) is impacted by the water movement over or within the landscape (Arndt and Richardson, 1988). A Minnesota study found that in an intensively tilled field, 20cm of soil has translocated from the upper slope to foot and toe slope when compared with an untilled landscape (Papiernik, et al., 2007). Differences in soil texture and soil deposition were found in wetlands with a cultivated landscape by higher soil clay percent and five times the soil sedimentation rate when compared to wetlands associated with grassland landscapes (Martin and Hartman, 1987b).

Gustafson and Wang (2002) showed that anthropogenic activities have influenced wetland vegetation by increasing deposition of nutrients such as phosphate (PO_4^{3-}) and NO_3^- into wetlands through soil displacement. Other research has identified that undisturbed grassland landscapes have higher total N and OM content within the topsoil when compared to a cultivated landscape (Martin and Hartman, 1987b). According to Bedford et al. (1999), undisturbed wetlands with high plant diversity tend to have lower concentrations of soil nutrients when compared to wetlands with low plant diversity being linked to croplands. Species richness tends to be an indicator of soil nutrient availability meaning there is a decline in species when soil nutrient availability increases beyond the needs of the ecosystem (Bedford, et al., 1999). Further, altered landscapes by residential development and aquaculture (shrimp and fish farming) in proximity to mangrove wetlands have shown soil changes in metal accumulation of Cu, Zn and Pb over 19 years (Ren, et al., 2011, Xin, et al., 2014).

1.8. Hydrology

Hydrology plays a major role in wetland function and formation (Winter, 1988, Brinson, 1993a). Hydrology affects vegetation and movement of chemical element concentrations, clays, and salts laterally and vertically within the landscape topography (Arndt and Richardson, 1988, Hubbard, et al., 1988, Winter, 1988, Winter and Woo, 1990, Brinson, 1993a, Euliss and Mushet, 1996, Richardson, et al., 2001, Mitsch and Gosselink, 2007). Within the ecosystem, element biogeochemical processes are also impacted by water movement and soil development and formation (Arndt and Richardson, 1988, Hubbard, et al., 1988, Winter and Woo, 1990, Winter, 2001).

Hydrology plays a role in the overland flow affecting the landscape through erosion that cause sedimentation in and possibly degradation of wetlands and changes in their chemistry (Godwin, et al., 2002, Byrd and Kelly, 2006, Dahl, 2014). Within tilled landscapes, there is reduced plant cover and water infiltration compared to undisturbed, natural, landscapes causing runoff down the landscape, which subsequently results in varied seasonal water levels in wetlands. This water level fluctuation (changes in maximum and minimum water depth) has direct impact on wetland vegetation. Wetlands with a tilled landscape) had water levels varying by 14.14 cm while wetlands with grass landscapes had water level variation of 4.27 cm. In addition, sedimentation rate is increased in tilled landscapes (Euliss and Mushet, 1996). This creates differences between wetlands with different degrees of disturbance and impacts the condition of the wetland (Dahl, 2014). A study by Freeland et al. (1999) found significant differences in the soil profile development of the A horizon and variations of soil texture and OM between cultivated and grassland landscapes. There was soil accumulation due to erosion, tillage, sedimentation, deposition, and vegetation differences in the wetland.

1.9. Restoration

Wetland restoration requires consideration of many factors. Often the relationship between wetland and landscape functions are not thoroughly understood (Bedford and Preston, 1988, Matthews, et al., 2009). For instance, landscape affects the hydrologic regime, which affects the vegetation biodiversity, soil, water quality, and wetland ecosystem (Gleason and Euliss, 1998, Bedford, 1999, Zedler, 2000, Matthews, et al., 2009, Paradeis, et al., 2010, Cowdery and Brigham, 2011). The landscape also impacts the size, variability, hydrology, multi-element composition, and biological diversity of the wetland ecosystem (Bedford, 1999). Including the landscape as one of the factors in restoration would be beneficial in determining the success of restoration measured through wetland biodiversity (Gwin, et al., 1999, Godwin, et al., 2002, Paradeis, et al., 2010).

In order for wetland restoration to be successful, knowledge about the biogeochemistry in the undisturbed native condition should be included. Little is understood of how the different elements other than the ‘usual suspects’ (such as N, P, and C) play a role in wetland functions. Knowledge about biogeochemistry, also in relation to less-studied elements, is essential for our understanding of wetland function. Wang et al. (2011a) looked at rare earth elements (REE) of soil in Xianghai wetlands in China and found that the wetlands had lower concentrations of REE when compared to upland soil at depth. While comparing disturbed and undisturbed lakes, it was found that using multi-element chemical analysis as a tool, aided in improving the understanding of how natural and anthropogenic influences affect lakes (Mikac, et al., 2011). By establishing a soil element concentration baseline, we can begin to establish an understanding of how the parent material, soil type, vegetation, landscape, and climate along with the impacts by anthropogenic activities influences the wetlands and start to create a wetland timeline (Gustavsson, et al., 2001). If the past and present biogeochemistry in the ecosystem can be identified, it can aid in the way the restoration is carried out and assessed (Bedford, 1999).

The findings from previous studies on wetlands lack thorough analyses of the chemical elements. For instance in German river sediments, Al, Na, potassium (K), Ca, Mg, Mn, and Fe were studied and found to be at parent material background concentrations while Zn, Cu, and Pb were higher (Devai, et al., 2005). Callaway et al. (1998) studied European wetlands that included soil analysis of Cu, Cd, chromium (Cr), Cs, Fe, Pb, Mn, nickel (Ni), and Zn. They further identified historical metal inputs of identified pollutants. Another study on cobalt (Co), Cu, Cr, Fe, Mn, Ni, Pb, thorium (Th) and uranium (U) concerning the influence of metals and OM in soils showed redox processes and pH influenced the mobility of the element concentrations (Grybos, et al., 2007). Martin and Hartman (1987a) studied arsenic (As), Cd, Pb, Hg and selenium (Se) to find the level of metal concentrations in the PPR. A study on As, Cd, Pb, Hg, and Se only in the topsoil observed differences between element concentrations in prairie pothole and riverine wetlands (Martin and Hartman, 1984). Jacob et al. (2013) identified Cd, P, and Zn in the wetland topsoil to be possibly tied to cultivated landscapes with Cd concentrations tied to the underlying parent material or fertilizer additions. In conclusion, the biogeochemistry of most element concentrations in wetlands and their associated landscape has not been adequately researched.

A baseline to establish the historical health of wetlands in the PPR is essential to understand the anthropogenic and natural impacts over time. Wetland quality assessment techniques, such as the Index of Plant Community Integrity (IPCI) do not typically include the element composition within of soils (Mita, et al., 2007, Hargiss, et al., 2008). Chemical disturbances occurring within a system may not be immediately evident through vegetation changes, but may still be important for maintaining ecosystem services, and therefore the successful protection, preservation, and restoration of wetlands. Wetland soil timelines are not clearly obvious from physical observations of wetland soil profiles, as is common in dryland soils, because hydric wetland soils typically display very poor differentiation of deposited layers. However, changes in the chemistry or soil texture throughout the soil profile may show differences in the characteristics related to specific periods of anthropogenic activity.

1.10. Historical Dating Methods

Pollen, soil grain size, isotopes, and radioactive dating are a few methods used to identify historic events within the wetland ecosystem timeline. A Mediterranean wetlands study concerned with food web was able to tie concentration of accumulated As, Cd, Zn, Cu, and Pb within crayfish tissues to nitrogen isotope signatures (Alcorlo and Baltanás, 2013). To date soil sediments with ^{210}Pb, ^{137}Cs, or pollen, a historic wetland timeline may be developed. In developing a timeline, pollen can be used to identify change in wetland plant species. However, sometimes pollen count shifts have been linked to large storms. Pollen concentration and type, along with seeds have been used to figure out marsh development, related to open or shallow water (Khan and Brush, 1994). In northern Colombia, pollen identification from wetland soil cores established when the wetland first developed (Berrío, et al., 2001). To understand environment and vegetation change pollen, soil grain size, ^{210}Pb, and ^{137}Cs within wetland sediment identified 240 years of wetland history (Wang and Zhai, 2008). In south-eastern England peatlands, pollen profiles were used to see vegetation taxa shift but found that with different peatland sites it was difficult to find reproducibility of exact pollen profile (Waller, 1998).

Since the atmospheric nuclear bomb testing period, ^{137}Cs has been used as a dating and soil movement mechanism in landscape studies to identify sedimentation rates (Ritchie and McHenry, 1990). In the Xianghai wetlands in China, ^{137}Cs study by Wang et al. (2004) showed two different soil cores depths of 12-14 cm and 24-26 cm had the highest concentrations of ^{137}Cs, hence, tying the soil depth back to 1963 when there was nuclear testing fallout. In wetlands, ^{137}Cs, ^{90}Sr, and $^{239,240}Pu$ are used to date historic events of the nuclear testing, and identified the release of radionuclides incidents from Chernobyl in Ukraine and Kyshtym in Russia (Schell, et al., 1997).

1.11. Aims, Objectives, Outcomes

This study aims to assess if multi-element chemical fingerprinting of vertical soil profiles of prairie pothole wetlands can determine the depth of disturbance, restoration potential, and wetland soil history timeline. The overall hypothesis of the proposed project is that undisturbed wetlands will be different from disturbed wetlands. There will be vertical profile changes in multi-element composition in the undisturbed wetland, whereas disturbed wetlands will show distinct higher levels of element concentrations vertically relating to anthropogenic activity on the surrounding landscape. A wetland history timeline can be established with wetland soil sediment multi-element concentrations, which would aid in understanding the potential of multi-element concentration within the wetland system. Disturbed landscapes will have an impact of the wetland multi-element composition. Due to tillage, soil movement has accelerated deposition of sediments within the wetland. Within the soil, wetland sites close to roads may show elevated Pd concentrations, which are associated with catalytic converters, while wetlands in the western parts of ND might show sudden changes in U concentrations, because of past and current lignite mining activities. Agricultural activity can lead to increased concentrations of P, as well as As, Ce, Co, Cr, Eu, Hf, Hg, La, Ni, Pb, scandium (Sc), U, and vanadium (V) from PO_4 fertilizer application (Hamamo, et al., 1995, Mortvedt, 1996, Abdel-Haleem, et al., 2001). The recent soil layers/sediments may also contain elevated element concentration such as rare earth elements that are being used in recent technological advances, for example electronics.

The objective of our study was to assess if multi-element fingerprinting may be able to discern differences in soil profiles indicative of disturbances. The main research questions to be answered are: 1) What are the vertical variations of multi-element composition of wetland soils measured; 2) Are there differences between good quality, relatively undisturbed wetlands and poor quality, disturbed wetlands; 3) Can multi-element fingerprints be used to determine the feasibility of restoration; 4) Are there differences with disturbed or undisturbed landscapes; 5) Can multi-elements composition be tied to past historic events?

There are a few outcomes with this study. The multi-element concentrations are affected by plowing. We can roughly use 1861 as a date when the PPR in North Dakota was first tilled with maximum plowing accruing around 1910-1920 (State Historical Society of North Dakota, 2013) which allows us to tie tillage impacts of element concentrations to a timeline. As an example, Garcı´a-Marco et al. (2014) found Zn concentration in the topsoil higher in a reduced tilled field than in a tilled field. In the topsoil of a moldboard plowed field, Loke et al. (2013) found higher concentration of Cu when compared to a field with reduced till. Also, the addition of fertilizer influences cadmium, which aids in relating it to a multi-element timeline (Nicholson, et al., 1994, Mortvedt, 1996, Abdel-Haleem, et al., 2001).

Factors such as vegetation and landscape can be used to influence multi-element chemistry. Iron is influenced by vegetation and that Fe concentrations will be higher within the soil profile of a undisturbed wetland due to continuous vegetation over a growing season with iron plaque accumulation near the plant roots vs a tilled field (Kissoon, et al., 2010). In addition, cadmium concentrations will increase due to drier conditions with increasing elevation in the landscape (Jacob, et al., 2013).

A wetland timeline will identify events within human history timeline. Layers of volcanic ash are an identifier and Bluemle (1988) identified a layer of volcanic ash within the soil of south-central North Dakota. Wetland soil in the United State, since 1860, has had a steady increase of lead concentration and with higher concentrations occurring around 1978 which is related to the increase in industrial manufacturing and the change in gasoline additives (Schell, et al., 1997). With atmospheric testing of atomic weapons, record deposition occurred between 1963-1965, Cs-137 is another element that can be used for development of a timeline (Rose, et al., 1997, Hodgson, et al., 2001).

Overall, this study is to identify the baseline of multi-element concentrations in wetlands and observe if there is a difference in wetlands indicative of disturbances. In addition, understanding how the landscape plays a role with multi-elements composition within the wetlands can be useful in generating a wetland timeline using multi-element fingerprinting.

The following chapters address the relationship of multi-elements within the wetland and surrounding landscape that can aid in wetland restoration and provide guidance for wetland management. The chapters of this study each address 1) identify biogeochemical characteristics of PPR wetlands; 2) identifying differences or similarities in biogeochemical characteristics of the landscape; 3) assess the vertical variation in chemical composition at depth and 4) interpret the soil chemistry of undisturbed sites (good quality; prairie vegetation) and disturbed sites (poor quality; cultivated) relative to differences in landscape position locations. The chapters are broken down by landscape position: Chapter 1 Wetland, Chapter 2 Wetland and Fringe landscape, Chapter 3 Footslope and backslope, and Chapter 4 an overall wrap-up of the landscapes.

1.12. References

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2. MULTI-ELEMENT COMPOSITION OF PRAIRIE POTHOLE WETLAND SOILS ALONG DEPTH PROFILES REFLECTS PAST DISTURBANCE TO A DEPTH OF AT LEAST ONE METER[1]

2.1. Abstract

Wetlands are influenced by direct disturbances due to agricultural practices, as well as by indirect effects from the surrounding landscapes. Management and restoration require condition assessments, which are usually based on properties of the vegetation and soils near the surface. Less knowledge exists about the effects of disturbance deeper down the soil profile. In this study, multi-element analysis along soil profiles was used to assess changes due to past disturbances. Soil cores were obtained from undisturbed and disturbed Prairie Pothole wetlands in North Dakota, USA. The objectives were to: 1) assess the vertical variation in multi-element composition of wetlands soils, 2) interpret the differences between undisturbed and disturbed wetlands and: 3) determine the relationships between the environmental variables and multi-element concentrations. We expected that data on concentrations of elements, in addition to 'classical' assessments (organic matter, particle size distributions, profile descriptions) would provide more detailed information about the depth to which past disturbance could be detected. Classical methods of assessment of disturbance identified impacts down to 60 cm depth, but the concentrations of Ca, Ba, Sr, Nb, La, Pr, Tb, Bi, Tl and Th showed that differences due to past disturbances persist to a depth of at least one meter.

2.2. Introduction

Wetlands provide major ecosystem services, such as improving water quality, recharging existing aquifers, enriching plant diversity, regulation of carbon sequestration, and flood control (Oki and Kanae 2006, Gleason et al. 2008), but have been impacted through anthropogenic activities such as tillage, drainage, and fertilizer use.

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[1] The material in this chapter was co-authored by Carrie Werkmeister, Donna Jacob, Larry Cihacek, and Marinus Otte. Carrie Werkmeister had primary responsibility for collecting samples in the field. Carrie Werkmeister was the primary developer of the conclusions that are advanced here. Carrie Werkmeister also drafted and revised all versions of this chapter. Donna Jacob, Larry Cihacek, and Marinus Otte served as proofreader and checked the math in the statistical analysis conducted by Carrie Werkmeister.

This is particularly true for the Prairie Pothole Region (PPR), the US portion of which is located across Montana, North Dakota, South Dakota, Minnesota, and Iowa, and which consists of about 2.6 million ha (Dahl 2014). Wetlands make up 9% of the surface area of the PPR and were formed during the last glacial period (Sloan 1970, Dahl 2014). These wetlands receive water mainly as precipitation in the form of rain and snow. Their chemical characteristics are unique to PPR soils, reflecting the underlying glacial material (Richardson and Arndt 1989, Winter and Woo 1990). Over time, the number of wetlands in the PPR has been reduced by about 50%, mainly due to agricultural practices (Martin and Hartman 1987a, Dahl 1990, 2014). The PPR of ND has been cultivated for more than 100 years (Stewart and Kantrud 1971). Rainfall solubilizes naturally occurring soil salts or nutrients in surface runoff, and transports soil sediments from the surrounding landscapes into the wetlands. In addition, vegetation and near sub-surface hydrology affect wetland biogeochemistry (Wang and Zhai, 2008, Wilson et al. 2008, Jacob et al. 2011).

Wetlands have an intimate relationship with the surrounding landscapes (Bedford, 1996) in relation to topography, soil development, hydrological properties, and parent material (Bedford 1996, Cook and Hauer 2007). In the PPR, cropping and cattle grazing are the main factors affecting hydrology, sedimentation, soil quality, and biodiversity (Brinson 1993a, b, Brubaker et al. 1993, Bedford 1999, Guntenspergen et al. 2002, Byrd and Kelly 2006, Skagen et al. 2016). Wetlands disturbed by tillage generally have evidence of deposition of soil from erosion (Brubaker et al., 1993, Skagen et al. 2016).

Wetland quality assessment techniques, such as the Hydrogeomorphic Approach to Assessing Wetland Functions of Prairie Potholes (HGM, Gilbert et al. 2006) and the Index of Plant Community Integrity (IPCI) developed for the PPR (DeKeyser et al. 2003, Mita et al. 2007, Hargiss 2009) do not typically include the chemical composition of soils and sediments. These rank wetlands according to wetland plant communities into categories ranging from very good to very poor. Wetlands of very poor condition typically had their soils disturbed by intensive agricultural activities, such as cropping, while wetlands of very good condition have not (DeKeyser et al. 2003).

Our previous research (Yellick et al. 2016) showed that the element composition of surface soils in seasonal, recharge wetlands of the PPR in the very good and very poor categories differed markedly, with very good wetlands having high organic matter (OM) content, high sulfur (S), and selenium (Se) concentrations, but low metal concentrations. Very poor wetlands showed the reverse, with low OM content, low S and Se concentrations, and high metal concentrations. As the previous work only focused on surface soils, the research presented here focused on variation in element composition with depth across the soil profile, comparing undisturbed native prairie wetlands with wetlands that had been tilled and had poor composition of the vegetation. The objectives of this study were to: 1) determine the vertical variation in the multi-element composition of PPR wetland soils; and 2) compare the vertical multi-element profiles of 'very good' undisturbed wetlands (UW) and 'very poor' disturbed wetlands (DW). Such information is important for restoration of wetlands and may be used to determine the impacts of past disturbances and to what depth such disturbances would have impacted and persist in the wetlands. We expected the following outcomes: 1) Based on Yellick et al. (2016), disturbed wetlands (DW) would have lower OM content, lower concentrations of S and Se, and higher metal concentrations compared to undisturbed wetlands (UW), at least near the surface, 2) Due to increased soil porosity near the surface, more mobile elements, such as Na and K would have migrated down the profile, resulting in higher concentrations of such elements lower in the profile of DW compared to UW, and 3) Multi-element analysis of soils will provide more detailed information about the depth to which disturbances of wetland soils have been impacted, than assessments based on vegetation, near-surface soil characteristics, particle size distributions and visual descriptions of soil profiles.

2.3. Materials and Methods

2.3.1. Field and Lab Analysis

This study focused on seasonal, recharge wetlands on the Missouri Coteau of North Dakota, previously included in studies by DeKeyser and co-workers (DeKeyser et al. 2003, 2009) and our research group (Jacob et al. 2013, Yellick et al. 2016). Twelve wetlands between latitudes 47.3^{o} to 47.9^{o} N and longitudes 100.5^{o} to 101.1^{o} W, were evaluated (Table 2.1). The soils of the landscape surrounding both the UW and DW are of glacial moraine origin. Predominant soil series include complexes of the Williams (fine-loamy, mixed, superactive, frigid Typic Argiustolls), Zahl (fine-loamy, mixed, superactive, frigid Typic Calciustolls), Zahill (fine-loamy, mixed, superactive, frigid Typic Calciustepts), Bowbells (fine-loamy, mixed, superactive, frigid Pachic Argiustolls) and Max (fine-loamy, mixed, superactive, frigid, Typic Haplustolls) series. The Williams and Bowbells have a Bt (argillic) horizon occurring between 15 and 60 cm below the soil surface while all the series have a Bk (calcareous) horizon occurring from at a 10 to 60 cm depth.

Six wetlands classified as disturbed wetlands (DW) and six wetlands as undisturbed wetlands, (UW), previously identified by DeKeyser, et al. (2003) as being either of very poor or very good condition, were selected, as they represent the extremes in condition, making it more likely that we would find clear differences, if any such differences did indeed occur. In 2012, after a period of relatively low rainfall, most seasonal wetlands were dry, making access by vehicle possible. During August and September 2012, seven soil cores to about 1m depth were obtained by using a truck-mounted hydraulic Giddings probe within the interior portion of each wetland (Figure 2.1). Soil organic matter (OM) content based on loss-on-ignition (LOI), pH and electrical conductivity (EC) were determined in samples of all seven cores for each wetland, two cores were randomly chosen for soil description (Schoeneberger, et al., 2012), one

Table 2.1. Study sites, level of disturbance (Undisturbed Wetland, UW, or Disturbed Wetland, DW) and coordinates.

Undisturbed Wetland (UW) or Disturbed Wetland (DW)	**Latitude**	**Longitude**
UW	47.79321	-100.861
UW	47.39968	-100.647
UW	47.63833	-100.578
UW	47.89241	-101.047
UW	47.78067	-100.929
UW	47.59677	-100.815
DW	47.32008	-100.658
DW	47.36403	-100.81
DW	47.82481	-101.109
DW	47.75436	-101.063
DW	47.76762	-101.128
DW	47.66138	-100.476

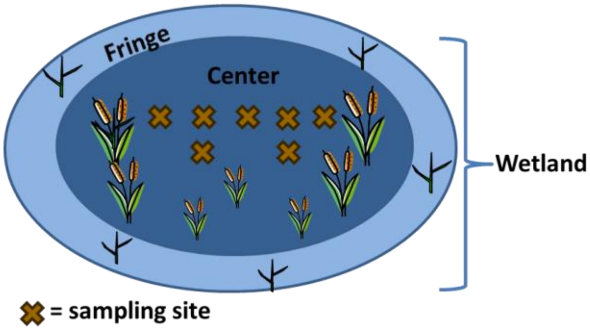

Figure 2.1. Schematic representation of wetland sampling locations relative to the wetland fringe and boundaries.

core of which was used for texture analysis. The remaining five cores were used for determination of bulk density (BD) and multi-element analysis by Inductively Coupled Plasma (ICP) analysis.

The soil cores were contained in metal free, acetate liners to prevent moisture loss and external contamination, sealed, and labeled, and stored in a cold room (2^{o}C) until processed. For soil sampling, the soil cores were segmented in 10 cm increments from the mineral surface to a depth of 30 cm, and then at 15 cm increments to a depth of 1 m (Figure 2.2).

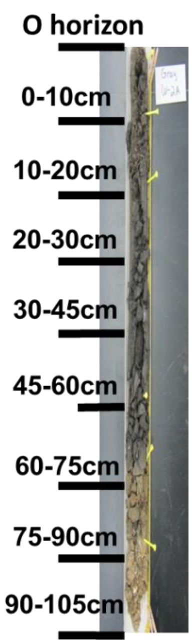

Figure 2.2. An example of a soil core and sub-sample divisions.

If present, organic matter on the mineral surface (O layer) was separated and analyzed separately. The soil samples were air-dried, hand crushed and passed through 2 mm stainless steel sieves to prevent trace metal contamination, which often occurs from standard brass sieves and mechanical grinders (Thompson and Bankston 1970, Hickson and Juras 1986). Subsamples were analyzed for pH and electrical conductivity (EC) on 1:1 basis (Watson and Brown, 1998, Whitney, 1998). Bulk density (BD) analysis followed the abbreviated core method of Blake and Hartge (1986). Organic matter was determined by loss of weight on ignition (Combs and Nathan, 1998). Particle-size analysis was obtained by the hydrometer method of Gee and Bauder (1986). A subsample was milled using carborundum to <180 μm for aqua regia digest and analysis by Inductively Coupled Plasma Mass - Spectrometry (ICP-MS) by Activation Laboratories, Ancaster, Ontario, Canada (actlabs.com), Ultra Trace 2 method, for multiple elements. The methods used were exactly the same and had the same detection limits as those used in our previous study (Yellick et al. 2016).

2.3.2. Data and Statistical Analysis

All element concentrations were received from Activation Laboratories in either ppm or ppb, which were converted to μmol g^{-1}. If more than half the concentrations for a given element were below the detection limit of that element, data on that element were excluded from further consideration. If less than half of the element concentrations were below the detection limit, but the remainder of the values were within detection limits, then the values below detection were replaced with half the detection limit and included in the analysis (Farnham, et al., 2002).

Because of limitations in resources and logistics, not all analyses could be carried out on all samples. For example, the cores analyzed for texture could not be used for element analysis as well, and financial and time constraints meant that not all layers could be analyzed for texture. In addition, due to local soil conditions, not all cores could be collected to the same depth. However, as the focus of our study was to compare wetlands in the two categories of condition, Undisturbed Wetlands (UW) and Disturbed Wetlands (DW), the data were averaged for each depth in each wetland. In some wetlands, only one sample reached to below 105 cm, but we had at least one sample at that depth for every wetland. For most other layers, we had four to five samples per wetland. Therefore, the data were averaged for each depth in each wetland, so that wetlands within each category and at every depth were replicated, n=6.

Statistical analyses followed procedures described by Sokal and Rohlf (1995), and Reimann et al (2008). Relationships between the environmental variables and element concentrations were assessed using redundancy analysis (RDA), following ter Braak and Smilauer (2002, 2012) and our previous studies (Kissoon et al. 2015; Yellick et al. 2016), using Canoco 5. The RDA models were determined by the manual forward selection procedure with Monte Carlo permutation tests.

To compare differences between layers of the two categories of wetlands, we used Analysis of Variance, where possible. For that purpose, if the data were not normally distributed, they were either $\log^{10}$ or Johnson transformed to obtain normal distributions with Minitab, Version 18, statistical software. If no suitable transformation could be obtained, differences between wetlands at the same depth were tested for significance by the non-parametric Kruskal-Wallis test. Comparison between entire profiles of the two categories is complicated by the fact that variables along profiles are not independent. Therefore, the mean values along profiles in the two categories were compared using the non-parametric Friedman's test, where wetland category (UW or DW) was considered the 'treatment' and the layers within the profiles 'blocks'.

2.4. Results

Quality control was carried out by Activation Laboratories as a standard practice of their procedures. This project included more samples than the ones reported on in this publication, and three more such certification reports were supplied by Activation Laboratories. All four showed the same information, with values for all elements falling within acceptable ranges.

2.4.1. O-Horizon

Because an O-horizon was lacking in several wetlands, there were not enough values to test differences between UW and DW. These data will therefore not be discussed further.

2.4.2. Mineral Soil Below the O-Horizon

2.4.2.1. pH and EC

The pH of undisturbed wetlands (UW) was significantly lower (5.8-6.1) than that of disturbed wetlands (DW) in the 0-10 and 10-20 cm layers (7.1-7.3, $P<0.05$), but not at lower depth (averaging around 7) (Figure 2.3).

Electrical conductivity (EC) was measured on the same samples (Figure 2.4). EC data were not normally distributed, and no suitable transformation could be identified. Therefore, differences in EC between UW and DW were tested using the non-parametric Kruskal-Wallis test, and not found to be

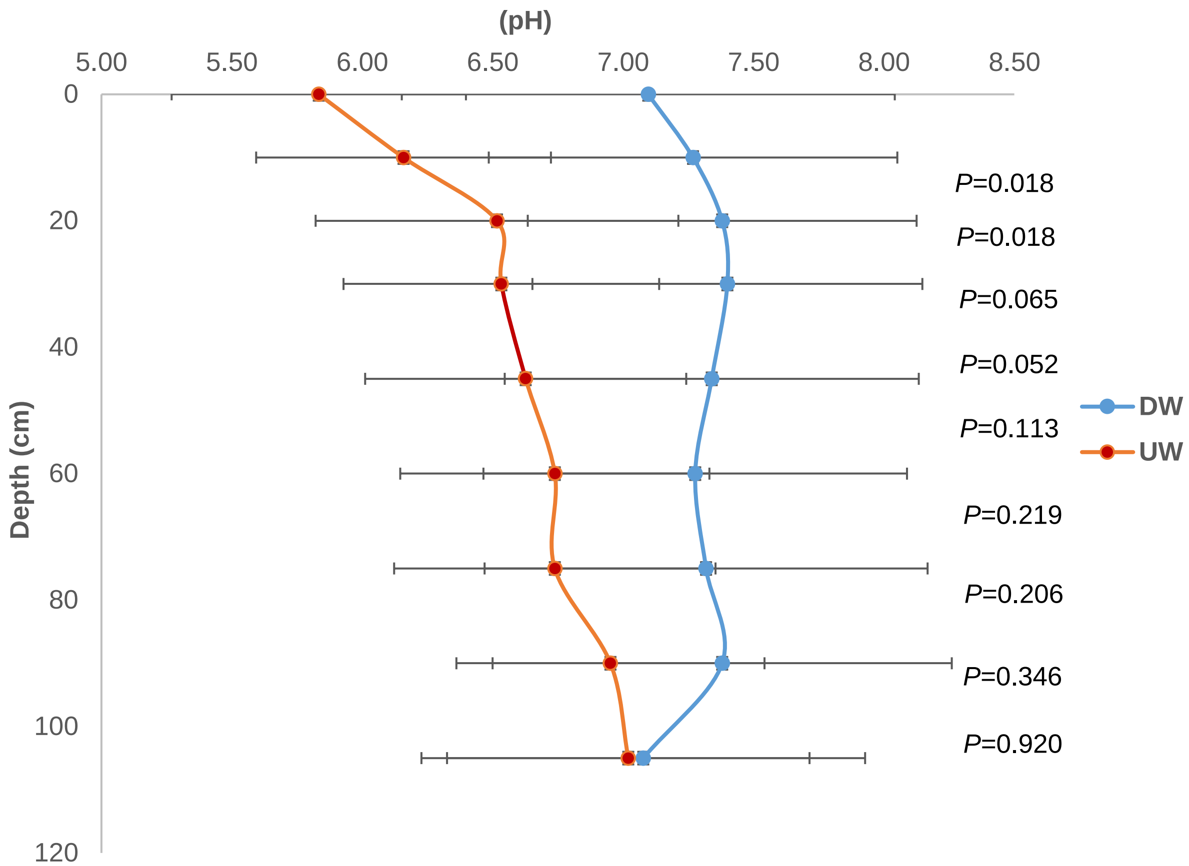

Figure 2.3. Average pH for undisturbed wetlands (UW) and disturbed wetlands (DW) with depth. Bars indicate standard deviation. The value at 0 = 0-10 cm below the mineral surface, 10 = 10-20 cm, 20 = 20-30 cm, 30 = 30-45, 45 = 45-60cm, 60 = 60-75cm, 75 = 75-90cm, 90 = 90-105cm, and 105cm = >105 cm to a maximum of 120 cm. Differences between UW and DW at each depth were tested by One-way ANOVA, n=6, normally distributed, so not transformed, *P*-values provided at each depth.

significant at any depth. But when tested by Friedman's Test on the means for each depth, the EC of UW (254 to 272 µS cm^{-1}) was significantly lower (*P*=0.003) and less variable than that of DW (400-860 µS cm^{-1}).

2.4.2.2. Texture, Bulk Density and Organic Matter Content

The sand (21-32 %) and silt (33-53%) fractions along the profiles did not differ significantly between UW and DW, but the clay fractions, ranging between 21 and 41%, were significantly higher in the top mineral layer at 0-10 cm below the mineral surface of DW compared to UW (Figure 2.5). The bulk density (BD, Figure 2.6), which ranged from 0.76 to 1.66 g cm^{-3}, did not differ significantly between UW

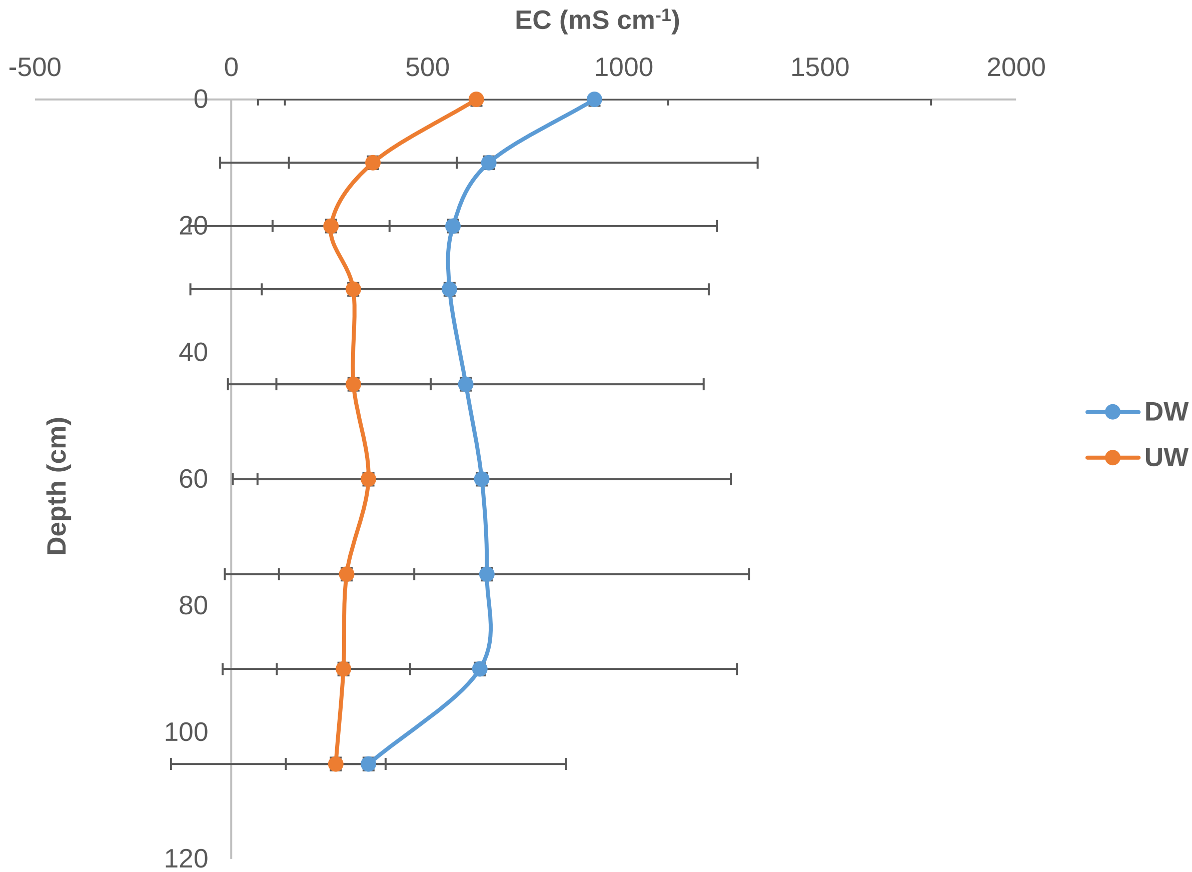

Figure 2.4. Average Electrical Conductivity (EC) for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (not normally distributed, and no suitable transformation, Kruskal-Wallis Test), but across the entire profile were at *P*=0.003, when tested by Friedman's Test.

and DW when tested for each layer (one-way ANOVA, untransformed), but across the entire profile, the BD of UW was significantly higher than DW (Friedman's Test, *P* = 0.020).

Organic matter (OM) as determined by loss on ignition (Figure 2.7) was significantly higher in the 0-10 cm layer of UW than DW, but not at any other depth.

2.4.2.3. Element Concentrations

The concentrations of Au, Ge, Hg, Hf, In, Lu, Re, Ta, Tm, W were below the detection limit and these elements were therefore excluded from further analysis.

Initial exploration of the remaining elements was done using RDA (Table 2.2), for all the data of all sites combined (Figure 2.8), and separately for the Undisturbed Wetlands (UW, Figure 2.9) and for the Disturbed Wetlands (DW, Figure 2.10). When all data from both undisturbed and disturbed together were

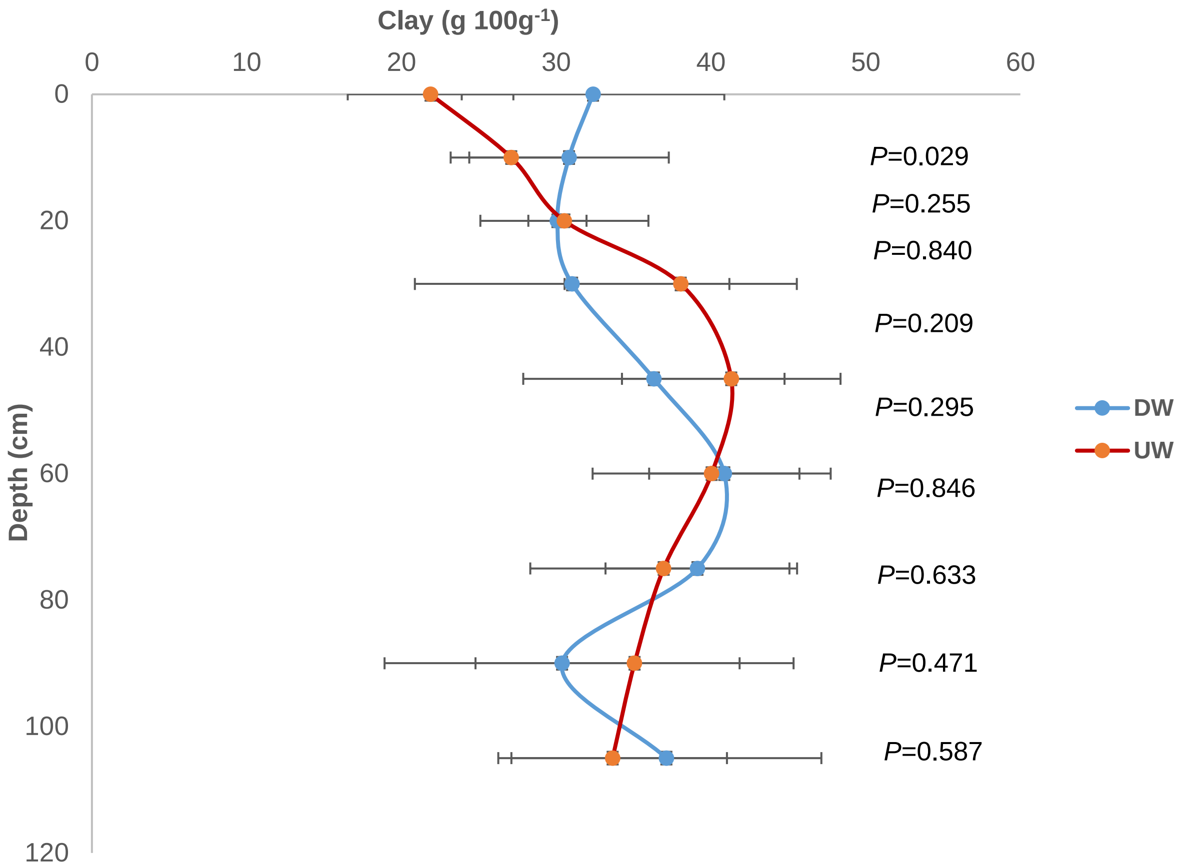

Figure 2.5. Average Clay content for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth were tested by One-way ANOVA, n=6, data were normally distributed, no transformation, *P*-values provided at each depth.

analyzed, EC was the most important factor explaining variation among the elements, followed by depth, clay, site and OM. When the data were analyzed separately for UW and DW, the importance of the environmental variables changed, with OM explaining most of the variation in element concentrations in undisturbed wetlands, and EC in disturbed wetlands, and other factors explaining much smaller amounts of variation. Several relationships stand out: (1) Nb is correlated with OM in all three RDAs; (2) Na correlates with EC in all three RDAs; and, (3) S correlates with OM in undisturbed wetlands, but with EC in disturbed wetlands. It is further evident from the RDA analysis that metals of the transition and lanthanide series cluster together and that site and depth explain a small but significant amount of variation.

2.4.3. Spatial Variation

We further explored the variation between wetlands, undisturbed and disturbed, and with depth along the soil profiles. The following elements showed no significant variation between the types of wetlands or with depth: Ag, Al, As, Be, Cd, Ce, Cu, Cs, Dy, Er, Eu, Ga, Gd, Ho, K, Mn, Mo, Nd, Pb, Rb, Sb, Sm, Sn, Te, U, Y, Yb, and Zn. But Friedman's test showed significant differences for concentrations along the soil profile (UW and DW as 'treatments', Depth as 'blocks') for Na (Figure 2.11), S (Figure 2.12), Ca (Figure 2.13), Ba (Figure 2.14), Sr (Figure 2.15), La (Figure 2.16), Pr (Figure 2.17), Tb (Figure 2.18), Bi (Figure 2.19), Tl (Figure 2.20), Nb (Figure 2.21) and Th (Figure 2.22).

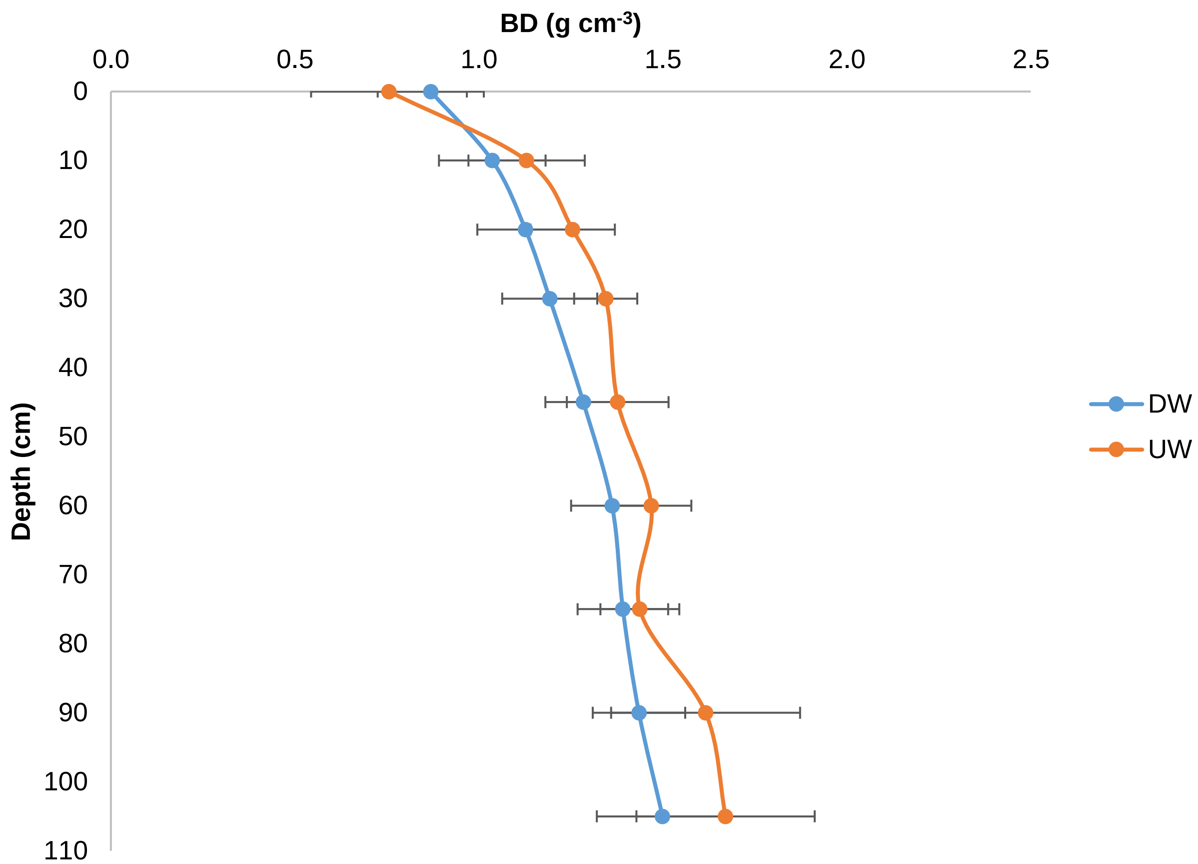

Figure 2.6. Average Bulk Density (BD) for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (One-way ANOVA, no transformation), but across the entire profile were at *P*=0.020, when tested by Friedman's Test.

2.5. Discussion

2.5.1. pH and EC

Both pH and EC varied both vertically and horizontally, and were significant factors in explaining the distribution of elements. However, it must be noted that we determined both using protocols that are standard for dry, well-aerated soils, and involve drying and homogenization. Under wetland conditions, the pH tends to be buffered around neutral (Reddy and DeLaune 2008), but drying will oxidize the soil, and alter the pH. Similarly, the EC of a soil changes with the moisture content. Both pH and EC in our study therefore are indicators of differences between the soils, but they are not measures of *in-situ* values. The lower pH in the top layers of the undisturbed wetlands compared to the disturbed wetlands suggests that, at least upon drying and homogenization of the soils, more protons were available. One likely source is organic matter (Brubaker, et al. 1993), the content of which was higher in the top layer of the undisturbed wetlands than the disturbed wetlands.

The EC of disturbed wetlands was generally higher than that of undisturbed wetlands throughout the soil profile. The differences can be explained by tillage on the surrounding landscapes, which increases movement of salts into the wetlands. The groundwater table influences the water level in the wetlands (Stewart and Kantrud 1971, Niemuth et al. 2010), which is altered by cultivation. Undisturbed wetlands and surrounding landscapes have a permanent vegetation cover which utilizes moisture throughout the growing season. This slows down percolation of water down the soil profile, preventing soluble salts from moving downwards to the water table (Winter 1988). When disturbed by tillage, the vegetation cover is changed from a permanent to a seasonal cover that does not utilize all the precipitation that occurs over the effective plant-growing season. Annual crops in this area typically are cereal grains (spring wheat, barley) with a short growing cycle (~90-days), which means there is a greater chance that precipitation does not get utilized, in turn resulting in deep percolation. This raises the water table resulting in lateral water movement along subsurface layers of reduced permeability (Arndt and Richardson 1988, Winter 2001). In this region, glacially derived soil parent materials are of marine origin (primarily Pierre shale) which are saline with elevated Na content. When water moves through these materials, salts are leached from the parent material. As a result, salts are moved to the wetlands from the surrounding land. In addition, capillary rise of water from the water table to the soil surface due to

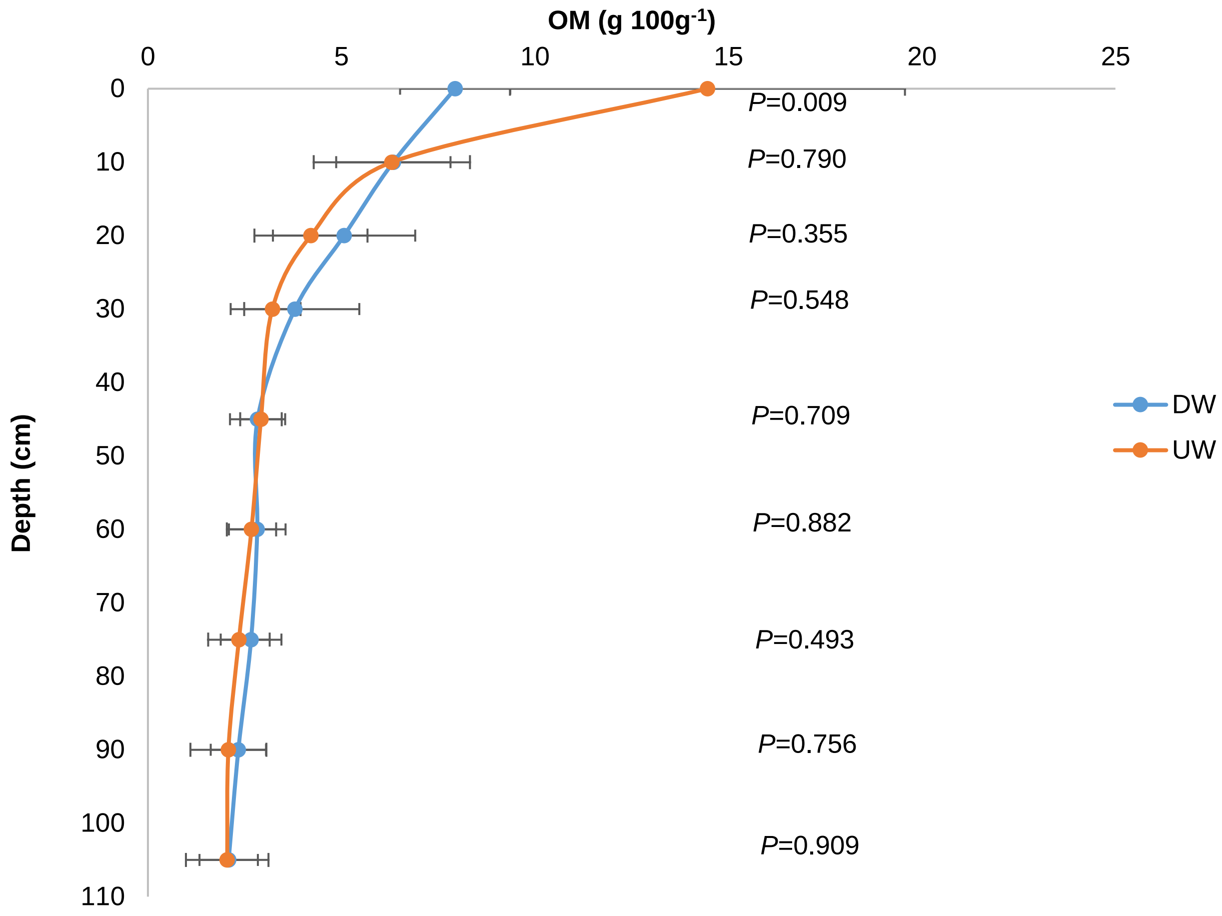

Figure 2.7. Average organic matter content (measured as Loss-on-Ignition) for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth were tested by One-way ANOVA, n=6, Johnson-transformation, *P*-values provided at each depth.

evapotranspiration, particularly during the dry periods of these seasonal wetlands, also deposits salts on the surface. The capillary rise can be from 1-2m depending on soil texture (Arndt and Richardson, 1988). Salts at the soil surface are subsequently transported in runoff. The overall result is an increase in salts, and therefore EC, in the wetlands. (Arndt and Richardson 1989, 1993, Richardson and Arndt 1989, Richardson et al. 1994, 2001, Freeland et al. 1999).

2.5.2. Texture, Bulk Density and Organic Matter Content

As soil development occurs, soil components move within the system (Brady and Weil 2002). The undisturbed and disturbed wetlands did not differ in sand or silt content, but the fraction of clay was significantly higher in the top 0-10 cm layer of disturbed wetlands compared to undisturbed wetlands.

Clay is generally transported with the direction of water movement due its small grain size (≤0.002 mm), either through eluviation (vertical movement) or by surface transport (erosion) and suspension (Brinson 1993ab, Brubaker et al. 1993, Schaetzl and Anderson 2005). Furthermore, the profiles for clay for both undisturbed and disturbed wetlands suggest accumulation of clay within the B horizon at around 60 cm depth, the Bt horizon (Schaetzl and Anderson 2005). In the DW, the higher clay content in the 0-10 cm layer is likely due to sediments originating from the Bt horizons now found on the soil surface of the landscapes. Decades of tillage and erosion events have removed much of the original topsoil of these landscapes, leaving the higher clay Bt horizons exposed on the soil surface. The downward shift in maximum clay content of the DW compared with UW indicates the average amount of sedimentation that has occurred in the DW wetlands. Recent deposition of sediments eroded from the exposed Bt horizons on surrounding agricultural landscapes is likely causing the increase in clay at the surface of the DW soil profiles.

Organic matter (OM) is one of the main factors affecting element chemistry of wetlands (Davranche et al. 2011, Demers et al. 2013, Yellick et al. 2016). Being formed predominantly by organisms growing at or near the surface, OM content typically decreases with depth, as it did in our study. Generally, an undisturbed wetland will have higher OM levels compared to disturbed wetlands surrounded by cropland (Martin and Hartman 1987b). The OM content of the soil in this study showed the reverse pattern to clay content – undisturbed wetlands had higher organic matter content in the top 0-10 cm layer compared to disturbed wetlands. This agrees with our earlier findings (Yellick et al. 2016), and suggests that disturbance of the soil, probably due to tillage, increased the degradation, oxidation and leaching of OM. At the same time, erosion from the surrounding landscape led to deposition of clay, resulting in dilution or burying of organic matter.

Although it might be expected that tillage would lead to compaction of soil due to the use of machinery, increasing bulk density (BD), (Brubaker et al. 1993, Freeland et al. 1999, Skagen et al. 2016), the BD of the disturbed wetlands in our study was in fact lower (1.24 g cm^{-3} on average) compared to that of undisturbed wetlands (1.33 g cm^{-3}), a difference of about 6.5%. This suggests that in the case of these wetlands, compaction is not a major feature of disturbance. Perhaps removal of OM and salts from the profile to at least a depth of one meter left the soils in DW more porous, but we lack a proper explanation

Table 2.2. Results of RDA model of element concentrations in wetlands to 1m depth using environmental variables, determined by manual forward selection procedure with Monte Carlo permutation tests according to ter Braak and Šmilauer (2002) ($p<0.05$). EC = Electrical Conductivity, Depth = 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105+ cm, Sand = Sand content (%), Clay = Clay content (%), Site = UW and DW, 6 replicate sites each, organic matter content (OM, %), pH, and BD = Bulk Density. UW = undisturbed Wetland, DW = Disturbed Wetland.

Environmental Variable	**Variance Explained (%)**	**Probability (*P*)**
	Data from UW and DW combined	
EC	28.2	0.001
Depth	8.6	0.001
Clay	3.6	0.001
Site	1.7	0.001
OM	0.6	0.004
Total	42.7	
	Data from UW only	
OM	36.8	0.001
Sand	8.4	0.001
EC	6.2	0.002
Site	4.7	0.003
pH	0.8	0.009
Total	56.9	
	Data from DW only	
EC	46.1	0.001
BD	8.2	0.001
OM	5.2	0.001
pH	2.5	0.004
Depth	0.8	0.004
Total	62.8	

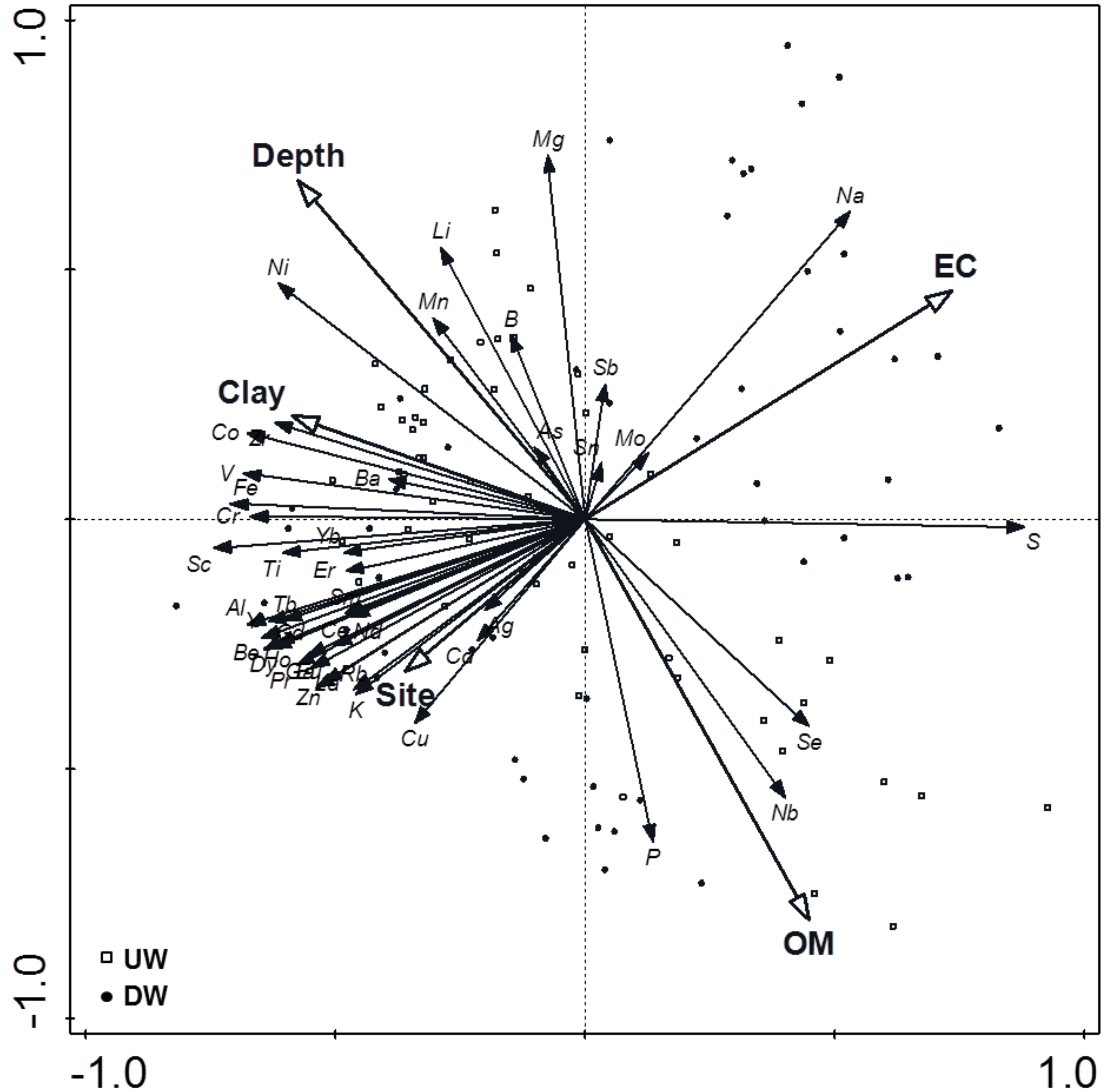

Figure 2.8. Ordination plot of RDA of element concentrations in UW and DW combined to 1m depth, constrained by (in bold): EC = Electrical Conductivity, Depth, Clay, Site, and organic matter content, OM. Element data were log transformed and centered to normalize weights due to differences in orders of magnitude and ranges.

2.5.2.1. Element Concentrations

Comparison of environmental data with other studies is always helpful for assessment of accuracy and to determine differences that point to enrichments and depletions, particularly so regarding multi-element composition of soils and organisms (Markert et al. 2015). However, there are very few

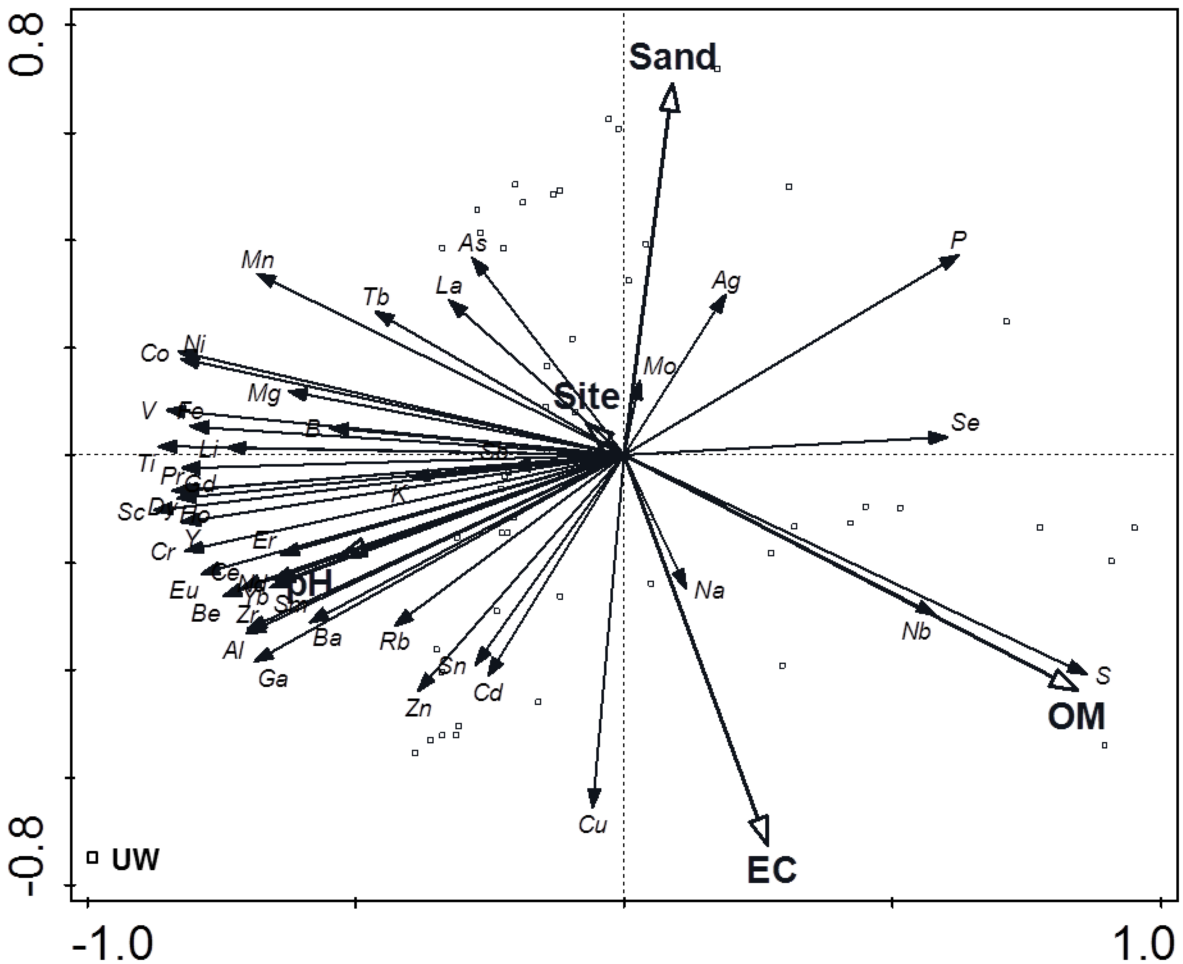

Figure 2.9. Ordination plot of RDA of element concentrations in UW to 1m depth constrained by environmental variables (in bold): OM = Organic Matter, Sand = % Sand, EC = Electrical Conductivity, Site = 6 Sites, and pH. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

studies to compare our results with. The largest studies so far that involved multi-element analysis of soils were the Kola Ecogeochemistry Project (http://www.ngu.no/Kola/, e.g., Niskavaara et al. 1997, Reimann et al. 1997, 2001), and the United States Geological Survey's National Geochemical Survey (USGS-NGS, Grossman et al. 2004). But these studies did not include wetlands, the biogeochemistry of which, and therefore the element composition of their waters and soils, is very different from drylands (Reddy and DeLaune 2008). And those studies that did involve wetlands addressed much fewer elements than we did in our study, and, more importantly, were in very different wetland systems than the ones studied here (e.g., Markert and Thornton 1990). The most valid comparison then is with our previous study (Yellick et al. 2016), and we conclude that the values for element concentrations are similar.

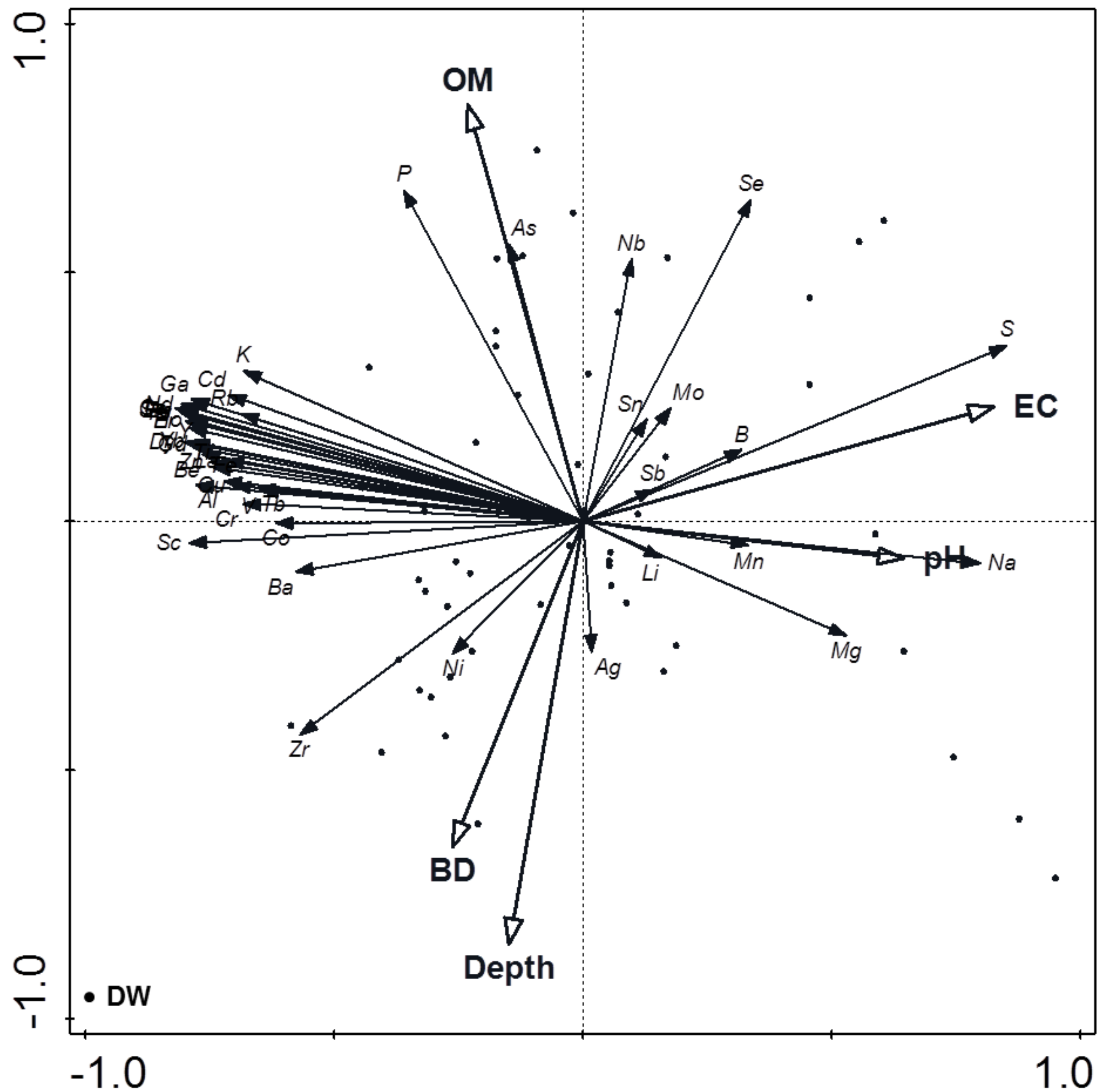

Figure 2.10. Ordination plot of RDA of element concentrations in DW to 1m depth constrained by environmental variables (in bold): EC = Electrical Conductivity, BD = Bulk Density, OM = Organic Matter, pH, Depth = 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105+ cm. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

The strong correlation between Na and EC shown by the RDA was evident from both soil profiles. This was to be expected, because EC is a function of dissolved salts, dominated by Na. Contrary to our expectations, however, Na concentrations did not vary particularly with depth. Lateral movement of Na from the surrounding landscape of disturbed wetlands led to higher concentrations compared to

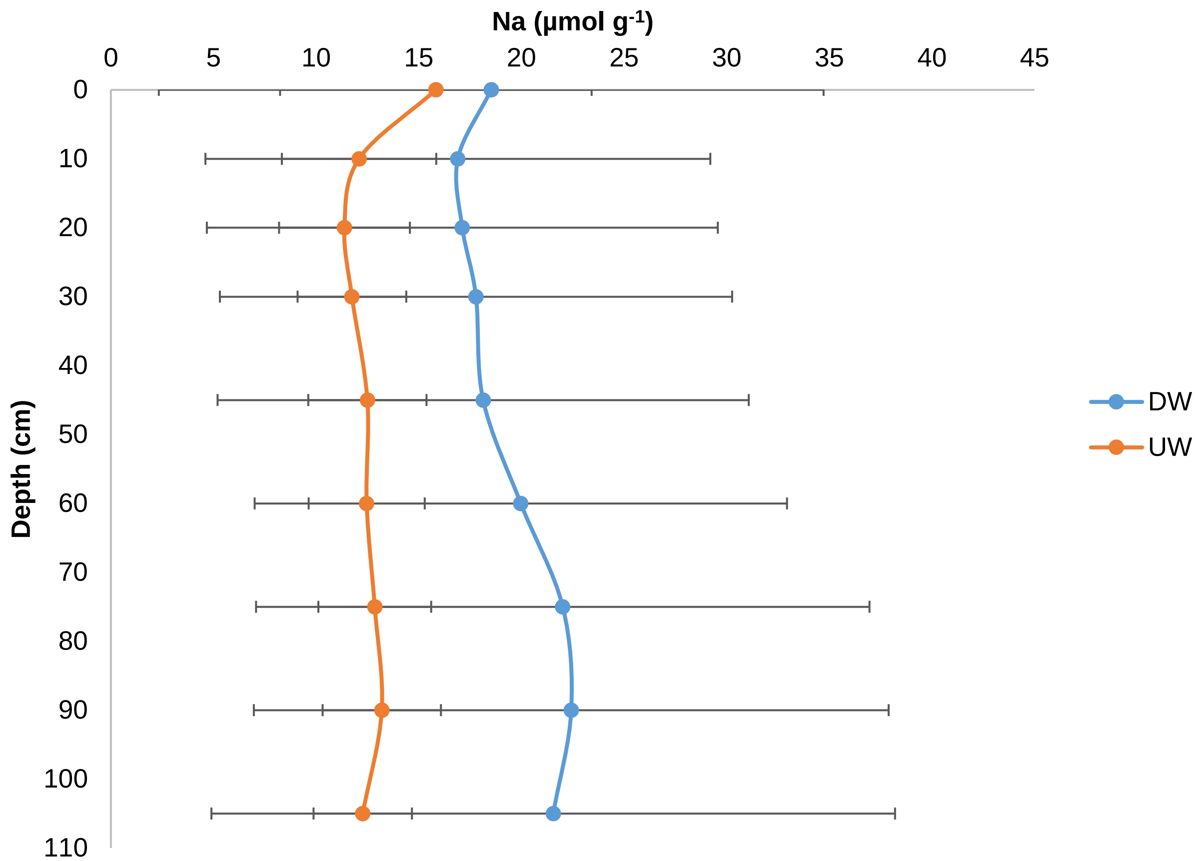

Figure 2.11. Average concentration of Na for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (One-way ANOVA, Johnson transformation), but across the entire profile were at *P*=0.003, when tested by Friedman's Test.

undisturbed wetlands, and thus a higher EC, but it appears that the permeability of the soils is such that Na does not accumulate at any specific layer below the surface, at a depth of at least one meter.

Another element contributing to salinity and EC in this region is S. The biogeochemistry of S in the PPR wetlands is driven mainly by three processes: (1) redox reactions, in which S is present in the form of sulfate and sulfide (Vasilas et al. 2010), (2) binding and precipitation of sulfate to Ca and Mg, which precipitate out of solution (Goldhaber et al. 2014), and (3) inclusion of S in organic compounds due to uptake and cycling, mostly through vegetation (Jokic et al. 2003, Tabatabai 2005). The PPR region has naturally high levels of sulfate in the soils, due to the marine origin of the sediments. This dominates some of the biogeochemistry of S in the region (Goldhaber et al. 2014), but Yellick et al. (2016) also found a strong, and likely causal correlation between S and OM. These processes explain the

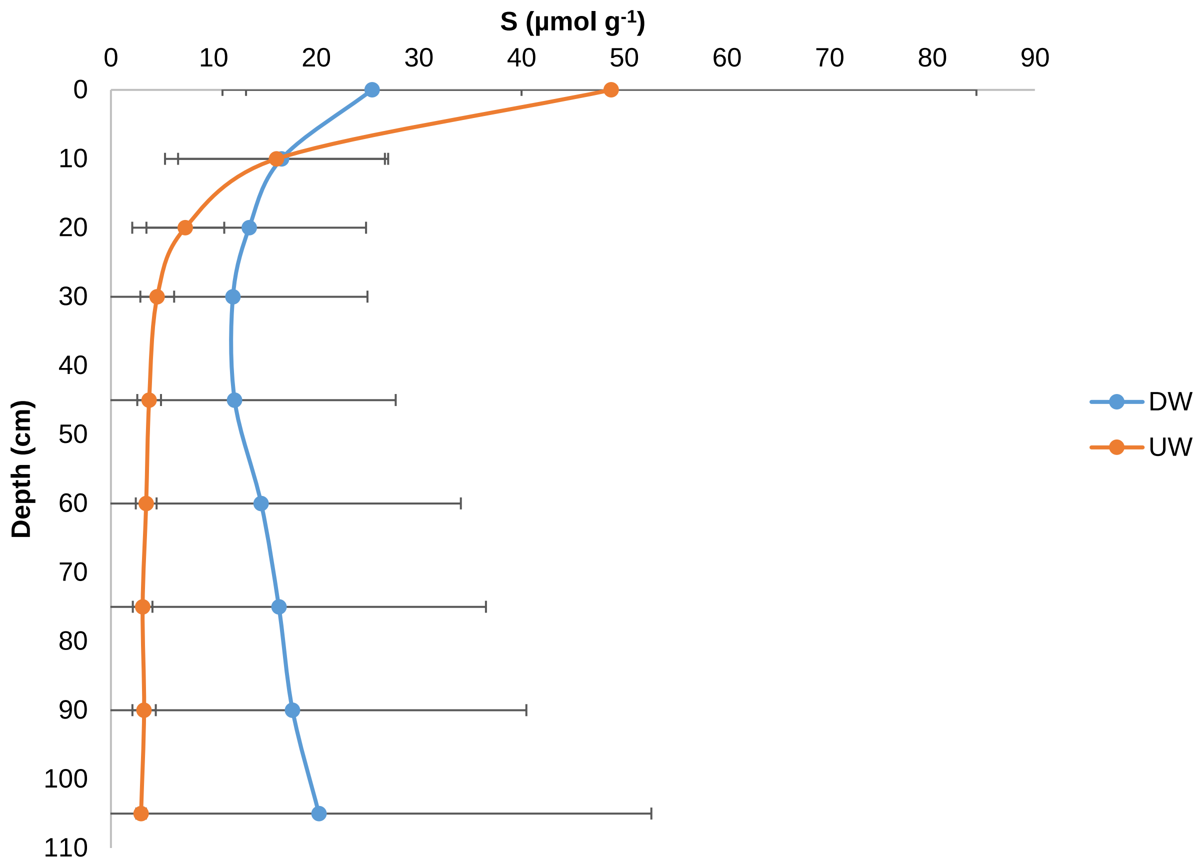

Figure 2.12. Average concentration of S for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (One-way ANOVA, Johnson transformation), but across the entire profile were at P=0.020, when tested by Friedman's Test.

observations in our study presented here. When all sites are considered in the RDA, S was correlated with both OM and EC. But when the data were separated for undisturbed wetlands (UW) and disturbed wetlands (DW), S strongly correlated with OM in UW, but with EC instead in DW. This can be explained by the organic matter rich O-horizon being intact in undisturbed wetlands, which reduces evapotranspiration from the soil surface. Evapotranspiration and fluctuating water levels bring S from deeper horizons to the surface. In addition, S bound to organic matter accumulates from decaying plant material. In contrast, in disturbed wetlands, the organic matter content in the top horizons is much reduced, because of oxidation and leaching further down into the profile. Under these conditions, S dynamics are driven by dissolution and precipitation as sulfates. The relative lack of plants and OM near

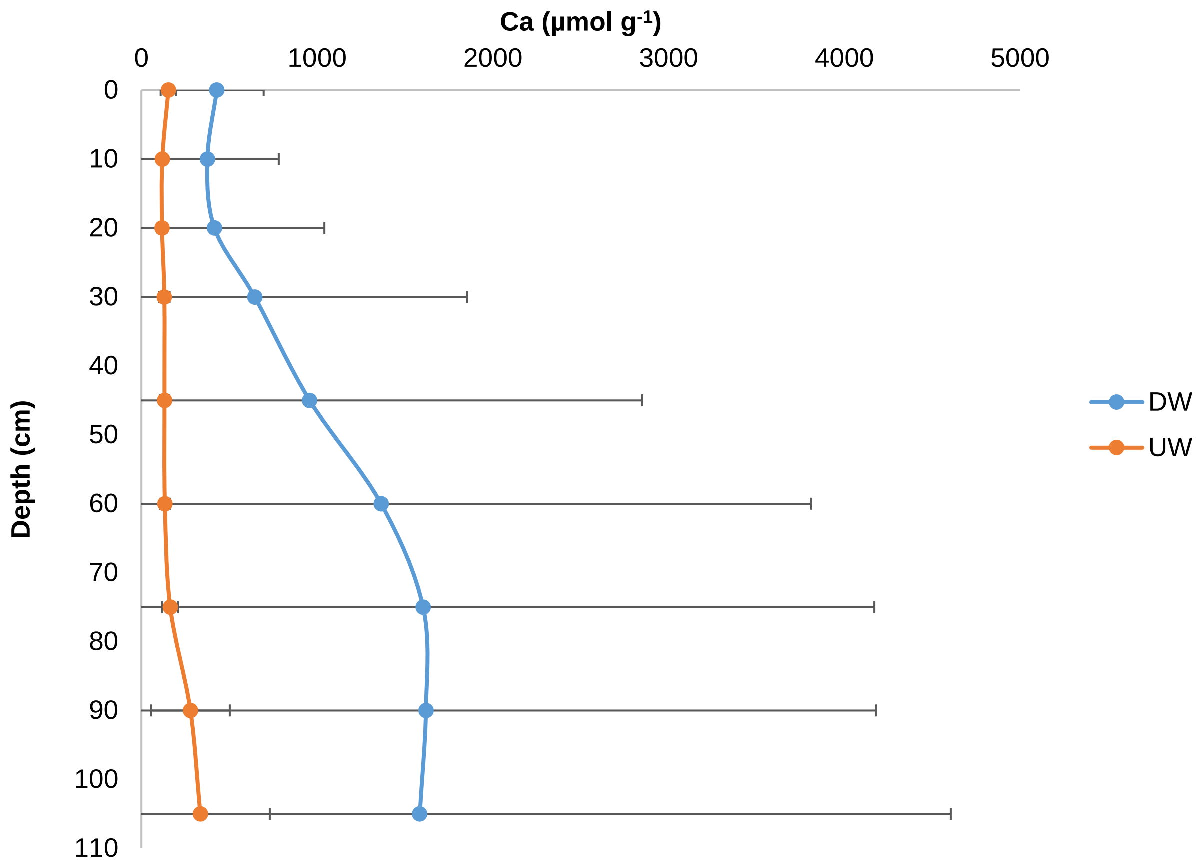

Figure 2.13. Average concentration of Ca for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately could not be tested, because the data were not normally distributed and no suitable transformation was found. However, across the entire profile differences between UW and DW were significantly different at *P*=0.003, when tested by Friedman's Test.

the surface of DW means that S only can be retained when it precipitates out as salts, explaining the correlation with EC rather than OM.

Calcium, Ba and Sr are alkaline earth metals with similar biogeochemical behavior (Drouet and Herbauts 2008). It is therefore not surprising to find very similar soil profiles for these elements. All three showed significantly higher concentrations in the disturbed wetlands compared to the undisturbed wetlands, with the highest concentrations below 60 cm. This coincides with the observation that a Bt horizon existed at that same depth, and suggests that these elements, particularly Ca and Sr, are good indicators of eluviation.

Across all sites (Figure 2.8), Nb, P and Se, and to some extent S, were positively correlated with OM, while Ni, Mn, Li and B showed strong negative correlations. Many of the transition metals, including

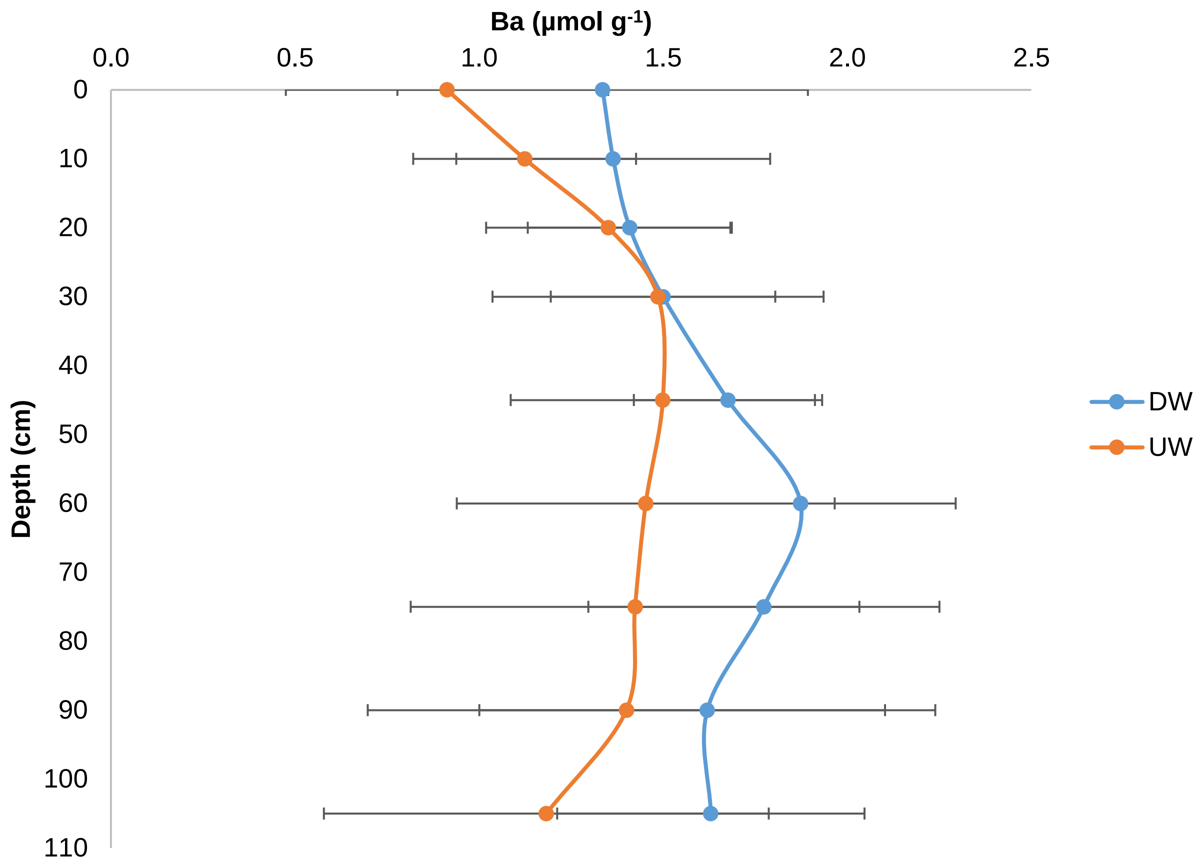

Figure 2.14. Average concentration of Ba for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (One-way ANOVA, normally distributed, so no transformation), but across the entire profile were at P=0.003, when tested by Friedman's Test.

Fe, Zn, Cd and Cu, as well as metals in other groups of the Periodic Table, such as K, Al, Ni, Dy and Co, varied more with clay content, which was negatively correlated with EC and Na. This was in line with previous observations by Yellick et al. (2016). These elements also varied strongly with Site. When considered separately, the two types of wetland conditions show striking differences in relation to element concentrations and correlations with environmental variables. In UW (Figure 2.10), the relationship between Nb and Se with OM is again clear. In DW, the relationship between OM and Nb is still strong, but S is correlated more strongly with EC.

The correlation between OM and Nb is consistently present in this study, regardless of the condition of the wetlands, but was not observed by Yellick et al. (2016). In fact, Nb showed a negative correlation with OM in the latter study, aligned with most other transition metals. This can be explained as

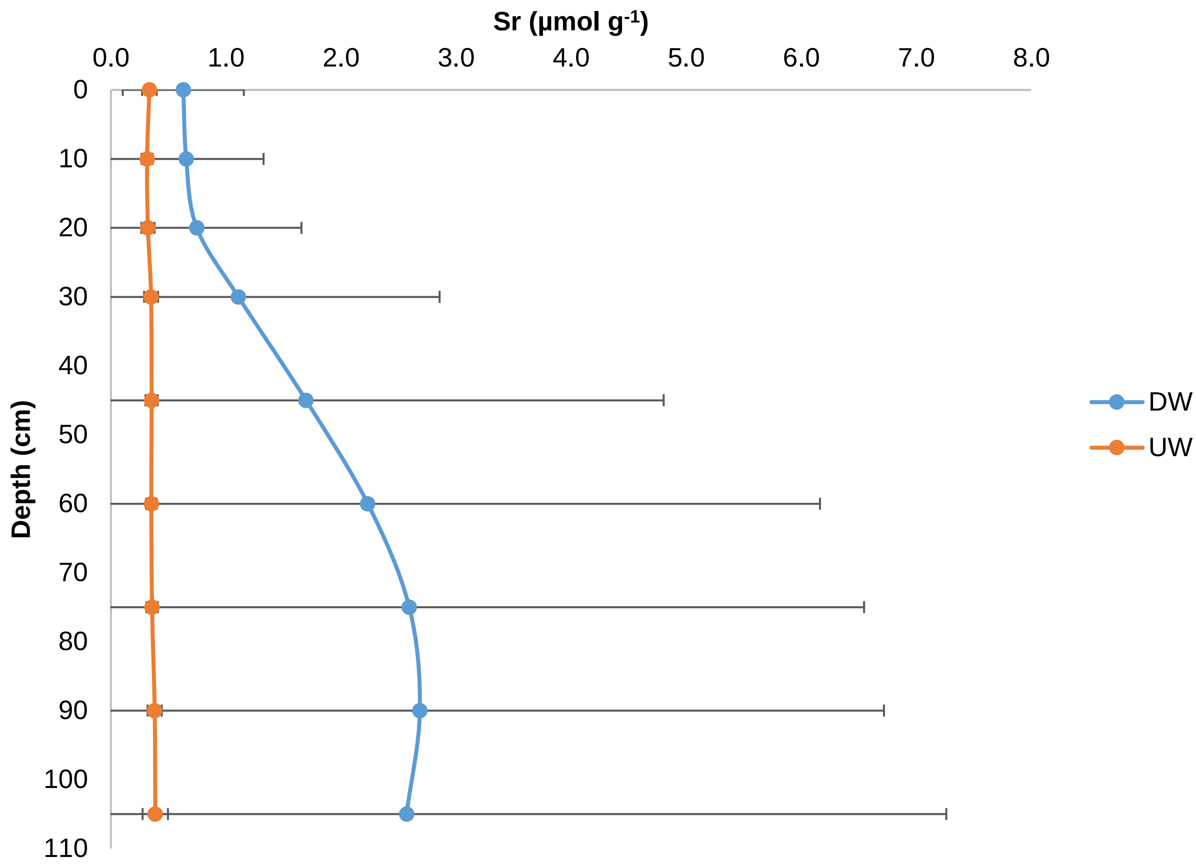

Figure 2.15. Average concentration of Sr for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately could not be tested, because the data were not normally distributed and no suitable transformation was found. However, across the entire profile differences between UW and DW were significantly different at *P*=0.003, when tested by Friedman's Test.

follows. Although little is known still about the biogeochemistry of Nb and its behavior in soils (Söderlund and Lehto 2012), it can accumulate in the root zone, due to the action of plant roots, upward movement of water, and complexation with soluble organic matter (Echevarria et al., 2005). The relationship between organic matter content of the soils and Nb is therefore not necessarily causal; Nb was higher in the upper horizons and so was OM content, but the underlying mechanisms are different: Nb moves along the profile with salts, but OM is supplied from the surface and leaches downwards. In the case of Yellick et al. (2016), variation in element concentrations and organic matter content in the soils were assessed across the landscape in the top 10 cm only, with many other factors affecting both Nb concentrations and OM content, and the relationship observed in this study would therefore not be apparent.

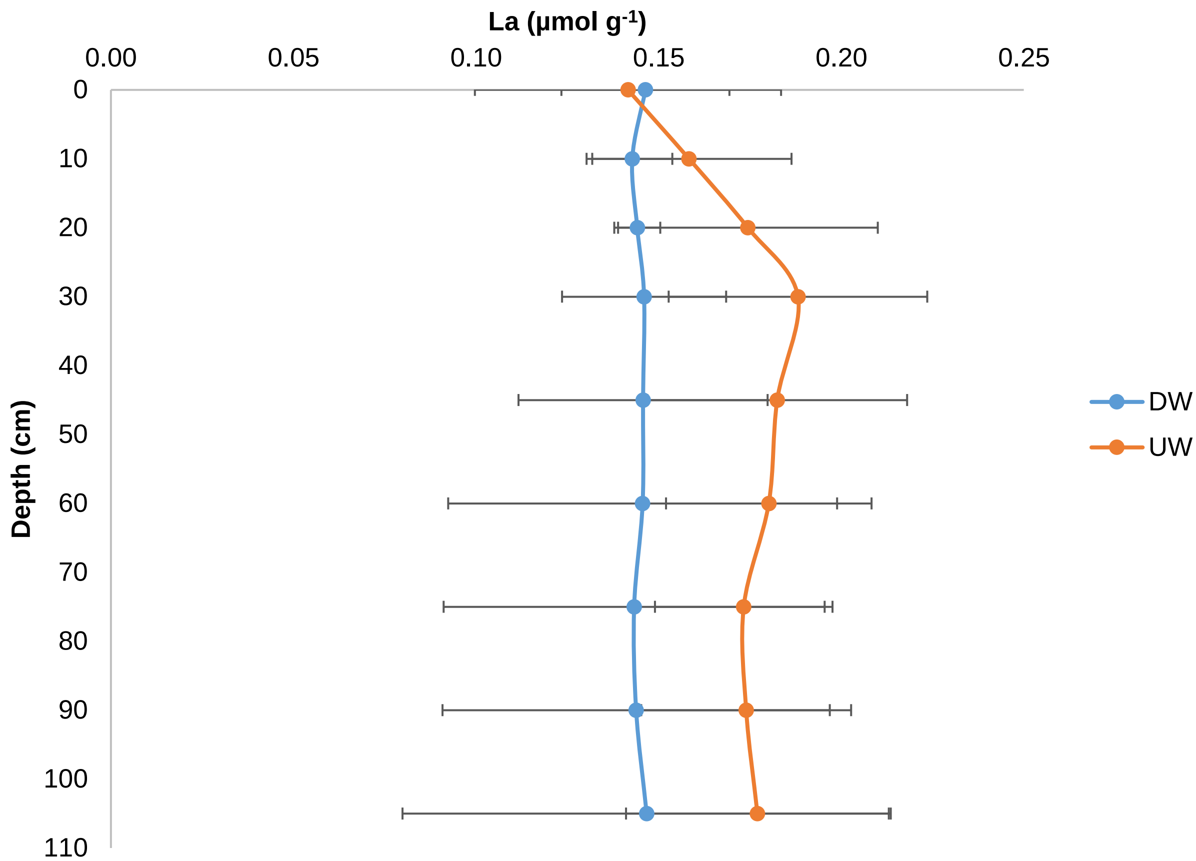

Figure 2.16. Average concentration of La for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (One-way ANOVA, Johnson transformation), but across the entire profile were at P=0.020, when tested by Friedman's Test.

As was also observed by Yellick et al. (2016), Se behaves like S and correlates with OM and EC. Selenium is mobile in soils because it generally occurs in the soluble forms as selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}). In addition, areas of high Se can occur in the PPR due to parent materials of marine origin enriched in Se (Boon, 1989). These Se ions are analogs of phosphate and sulfate and are often found associated with salts in soils with adsorption to soil influenced by higher organic carbon (OM) or calcite (Mayland et al. 1991). Further in accordance with previous observations (Yellick et al. 2016), P is correlated with OM, and the same explanation applies: high OM is associated with undisturbed wetlands, which have relatively high levels of P compared to disturbed wetlands. It is therefore unlikely that P in these wetlands is particularly affected by fertilizer applications, because in that case we would have expected to see high levels of P in disturbed wetlands, not in the undisturbed wetlands. Sodium is

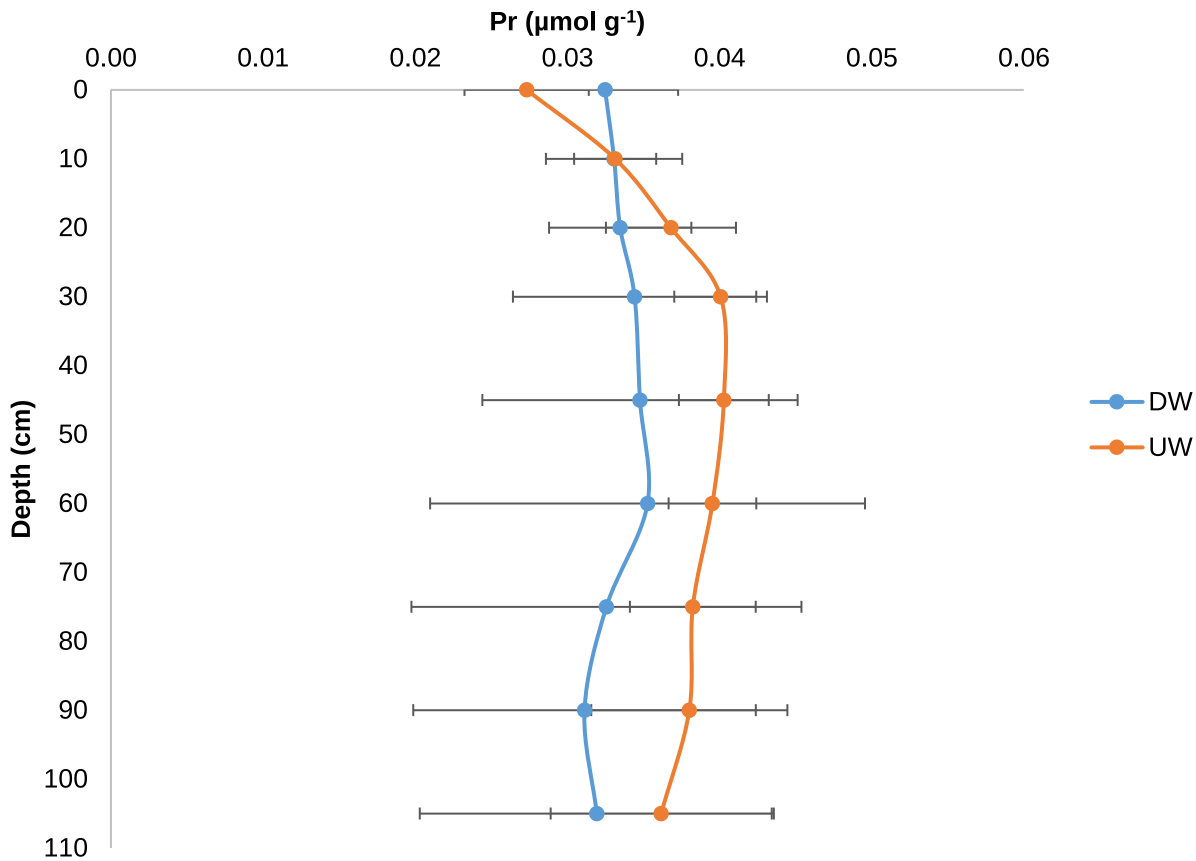

Figure 2.17. Average concentration of Pr for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately were not significant (One-way ANOVA, Johnson transformation), but across the entire profile were at P=0.020, when tested by Friedman's Test.

naturally found in soil parent materials in the PPR with variable levels related to the composition and original levels of the glacial soil parent materials (Bluemle 1980). It is highly soluble as chlorides and sulfates, and is a major determinant of the EC (Richardson and Arndt 1989, Timpson et al. 1986). This further explains why Na and S are closely correlated (Sparks 1996).

Lanthanum, Pr and Tb are elements of the lanthanide group. They are known for their very similar geochemical behavior (Sigel and Sigel 2003), but as our previous research has shown (Jacob et. al 2011), interactions between plants and soil may affect their individual behaviors. The profiles of these elements in this study are very similar, but our data show that the profiles are affected by disturbance – concentrations in DW were higher across the profile compared to UW, as was also the case for Bi, Tl and Th. It is not clear what the underlying mechanisms are for these differences, but our observations suggest

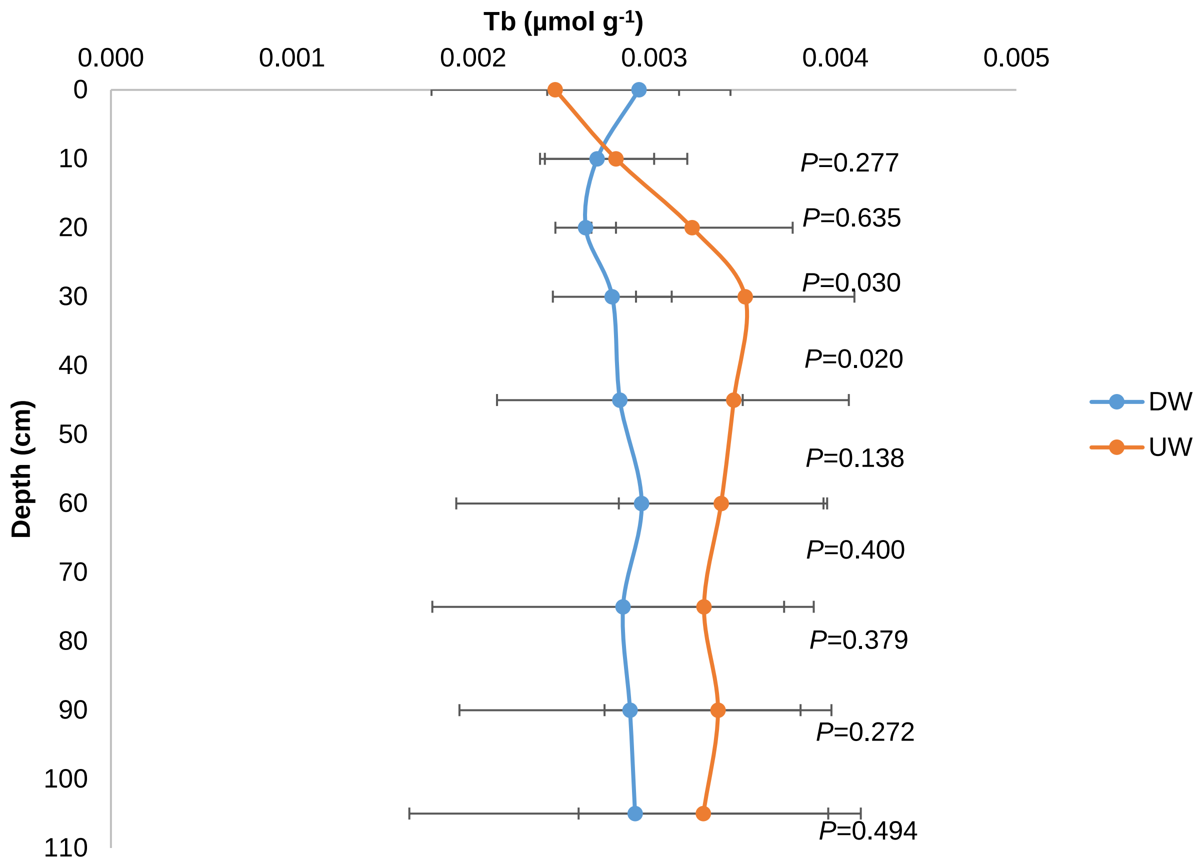

Figure 2.18. Average concentration of Tb for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth were tested by One-way ANOVA, n=6, Johnson transformation, *P*-values provided at each depth. In addition, differences between UW and DW across the entire profile were significant at *P*=0.020, when tested by Friedman's Test.

that the disturbances of the surface and surrounding landscapes have lasting effects on element distributions throughout the profile to a depth of at least one meter. This extends below the Bt horizon identified by other assessments, found at about 60cm depth.

2.6. Conclusions

Wetland soils typically show much less defined horizons compared to dryland soils, and more traditional methods of assessment of the impacts of disturbance (e.g., OM matter content, particle size distributions, pH, visual profile descriptions) are therefore limited in determining the depths to which soils are affected by disturbance. The determination of element concentrations throughout the profile, which is easily done using Inductively Couple Plasma analysis, has shown that disturbances lead to changes in element composition throughout the soil profile to a depth of at least one meter. This means that

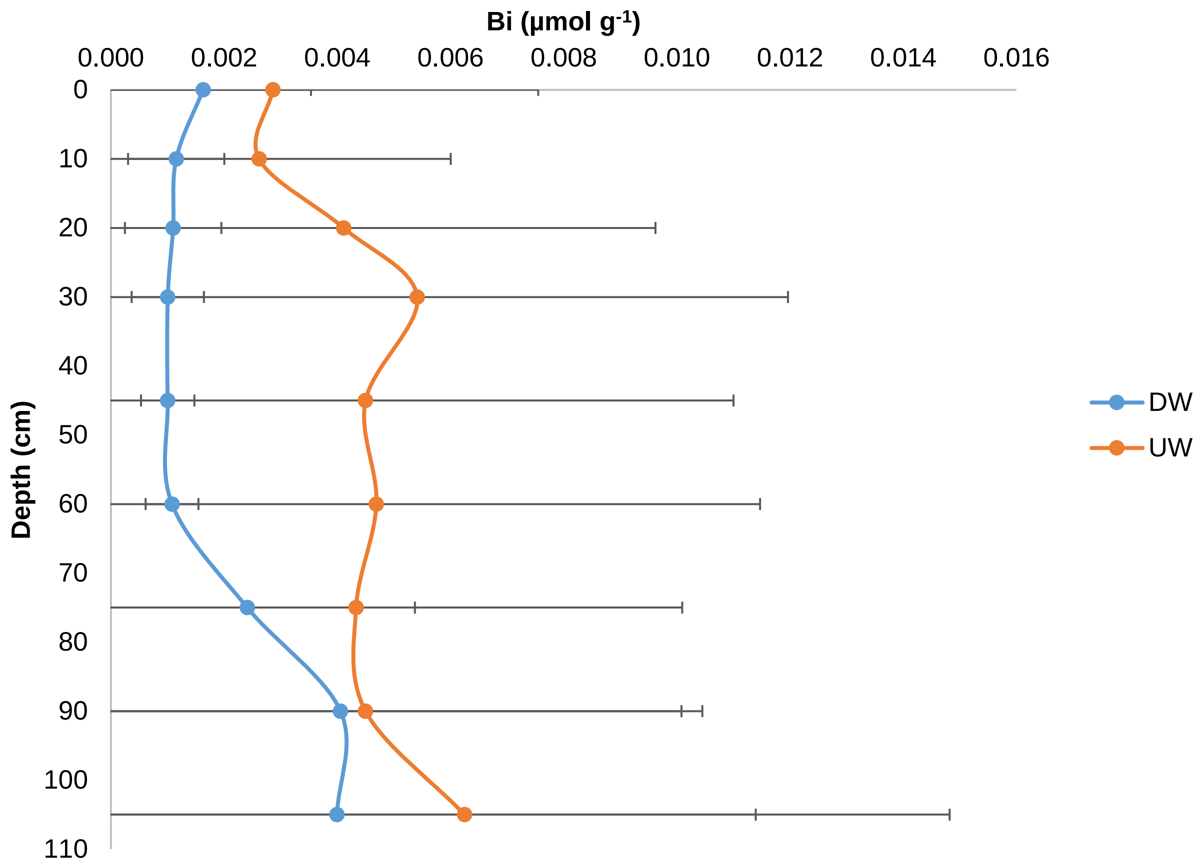

Figure 2.19. Average concentration of Bi for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately could not be tested, because the data were not normally distributed and no suitable transformation was found. However, across the entire profile differences between UW and DW were significantly different at *P*=0.003, when tested by Friedman's Test.

disturbance at the surface has consequences to greater depths than is generally acknowledged. Understanding the extents to which disturbances of soils affect the profile will help aid management and restoration efforts. This study further raises two questions: (1) Are the patterns in element distributions relating to disturbance observed here, particularly for the elements that showed differences due at greater depth (Ca, Ba, Sr, Nb, La, Pr and Tb) similar in other types of wetlands, and in even perhaps in the soils of the surrounding dry landscapes, and (2) how does the chemical speciation of these elements differ in response to disturbance throughout the profile?

2.7. Acknowledgments

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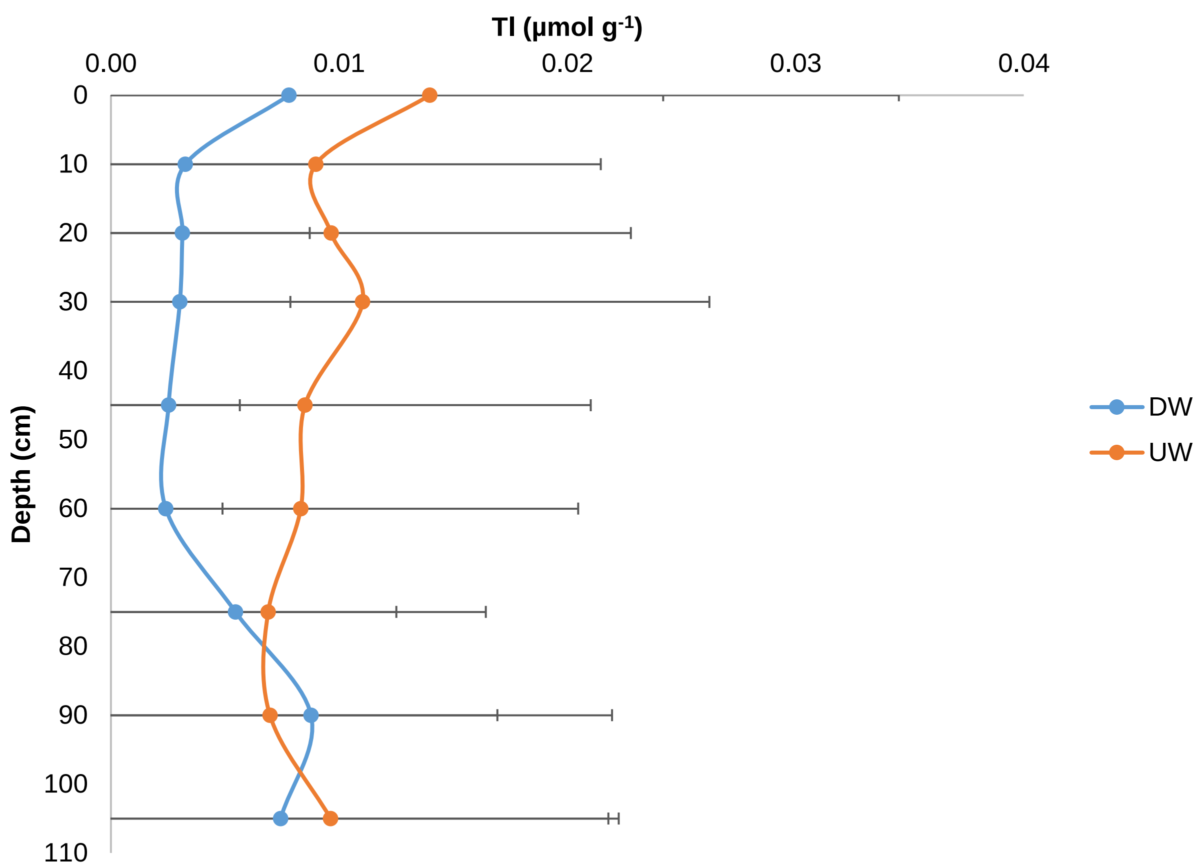

Figure 2.20. Average concentration of Tl for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately could not be tested, because the data were not normally distributed and no suitable transformation was found. However, across the entire profile differences between UW and DW were significantly different at *P*=0.020, when tested by Friedman's Test.

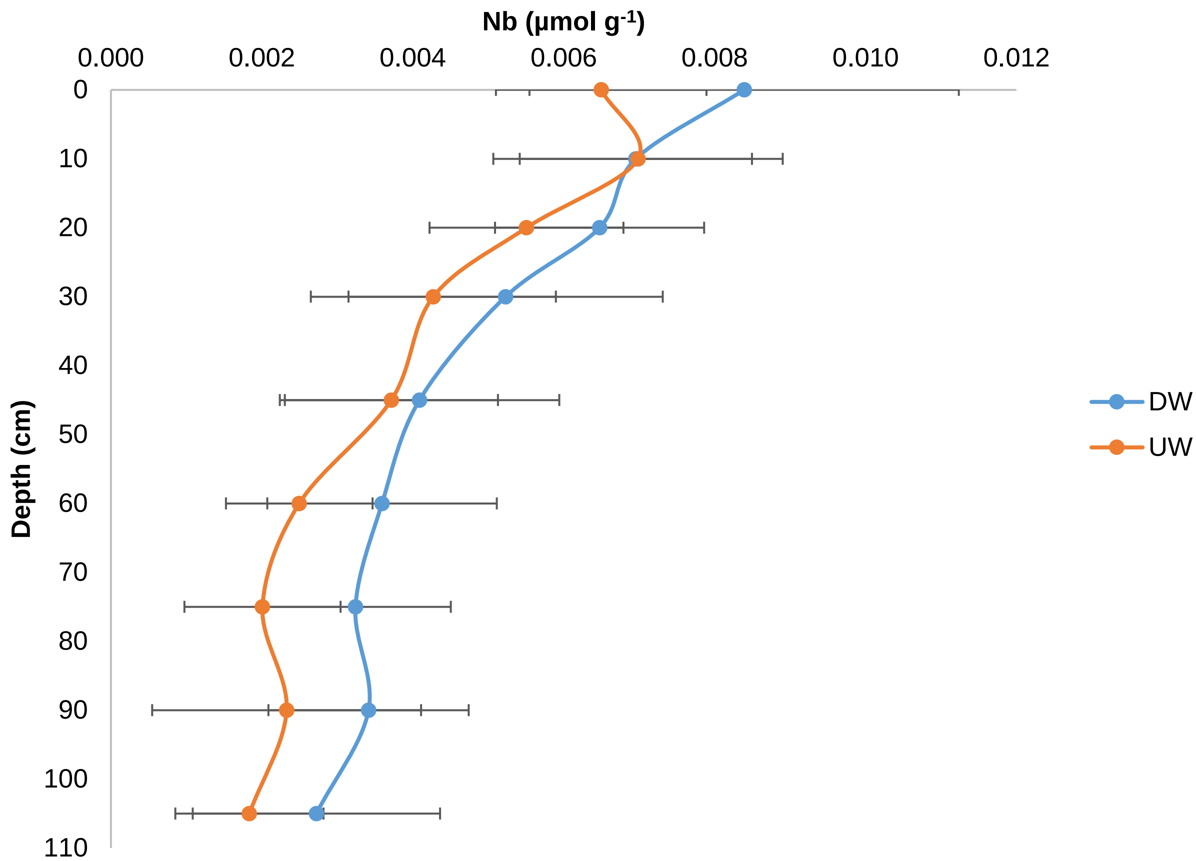

Figure 2.21. Average concentration of Nb for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth were tested by One-way ANOVA, n=6, Jonson transformation, but none were significant. However, differences between UW and DW across the entire profile were significant at P=0.020, when tested by Friedman's Test.

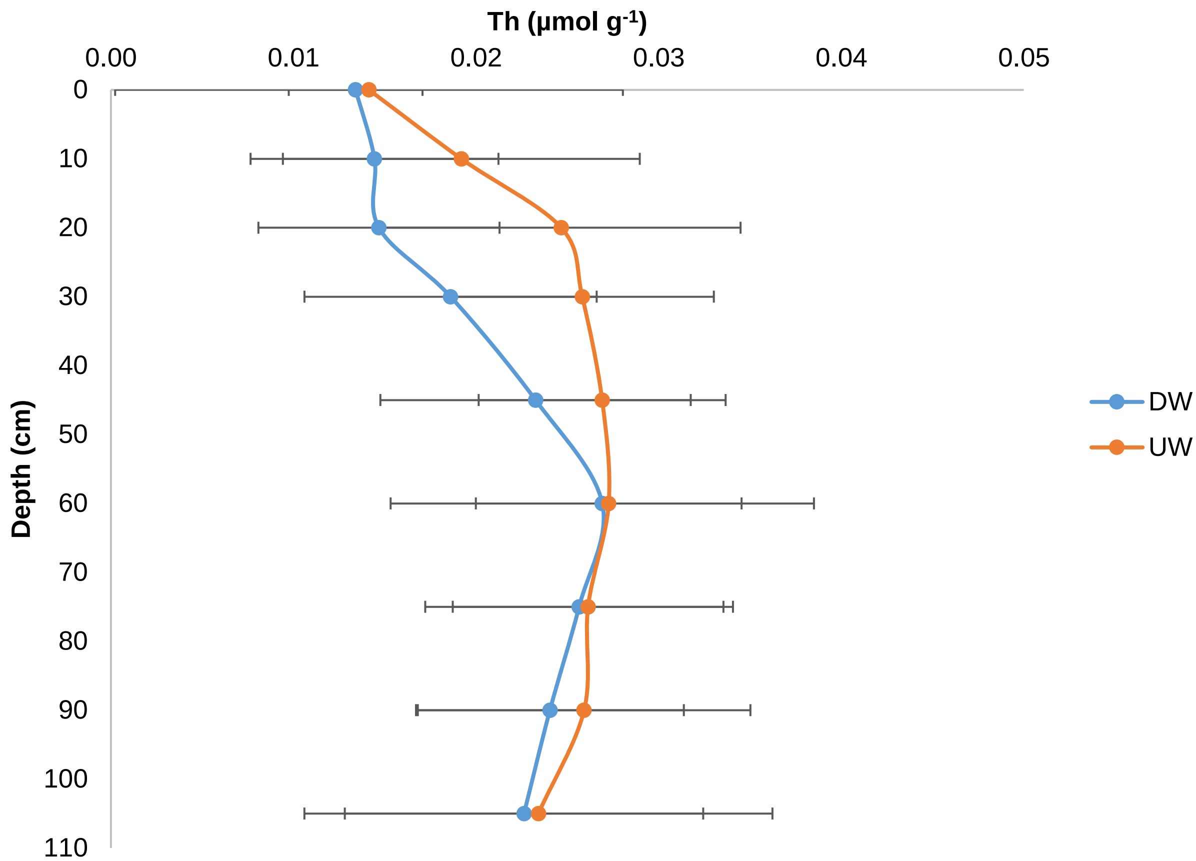

Figure 2.22. Average concentration of Th for UW and DW with depth. Bars indicate standard deviation. Abbreviations and depth values as for Figure 2.3. Differences between UW and DW at each depth separately could not be tested, because the data were not normally distributed and no suitable transformation was found. However, across the entire profile differences between UW and DW were significantly different at P=0.003, when tested by Friedman's Test.

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3. DEVELOPING THE MULTI-ELEMENT COMPOSITION OF WETLAND FRINGE SOIL PROFILES IN THE SURFACE 1M OF PRAIRIE POTHOLES

3.1. Abstract

Agricultural practices on landscapes surrounding Prairie Pothole Region (PPR) wetland ecosystems has been recognized but there is limited understanding of landscape influence on multi-element chemistry concentrations at depth. Knowledge base of multi-element chemistry composition in PPR is needed to aid in understanding soil development within the wetland fringe that can aid in restoration of debilitated wetlands and landscapes. The study objectives were to: 1) identify biogeochemical characteristics of PPR wetland fringe soils; 2) assess the vertical variation in chemical composition of wetlands fringe soils at depth; and 3) interpret soil chemistry reflected by undisturbed wetlands (UW) and fringe (UF) (good quality; prairie vegetation) and disturbed wetland (DW) and fringe (DF) (poor quality; cultivated) emphasizing differences between central wetland and wetland fringe zones to see if sampling fringes instead of wetlands is suitable. A field study was conducted on six DW, DF, and six UW, UF North Dakota (ND) PRR wetlands. Redundancy analysis (RDA) ordination plots of element concentrations to 1m depth in UW was constrained by one set of variables (clay%, depth, sand%, EC, pH) while in DW, a different set of variables (EC, OM, site, clay%, bulk density (BD)) provided constraint. The RDA ordination plots of element concentrations in UF to depth of 1m was constrained by one set of variables (sand%, EC, depth silt/clay%, pH) while in DF, a different set of variables (sand%, EC, OM, silt/clay%), provided constraint. This research indicates that anthropogenic landscape impacts on DW and DF likely influenced subsurface hydrology related to differing physical and chemical properties from UW and UF. Differences appear to be related to vegetation and soil health of surrounding landscapes. This research indicates that soil sampling in the fringes instead of wetlands is suitable in many cases and will yield similar data as sampling within the wetland as long as the relationships between the wetlands and their surrounding landscapes are understood.

3.2. Introduction

The Prairie Pothole Region (PPR), glacially formed ~10,000-12,000 years ago with undulating deposition of glacial till parent material and a closed hydrological system, is located in Montana, North Dakota (ND), South Dakota, Minnesota, Iowa, and the Canadian Provinces (Bluemle, 1980, Berkas, 1996, Dahl, 2014). Since 1780, 60% (2,000,000 acres, 809371 hectares) of ND PPR has disappeared due to land conversion for human use (tillage, drainage, grazing, construction) (Tiner, 1984, Martin and Hartman, 1987b, Winter, 1988, Berkas, 1996, DeKeyser, et al., 2003). In ND 85% of the wetlands are to some extent protected from anthropogenic conversion due Federal, state, local, and tribal agencies (Leitch and Baltezore, 1992). Wetland protection enables recharging existing aquifers, enriching biological diversity, and providing flood control within the region (Woltemade, 2000, Brady and Weil, 2002, Lamers, et al., 2006, Oki and Kanae, 2006, Gleason, et al., 2008, Hussain, et al., 2012). Today, relatively undisturbed prairie pothole wetlands can only be found in grazed native grassland landscapes (DeKeyser, et al., 2003, Mita, et al., 2007, Hargiss, et al., 2008, Paradeis, et al., 2010).

Wetland functions can be categorized through biogeochemistry, hydrology, vegetation, and environment (Brinson, 1993b). Wetlands which have been studied, characterized, and modeled by different classifications, such as hydrology, vegetation, salinity levels, topsoil, sediment, and human influence, can benefit from analysis of soil element content as a technique to distinguish between wetlands with different levels of disturbance in the PPR (Martin and Hartman, 1987b, Brinson, 1993a, Holmgren, et al., 1993, Hupp, et al., 1993, Euliss and Mushet, 1996, Bedford, et al., 1999, Gwin, et al., 1999, Beck and Sneddon, 2000, Winter, 2000, Voldseth, et al., 2007, Wilson, et al., 2008, Euliss, et al., 2010, Euliss and Mushet, 2011, Gleason, et al., 2011, Mikac, et al., 2011, Zhuang and McBride, 2013, Werkmeister, et al., 2018). Multi-element analysis can be an effective tool in studying soil chemistry due to advances in analytical technology. Multi-element analysis enables examination of detailed wetland chemistry in an efficient manner but wetland chemistry correlating with ecosystem functions can be confounding. There is still limited understanding of different ecosystem functions that may occur in natural, restored, or created wetlands (Mitsch, et al., 2012) and so the relationship between wetland ecosystems and the surrounding landscape linkages need to be better defined (Bedford and Preston, 1988). Use of biogeochemistry in studying these functions aides in a better understanding of how the element concentrations vary within a landscape (Glazovskaya, 1968). The analysis of soil element content is a potential technique to distinguish between wetlands with different levels of landscape disturbance in the PPR (Martin and Hartman, 1987a, Bedford, 1999, Beck and Sneddon, 2000, Wilson, et al., 2008, Mikac, et al., 2011, Zhuang and McBride, 2013, Werkmeister, et al., 2018).

Sound sample data collection procedures should be used throughout a study in order to maintain sampling consistency in addition to taking multiple cores to gather a representative picture of a wetland or a group (class) of wetlands (Yang and Rose, 2003, Dahlin, et al., 2012). Studies involving a sampling in two different areas of the wetlands or wetland vs streams can generate varying results relating to historical metal inputs or OM level depending on sampling location (Callaway, et al., 1998, Cowdery and Brigham, 2011). This research project will evaluate if soil sampling in the fringes instead of the wetlands, when the wetlands are saturated creating problematic sampling when trying to collect soil samples with a Giddings probe, would be suitable to yield data similar to soil sampling in the wetland itself. The fringe is the outer part of the wetland that has a very slight uprising in topography and a vegetive shift with a change in the plant community is seen in the grassland sites. A salt ring may also exist in this area and occasionally there is a tillage ring.

This study compares undisturbed wetlands (UW) (untilled soil, undisturbed native prairie wetlands) with, disturbed wetlands (DW) (tilled soil, poor wetland plant vegetation composition) and then within the wetland and representative undisturbed fringe (UF) and disturbed fringe (DF) areas by looking at soil biogeochemistry and element concentrations at various depths in the wetlands and fringe. The UW and DW sites were examined and identified by previous research that used Index of Plant Community Integrity (IPCI) (DeKeyser, et al., 2003). The objectives of this current study are to: 1) identify differences or similarities in biogeochemical characteristics of wetland and fringe soils in the PPR; 2) assess the vertical variation in the chemical composition of wetlands and fringe soils; and 3) interpret the soil chemistry reflected by UW and UF (good quality; prairie vegetation) and DW and DF (poor quality; cultivated) wetlands emphasizing differences between the central wetland and fringe zones in the wetlands. In this study, we hypothesize the following: 1) DW, DF, UW and UF will have distinctly different multi-element concentrations related to anthropogenic activity within the surrounding topography, and 2) at depth, there will be chemistry differences between the two groups of wetlands related to disturbances and topography. A secondary, underlying but important research question is whether soil sampling the wetland fringe could be used as a proxy for soil sampling the wetland in the case where water depth and saturated conditions in the wetland made collecting volumetric soil cores sampling difficult.

3.3. Materials and Methods

3.3.1. Field and Lab Analysis

A field study conducted in the PPR evaluated seasonal wetlands on the Missouri Coteau region of North Dakota. The PPR, contains small, shallow glacial basins and plant specific community zone which influence the characteristics of wetlands in the area (Stewart and Kantrud, 1971). Twelve ND PPR wetland locations, latitude 47.3º to 47.9º and longitude -100.5º to -101.1º, were evaluated in Burleigh, McLean, Sheridan, and Ward Counties of North Dakota (Bluemle, 1980). The sites were selected from wetlands in this region previously assessed for quality using the Index of Plant Community Integrity (IPCI) (DeKeyser, et al., 2003), where the soils and landscapes have developed from similar glacially derived parent materials, including lacustrine and palustrine sediments and landscapes (Kantrud, et al., 1989). The ND soils have mesic soil temperature regimes (8ºC -15ºC) and a ustic moisture regime (plant-available moisture during the growing season) (Soil Survey Staff, 2010). Six wetlands were classified as DW and six wetlands were classified UW by IPCI as either very good (VG) or very poor (VP) (DeKeyser, et al., 2003). In 2012, after a period of relatively low rainfall, most seasonal wetlands were dry and allowed vehicle traffic. In addition, landscape samples were taken to support in the explanation of the differences between UW and DW. The wetland sampling and results have been reported previously by Werkmeister et al. (2018). Within the fringe, three cores up to 1 m depth were collected using a truck mounted hydraulic soil probe (Figure 2.1). All three cores were used for pH and EC determination but two of these cores were also used for multi-element analysis and BD, and one core for soil characterization and textural analysis (Figure 2.1). Since the fringe is part of the wetland landscape position, the fringe is the outer part of the wetland that has a very slight uprising in topography and a vegetive shift with a change in the plant community is seen in the grassland sites. A salt ring may also exist in this area and occasionally there is a tillage ring. The soil cores were encased in acetate (metal free) liners to prevent moisture loss and contamination, sealed, and labeled, and stored in a cold room (2ºC) until processed. For soil sampling, the soil cores were segmented in 10 cm increments from the mineral surface to a depth of 30 cm, and then at 15 cm increments to a depth of 1 m (Figure 2.2). The soil samples were air-dried, hand crushed and passed through a 2 mm stainless steel sieve to prevent trace metal contamination which often occurs with standard brass sieves and mechanical grinders (Thompson and Bankston, 1970, Hickson and Juras, 1986). Subsamples were analyzed for pH and electrical conductivity (EC) on 1:1 (soil:water) basis (Watson and Brown, 1998, Whitney, 1998). Bulk density (BD) analysis followed the abbreviated core method of Blake and Hartge (1986). Organic matter was determined by loss of weight on ignition (Combs and Nathan, 1998). Particle-size analysis was obtained by the hydrometer method of Gee and Bauder (1986). A subsample was milled using carborundum media to <180 µm for aqua regia digest and analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Ultra Trace 2 method) for multiple elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Ge, Gd, Hf, Hg, 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, Zr) (Act Labs, 2016). Wetlands and fringes that had an organic matter layer (O horizon) on the surface had the layer separated from the mineral surface and sampled in a manner similar to the mineral surface. The organic material O horizon was air-dried, hand crushed with mortar and pestle with the aid of liquid nitrogen to <180 µm for digestion and analyzed by ICP-MS (Act Labs, 2016). However for this chapter, O horizon will not be addressed due to O horizon not being present in several wetlands and there were not enough values to test differences between W and F.

3.3.2. Data and Statistical Analysis

Elemental data received from the laboratory was presented in different concentrations (ppm, ppb) and converted to one standard unit (µmol g^{-1}). If the data were not normally distributed, they were either $\log_{10}$ or Johnson transformed to obtain normal distribution with Minitab statistical software (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018). For the element concentration data in the dataset: 1) if more than half of the samples had concentrations below the detection limit of that element, these were deemed non-detectable and not included in analysis; or, 2) if less than half of the element concentrations in the samples were below the detection limit but the remainder of the values were within detection limits, then the values below detection were replaced with half the detection limit and included in the analysis (Farnham, et al., 2002). Due to a large database and for logistical reasons, the multi-element data concentrations were averaged for each depth at each wetland and fringe and then averaged by wetland and fringe quality (very poor/disturbed i.e., tilled, or, very good undisturbed i.e., native grassland).

The environmental variables (EVs) were selected based on their quantifiability in the soils and landscapes. The EVs evaluated in this study were electrical conductivity (EC), pH, sampling depth (-0 O horizon, 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105+ cm), soil texture (sand, silt, clay), site location, organic matter (OM), and bulk density (BD). Generally, for each depth, samples from 5 cores (Werkmeister, et al., 2018) in the wetland and samples from 2 cores in the fringe (n=7) were used for EC, pH, BD, OM, and multi-element analysis except when the sample was not adequate (e.g., a core could not be collected to a 1m depth), while samples from one core each in both wetland and fringe was used to determine soil texture due to limited sample quantity (e.g. textural analysis requires large sample size). The strength of the relationships between the EV and multi-element concentration were assessed using redundancy analysis (RDA) (Yellick, et al., 2016) using Canoco 5 (ter Braak and Smilauer, 2012). The RDA model results of element concentrations using EV was determined by manual forward selection procedure with Monte Carlo permutation tests (ter Braak and Smilauer, 2002). The ordination plot of RDA for element concentrations is displayed as two-dimensional for the purpose of this paper, but it is actually three-dimensional within X, Y, and Z planes. A Pearson Correlation of the five most strongly related soil elements and selected soil physical properties in DW and UW to 1m depth ($p<0.001$) was conducted with PROC CORR in SAS v.9.2 (SAS Institute, 2008).

3.4. Results and Discussion

Soil can be translocated from the surrounding landscape through surface runoff of rain or snowmelt and aid in solubilizing the salts and nutrients within the soil and their deposit on along the landscape (Brinson, 1993a, Gustafson and Wang, 2002, Papiernik, et al., 2007, Renella, et al., 2014). In addition, the environmental factors corresponding to the surrounding vegetation along with sub-surface hydrology can play a role in affecting the biogeochemistry of the soil at depth (Matthews, et al., 2009, Cowdery and Brigham, 2011, Renella, et al., 2014). In the PPR, wetland as well as fringe soil pH can be impacted through various factors such position within the landscape, mobility of elements, hydrology, OM, and underlying parent material (Arndt, 1994, Cook and Hauer, 2007, Bailey Boomer and Bedford, 2008, Wilson, et al., 2008). A difference in pH values between DW, DF, UW, and UF was observed throughout

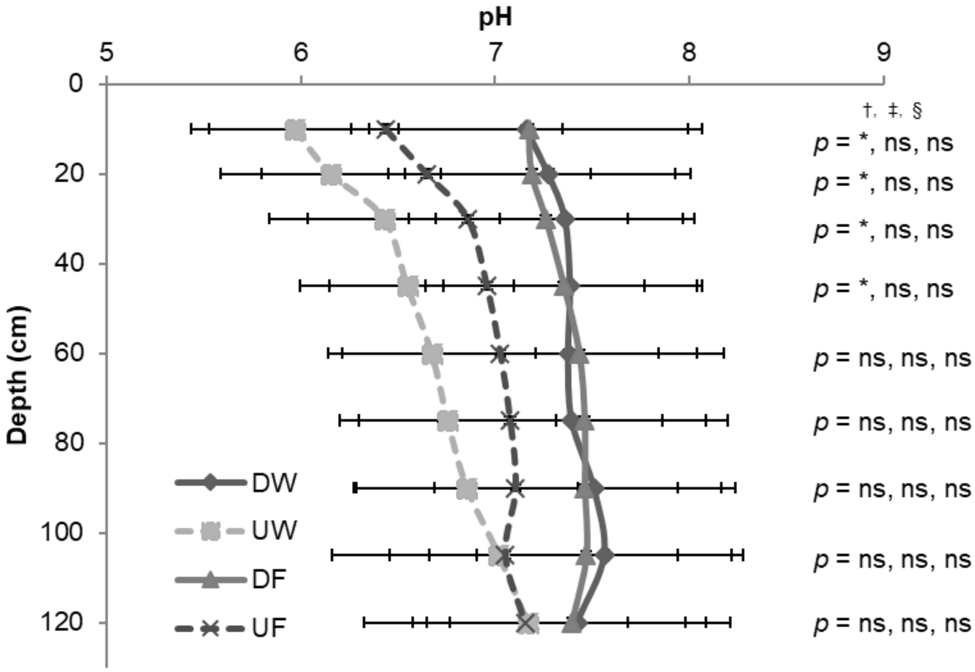

Figure 3.1. A comparison of averaged pH for DW, DF, UW, and UF at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

the soil profile (Figure 3.1). The UW and UF had lower pH throughout the soil profile when compared to DW and DF (Figure 3.1). The DW and DF had similar pH throughout the mineral soil profile section (Figure 3.1). The UW had an overall lower pH than the other three (DW, DF, UF) that converged with the UF at 100cm (Figure 3.1). At the 100cm depth, the UW and UF had pH similarities of the DW and DF which likely indicates that soil parent material likely occurs beyond this point to influence the pH (Bluemle, 1980). Comparison between the pooled wetland and the pooled fringe values showed no significant differences indicating that in this case the fringe can be used as a proxy for sampling. The higher pH values in the DW and DF likely reflect the deposition of soil components eroded from the surrounding calcareous glacial till landscapes over the period of time that these landscapes have been cultivated (calcareous soils have higher pH). In addition, salts may have accumulated in the fringe due to seepage inflow related to fluctuating local water table levels during wet and dry periods (Abdel-Haleem, et al., 2001). The landscapes surrounding the DW and DF have likely been cultivated for ≥100 years and play a

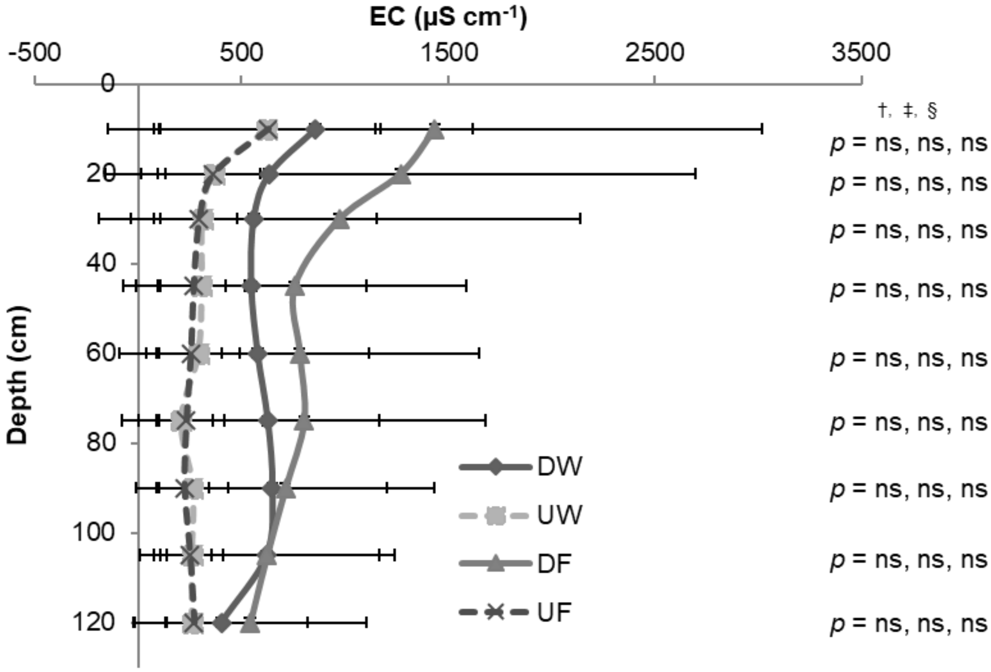

Figure 3.2. A comparison of averaged EC for DW, DF, UW, and UF at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

role with the OM levels observed (Stewart and Kantrud, 1971). Lower OM levels could be a factor in the observation of higher pH readings at depth due to calcareous soil material moving during disturbance of the landscapes at the sites. This in turn would hinder OM accumulation as well as the pH buffering effect by the OM with depth (Figure 3.2 and 3.6) (Brubaker, et al., 1993, Grybos, et al., 2009, Davranche, et al., 2011).

Starting at the mineral surface, the UW and UF have similar EC values throughout the soil profile in addition to having lower EC concentrations when compared to DW and DF (Figure 3.2). Anthropogenic disturbances on the landscape, (e.g., cultivation) affects the subsurface hydrology, by causing drastic vegetation changes hence creating a higher probability of saline seep formation in cultivated landscapes (Stewart and Kantrud, 1971, Parkin, 1993, Seelig, 2010). When an area has been disturbed by tillage, the vegetation cover is changed from a permanent vegetation cover to a seasonal annual crop cover that does not utilize all of the precipitation that occurs over the effective plant-growing season (April –

October). This unutilized moisture results in deep percolation of the excess water causing the local water table to rise. With a raised water table, increased lateral flow toward low points on the landscape becomes possible and salts dissolved in the ground water are moved to the wetlands and fringe area or to the soil surface in portions of landscapes surrounding wetlands creating saline seeps. This can be seen from the top of the mineral surface to 90cm depth for the DF, where the salinity levels converge with the DW soil. The DF have higher EC levels than DW, UW, and UF (Figure 3.2). As previously mentioned, diverse perennial vegetation on the landscape surrounding the UW/UF utilizes moisture from precipitation throughout the growing season resulting in reduced deep percolation of water in the soil profile. The fringe water level is shallower and as water evaporates, fringe soils become exposed. When wetland water levels decline, salt moves to these areas with salts deposited as the water evaporates from free water and by wicking from both the water table. When the percolating water in the landscape is reduced,

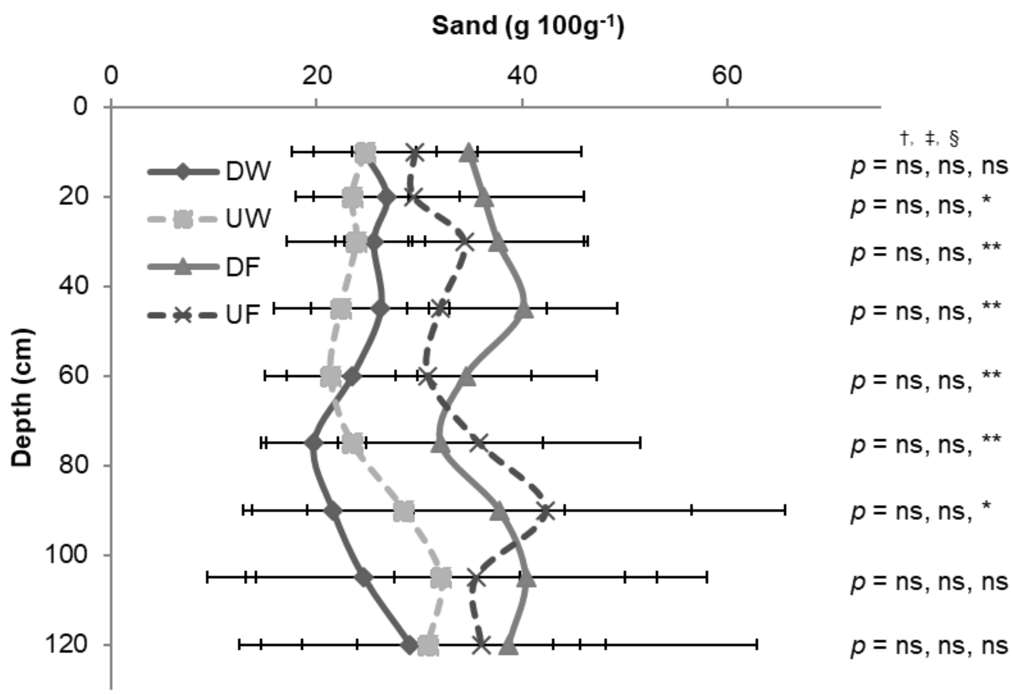

Figure 3.3. A comparison of averaged sand percent for DW, DF, UW, and UF at depth for the mineral horizons. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The p-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

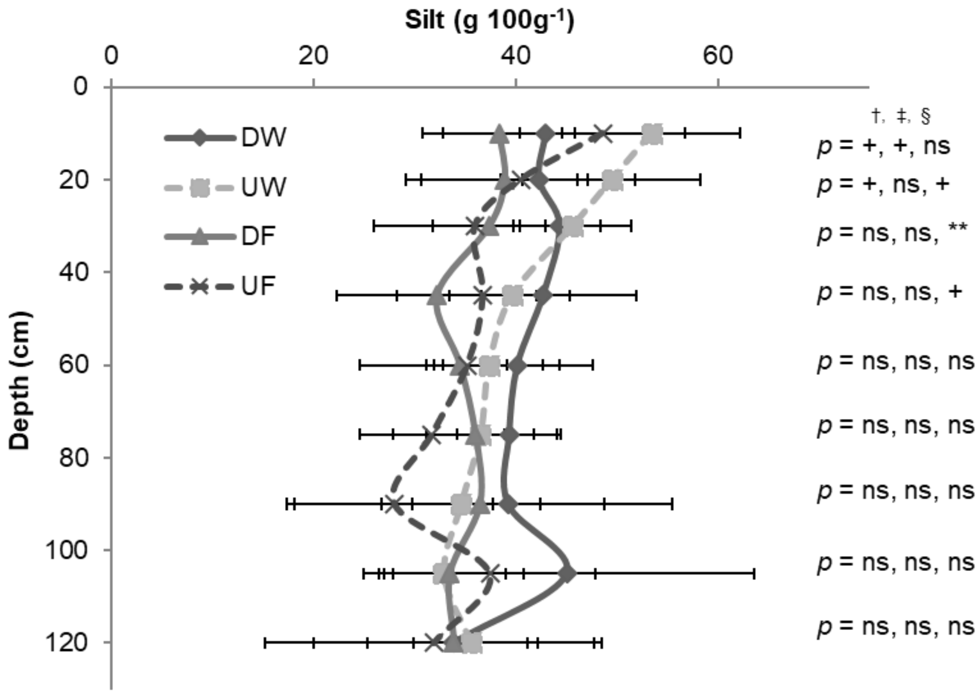

Figure 3.4. A comparison of averaged silt percent for DW, DF, UW, and UF at depth for the mineral horizons. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

soluble materials (salts) do not have the opportunity to move to the local water table (Winter, 1988, Parkin, 1993).

The soil texture on the landscapes surrounding the wetlands can influence the soil texture and soil textural component distribution in wetlands and the fringes as both natural and accelerated erosion occurs. Sediment detachment, transport and deposition in wetlands is related to landscape soil texture. An undisturbed landscape will be more resistant to intense erosion events than a disturbed landscape due to permanent vegetative cover. The two best indicators of cultivation on a landscape are sand and clay distribution and deposition in a wetland (Arndt and Richardson, 1988). The landscape position affects the percent sand within the landscape (Arndt and Richardson, 1988, Brubaker, et al., 1993, Byrd and Kelly, 2006). Due to the size of a sand particle (0.05-2.0 mm), after an intense erosion event, the sand will settle in the fringes as water inflows into the wetland water body speed decreases. Thus, sand will not normally be deposited in the interior of the wetland but will settle in fringe areas. As shown in Figure 3.3

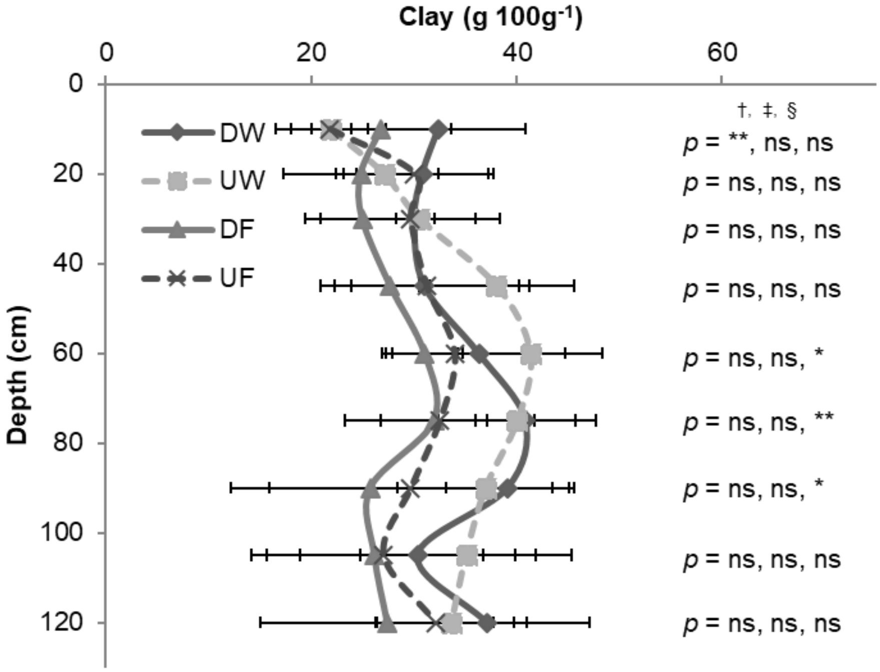

Figure 3.5. A comparison of averaged clay percent for DW, DF, UW, and UF at depth for the mineral horizons. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

and 3.4, the DW and UW have lower sand percent than in the fringe (DF and UF) position, but silt levels are similar.

Although clay is suspended in overland flow into the wetland during intensive erosion events, clay also has the ability to move within the soil profile due to its small particle size (≤0.002 mm) and is transported in the direction of water movement (Brady and Weil, 2002). Clay moves as soil development occurs by either eluviation (vertical movement) or by surface transport e.g., suspension in flowing water during erosion. In most soils, with the development of a B-horizon including changes in soil structure, color, and illuviation (zone of accumulation) of clay occur (Brinson, 1993b, Brinson, 1993a, Brubaker, et al., 1993, Schaetzl and Anderson, 2005). When clay accumulates within the B horizon (the horizon of developmental change) as a result of soil development it is designated as a Bt horizon (Schaetzl and Anderson, 2005). At 60cm depth (Figure 3.5), a separation in clay percent occurs in the UF and DF landscape positions with the wetland position have higher clay percent when compared to the fringe. The undisturbed wetland appears to have the B-horizon development starting at the 30cm depth. The clay percent (Bt horizon formation) in the UW soil is higher in the soil profile (between 30 and 80cm) while in the DW, clay increase occurs lower in the soil profile (between 50 - 90cm). The lowering of the position of the Bt horizon in the profile indicates the amount of clay sediments moving into and deposited in the wetlands. The UW and UF both have similar clay percent where the mineral layer starts while the DW and DF have a lower clay content. Within the fringe position, the UF and DF follow a similar clay percent throughout the soil profile (Figure 3.5). It is evident that fringes have less clay than wetlands due to the sorting of sediments within the fringe area of the wetlands (Figure 3.3).

Organic matter is one of the main EV's that influences the multi-element chemistry of both DW and UW (Davranche, et al., 2011, Demers, et al., 2013). The UW and UF have higher OM within the surface layer than the DW and DF (Figure 3.6). Organic matter with its net negative charge on particle

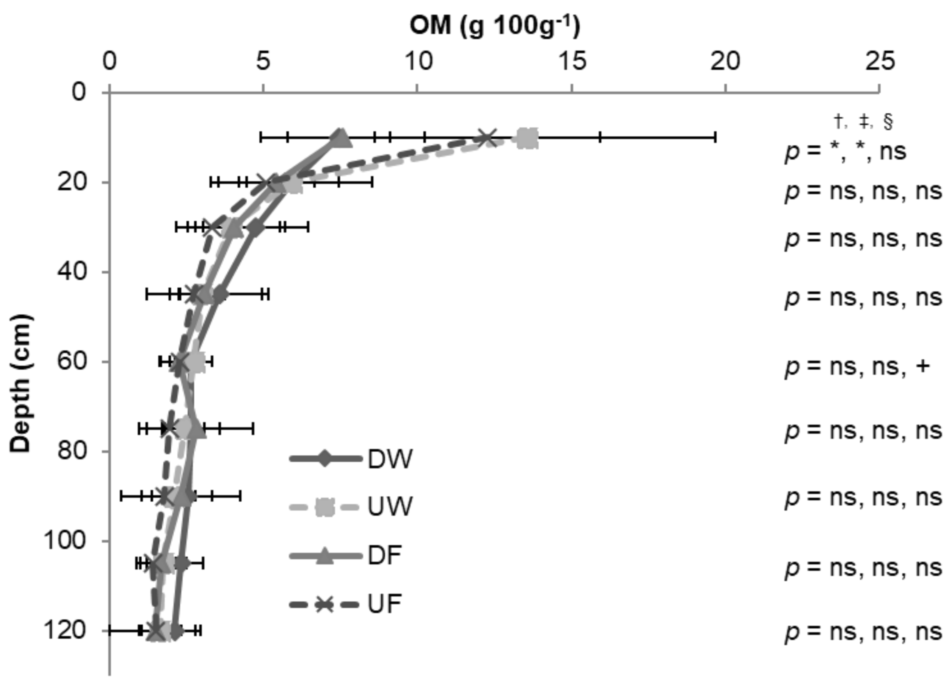

Figure 3.6. A comparison of averaged organic matter for DW, DF, UW, and UF at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20 cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The p-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

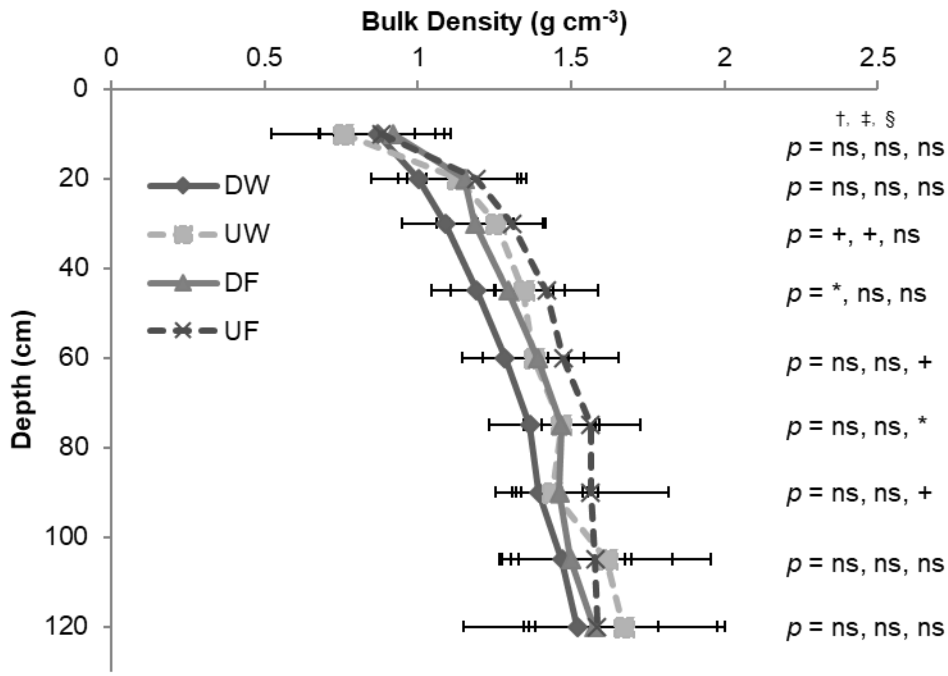

Figure 3.7. A comparison of averaged BD for DW, DF, UW, and UF at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DW and UW, ‡ = DF and UF, § = W and F at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

surfaces attracts positively charged particles, thus influencing the cation exchange capacity (CEC) of the soil (Brady and Weil, 2002) (not determined in this study), but the OM amount and quantity can also relate to wetland site quality (Martin and Hartman, 1987a, Gambrell, et al., 2001, Grybos, et al., 2007, Cowdery and Brigham, 2011, Werkmeister, et al., 2018). Generally, UW and UF will have higher OM levels compared to a DW and DF surrounded by cropland on the accompanying landscape (Martin and Hartman, 1987a). Organic matter decreases with depth and shows little difference between the DW and UW profiles was observed in the deeper portions of the soil profile. This is because deeper in the soil profile, root prevalence is diminished by periodic flooding and vegetation type (Feigum, 2000, Schaetzl and Anderson, 2005). Starting at the 20cm depth and below, the OM percent is similar for UW, UF, DW, and DF (Figure 3.6). It is evident that due to the relative uniformity of OM below 20cm in both the UW and DW, no catastrophic erosion events occurred over the history of the DW that would have buried an OM layer surface.

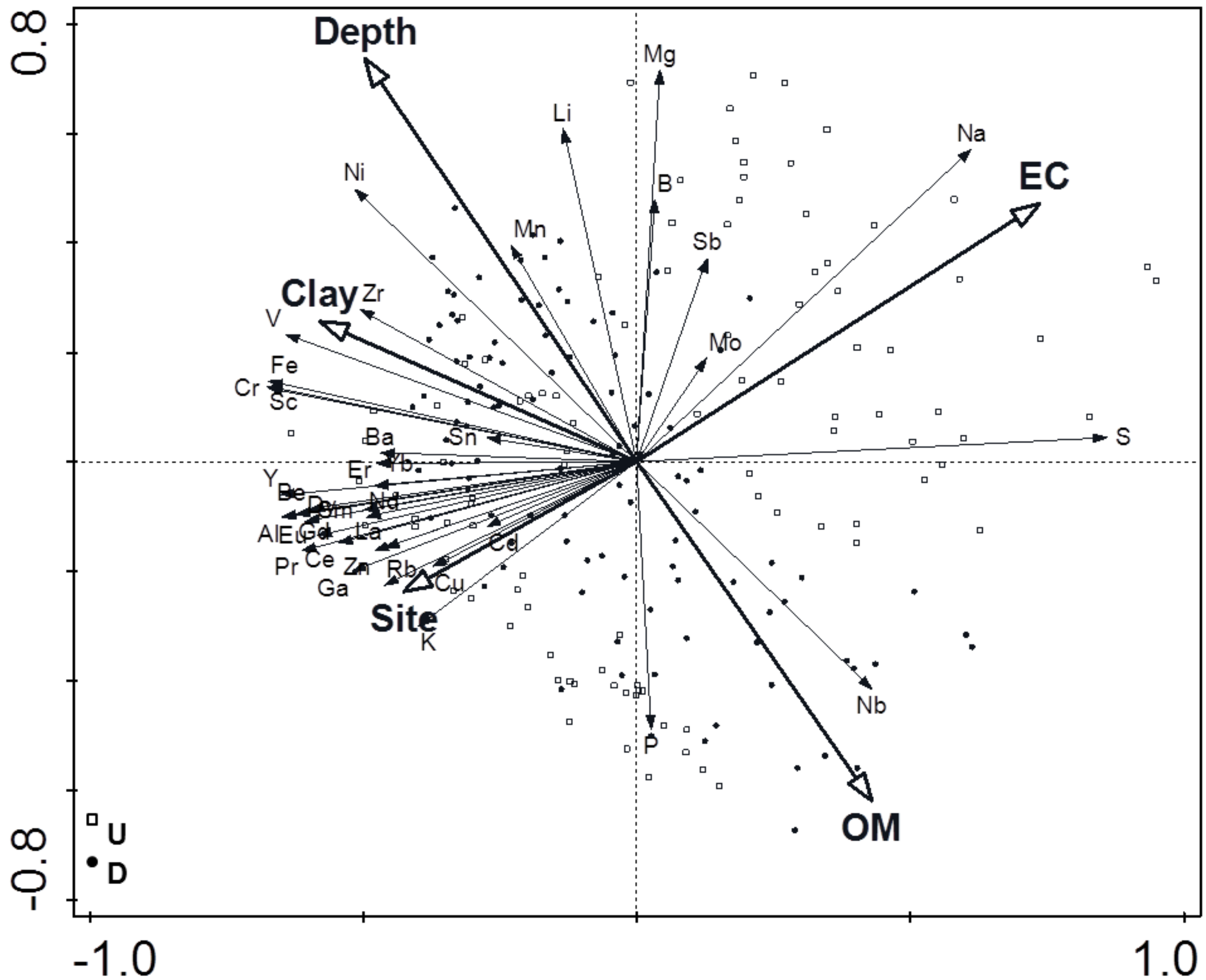

Figure 3.8. Ordination plot of RDA of element concentrations for combined data DW, DF, UW, and UF to 1m depth constrained by environmental variables (in bold): EC = Electrical Conductivity, Clay = Clay %, Depth = 1 m (0-105+cm), Site = 12 sites, and OM = Organic Matter. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

Sediment deposits in DW and DF due to erosion from surrounding tilled cropland may influence soil physical conditions (Brinson, 1993a, Freeland, et al., 1999, Skagen, et al., 2016). As shown in Figure 3.7, the BD trends lower in the DW and DF compared to the UW and UF throughout the soil profile for both wetland and fringe conditions. This illustrates an apparent anthropogenic impact in the DW, and DF while natural soil processes impact the UW and UF soil profile development. Perhaps due to disturbance, particle sorting by tillage could be occurring in the DW and DF.

Table 3.1. Results of RDA model of element concentrations in wetlands and fringe to 1m depth using environmental variables, determined by manual forward selection procedure with Monte Carlo permutation tests according to ter Braak and Šmilauer (2002) ($p<0.05$). EC = Electrical Conductivity, Depth = 1 m (0-105+ cm), Sand = Sand%, Clay = Clay %, Site = 12 sites fringe or wetland, OM = Organic Matter, pH, and BD = Bulk Density.

Environmental Variables	Explained Variance	*p*-value
	----%----	
------------- Combined Wetland & Fringe Data -------------		
EC	26.45	0.001
Clay	7.24	0.001
Depth	4.26	0.001
Site	1.59	0.001
OM	0.36	0.003
Total	39.90	
------- Undisturbed Wetland (UW) & Fringe (UF) ------		
Clay	30.78	0.001
Depth	11.14	0.001
Silt/Sand	5.24	0.001
EC	1.40	0.001
pH	0.03	0.001
Total	49.50	
-------- Disturbed Wetland (DW) & Fringe (DF) --------		
EC	34.36	0.001
OM	6.66	0.001
Site	3.60	0.002
Clay	2.07	0.001
BD	1.11	0.004
Total	47.80	

The RDA model of element concentrations for the combined DW, DF, UW, and UF to 1m depth identifies the primary environmental variables (EVs) EC, clay, depth, site, and OM (Figure 3.8 and Table 3.1). The variance of EVs explaining the highest percent of variance meant for individual RDA mode run for the combined data for UW, UF, DW, and DF are shown in Table 3.1 and with the same logic for only fringe EVs (Figure 3.11) for combined DF and UF data shown Table 3.2. Although the EVs ($p<0.01$) have high probability values for the data, only the substantial overall EV are identified (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018) based on concentrations to explaining the variable for environmental valuable effects. As seen in Table 3.1 and 3.3, the EVs are the same when the data for both the wetland and the wetland plus fringe are combined while the EVs for fringe data alone, have the same EV but differ for site. The only difference between Table 2.2 and 3.1 is that clay and depth are switched in the ranking order of importance in this analysis. A dramatic switch in explained variances was not observed between the wetland and fringe indicating a close relationship between fringe data and wetland data.

Site as an EV for DW or UW have previously been shown to relate to element concentration in the DW and UW but the fringe position has not been closely evaluated in the past (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018). The combined data RDA analysis for both wetland and fringe types in this study (Figure 3.8) showed that site was an important factor influencing the distribution of element data. Site appears as a critical EV which illustrates the importance of site quality (e.g., with or without disturbance) in multi-element concentrations within the wetland and fringe. The RDA ordination plots of element concentrations for disturbed sites and undisturbed sites show quality differences. The importance of site has been shown in both Table 2.2 and 3.1 while in Table 3.2 site does not appear as an EV likely due to the position of the fringe in the landscape (Figure 3.11, 3.12, and 3.13). However, site explains <2% of the EVs for the combined data and <4% of the EV for UW and UF (Table 3.1, with trend as shown in Table 2.2).

Figure 3.9 shows the RDA plot identifying different EVs and percent explained variance for UW and UF combined. The main EVs (clay, depth, sand, EC, pH) explaining the variance of element distribution for the correlated data in the UW and UF are shown in Table 3.1 and Figure 3.9. As seen, clay makes up >30% explained variance for UW and UF while only ~2% is due to clay for DW and DF (Table 3.1 and Figure 3.10). As natural soil development occurs on surrounding landscapes, a Bt horizon develops in the landscape soil profile. Then due to natural or accelerated erosion, clay is moved and deposited in the wetland. In the landscapes surrounding the disturbed wetland, most of the A horizon has been reworked and now sediments from the Bt are being deposited in the wetland (Figure 3.5). It is not clear whether the apparent Bt in the wetland is due to soil formation in place marking the natural soil profile of the landscape before anthropogenic influence for DW and DF. Overall, this shows the role of clay in soil formation and development in the two wetland positions. In addition, EC is a main EV for DW

Table 3.2. Results of RDA model of element concentrations in fringe to 1m depth using environmental variables, determined by manual forward selection procedure with Monte Carlo permutation tests according to ter Braak and Šmilauer (2002) ($p<0.05$). EC = Electrical Conductivity, Depth = 1 m (0-105+ cm), Sand = Sand%, Clay = Clay %, Site = 12 sites fringe, Site = 6 UF or DF, OM = Organic Matter, pH, and BD = Bulk Density.

Environmental Variables	Explained Variance	*p*-value
	----%----	
	-------------- Combined Data --------------	
Depth	10.96	0.001
pH	6.98	0.002
Clay	3.98	0.001
EC	2.33	0.021
Total	24.25	
	------- Undisturbed Fringe (UF) ------	
Sand	31.13	0.001
EC	13.40	0.001
Depth	5.61	0.001
Silt/Clay	2.72	0.007
pH	1.04	0.012
Total	53.90	
	-------- Disturbed Fringe (DF) --------	
Sand	29.59	0.001
EC	12.60	0.001
OM	7.75	0.001
Silt/Clay	1.66	0.031
Total	51.60	

and DF as well as with DW alone, and contributes >34% of explained variance while for UW it is slightly more than 1% of the explained variance, illustrating, the role EC plays in the biogeochemistry in the disturbed sites (Table 3.1). The EC reflects anthropogenic disturbances (e.g., cultivation) which not only accelerates erosion and sedimentation within the landscape but also alters subsurface hydrology (Stewart and Kantrud, 1971, Parkin, 1993, Seelig, 2010).

For the DW and DF, the RDA identifies different EV constraints (Figure 3.10). In Table 3.1, the main EVs explaining the variance of DW and DF element distribution for the factors correlated are shown to be EC, OM, Site, Clay, and BD. The results of the RDA ordination plot of element

Table 3.3. Pearson Correlation coefficients of select soil physical properties and the highest correlated soil chemical elements in wetlands and fringe to 1m depth. (p<0.001). In the PPR, elements in bold (Ni) are uncommon elements and elements underlined (Na, S, P, Mg) are common in wetland of the region.

EV	------------------------------------ Elemental Correlation (r^2) ------------------------------------				
	-- Combined Wetland & Fringe --				
EC	<u>*Na (0.716)*</u>	<u>*S (0.699)*</u>	pH (0.468)	Eu (-0.448)	Pr (-0.467)
Clay %	Al (0.685)	Cr (0.680)	Sc (0.656)	Fe (0.628)	Zn (0.627)
Depth	OM(-0.659)	**Ni (0.631)**	<u>*Mg (0.528)*</u>	Li 0.524)	<u>*S (-0.497)*</u>
Site	Pr (0.408)	Ce (0.371)	Nd (0.355)	Sm (0.355)	EC (-0.347)
OM	Depth (-0.659)	Silt% (0.536)	<u>*S (0.512)*</u>	BD (-0.504)	**Ni (-0.484)**
	---------------------------------- Undisturbed Wetland & Fringe (UW,UF) -----------------------------------				
Clay%	Al (0.858)	Ga (0.856)	Sc (0.831)	Cr (0.819)	Be (0.775)
Depth	**Ni (0.772)**	Li (0.725)	<u>*Mg (0.717)*</u>	<u>*S (-0.693)*</u>	OM (-0.686)
Sand%	Cu (-0.781)	Zn (-0.758)	Rb (-0.731)	Silt% (-0.702)	Al (-0.663)
EC	OM (0.586)	<u>*S (0.557)*</u>	<u>*Na (0.497)*</u>	Cd (0.349)	Silt% (0.341)
pH	<u>*Mg (0.700)*</u>	<u>*P (-0.539)*</u>	Silt% (-0.517)	<u>*Na (0.463)*</u>	Zr (0.426)
	--Disturbed Wetland & Fringe (DW, DF) -----------------------------------				
EC	<u>*Na (0.770)*</u>	<u>*S (0.764)*</u>	Al (-0.605)	Pr (-0.592)	Eu (-0.588)
OM	BD (-0.668)	Depth (-0.667)	<u>*P (0.489)*</u>	Th (-0.479)	Silt% (0.388)
Site	pH (-0.746)	<u>*S (-0.523)*</u>	EC (-0.472)	<u>*Mg (-0.470)*</u>	<u>*Na (-0.430)*</u>
Clay %	Zn (0.569)	Sand% (-0.540)	Cu (0.538)	K (0.524)	Cr (0.523)
BD	OM (-0.668)	Depth (0.641)	Th (0.462)	<u>*P (-0.404)*</u>	Zr (0.383)

in the correlated wetland and fringe data as constrained by EV shows a linkage between clay and depth, which can be seen in the upper left quadrant of RDA plot (Figure 3.8) which is the same trend as seen before in the DW and UW RDA (Figure 2.8). This is likely related to Bt horizon development through the movement of clay (eluviation) within the system and soil deposition (Figure 3.5). As can be seen from Figure 3.3, sand differences between the wetland and fringe are evident. Sand is not suspended in water nor can it be moved by illuviation. Due to their size, sand particles require substantial energy to move, requiring force provided by flowing water or wind compounded by gravity (erosion). When the energy needed for the movement of sand particles is reduced such as by vegetation in the wetland fringe, the movement of particles slows or stops. Thus, sand usually will settle in the fringes and will not normally be deposited in the interior of the wetland. In the RDA ordination plot of the UW and UF, sand appears

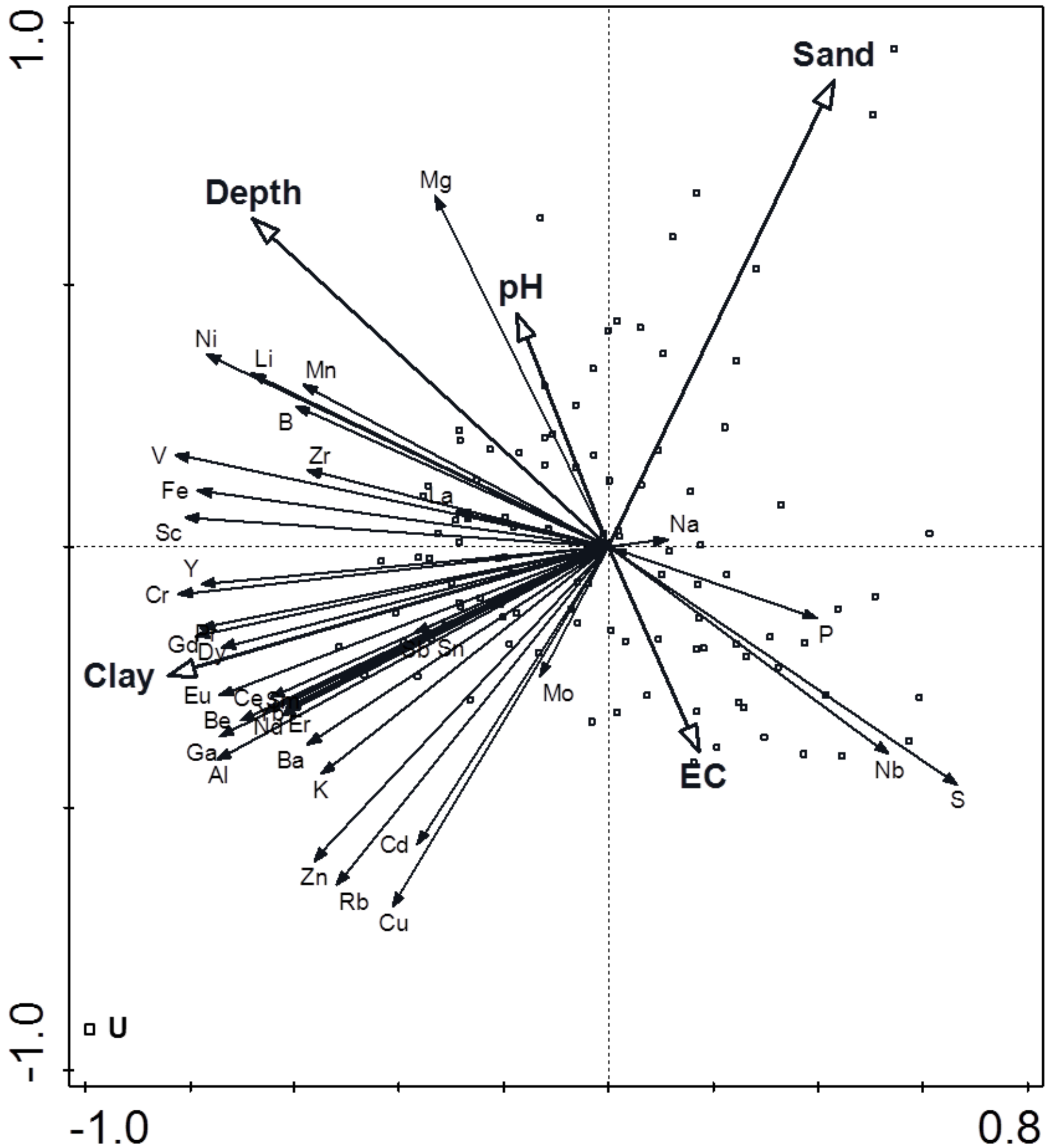

Figure 3.9. Ordination plot of RDA of element concentrations in UW and UF to 1m depth constrained by environmental variables (in bold): Clay = %, Depth = 1 m (0-105+ cm), Sand = %, EC = Electrical Conductivity, and pH. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

as an EV, likely due to low levels of clay deposition in the wetland resulting from an absence of tillage or erosional events on the surrounding undisturbed landscape (Figure 3.9). In Table 3.3, the chemical elements that are most highly correlated with the underlying EVs in the wetlands and fringe to a 1m depth are identified using Pearson correlation coefficients as well as in Table 3.4 for EVs in the fringe. The soil properties making how these correlations are similar or different between the combined wetland data

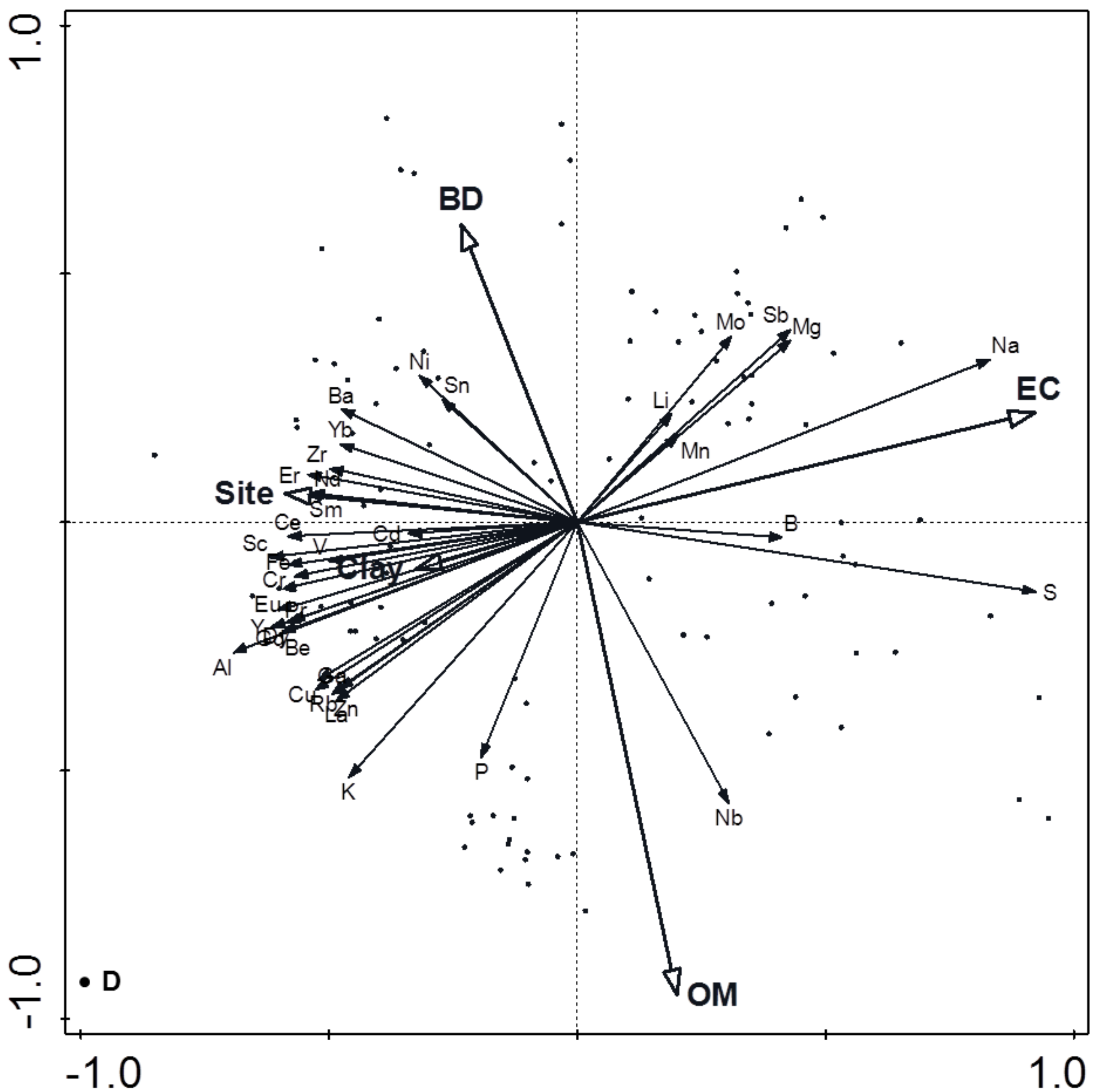

Figure 3.10. Ordination plot of RDA of element concentrations in DW and DF to 1m depth constrained by environmental variables (in bold): EC = Electrical Conductivity, OM = Organic Matter, Site = 12 sites, Clay = %, and BD = Bulk Density. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

and data specific to DW, DF, UW, and UF while Table 3.4 shows the correlation for the fringe.

The element Ni in Table 3.3 and 6 has not been previously noted in within wetland and fringe soil systems while the elements sodium (Na), sulfur (S), phosphorus (P), and magnesium (Mg) are commonly

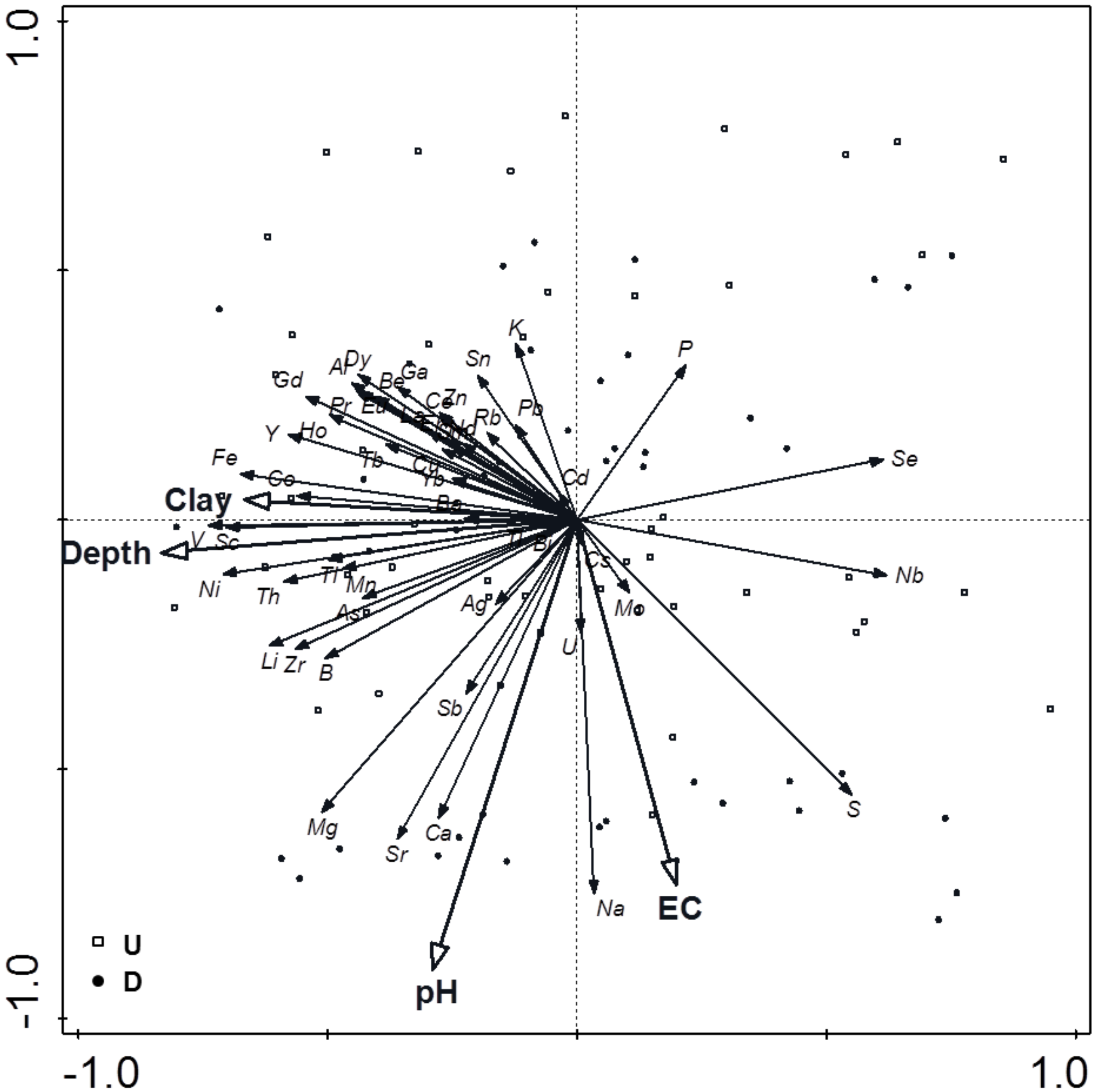

Figure 3.11. Ordination plot of RDA of element concentrations in UF and DF to 1m depth constrained by environmental variables (in bold): Depth = 1 m (0-105+cm), pH, Clay = %, and EC = Electrical Conductivity. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

observed in PPR soils (Werkmeister, et al., 2018). The presence of Ni may be related to the composition of the glacial parent materials in this region of the PPR. There is a difference between the wetland (Chapter 2) and the wetland and fringe data where Nb and Se were found to be an important factor within the wetland but not in the fringe location.

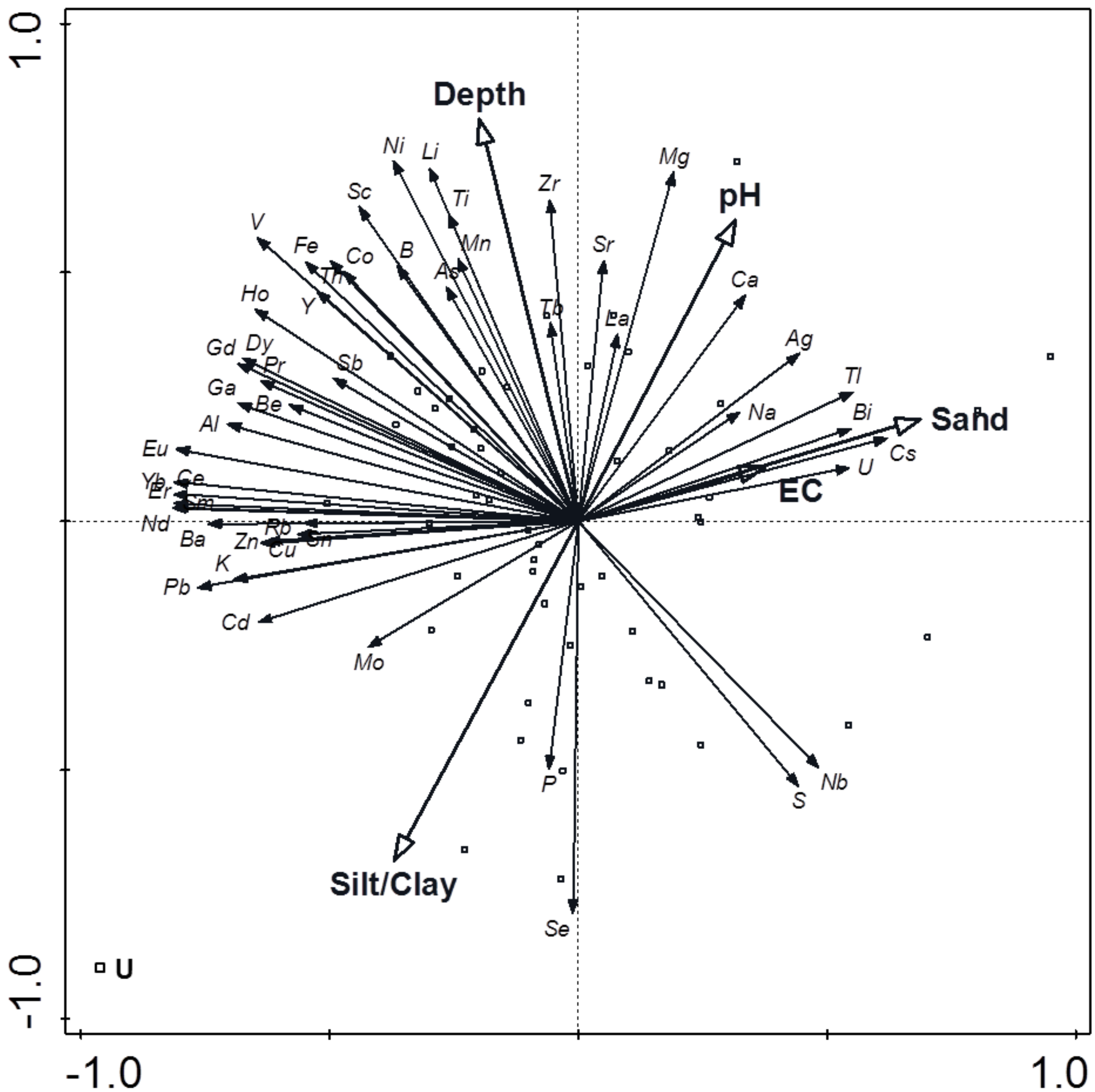

Figure 3.12. Ordination plot of RDA of element concentrations in UF to 1m depth constrained by environmental variables (in bold): Sand = %, EC = Electrical Conductivity, Depth = 1 m (0-105+cm), Silt/Clay = %, and pH. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

Sulfur is a common element found in PPR soils and occurs as variable sulfur concentrations (Bluemle, 1980). Unable to determination S species within the analytical methods used in this study, the S concentrations reported here are total S within the soils. To further understand the occurrence of S in these wetlands, background knowledge of S transformations is needed. Sulfur found in pyrites are often found in anaerobic wetland soils due to reduction of sulfates to sulfides (Bluemle, 1980) and resorting

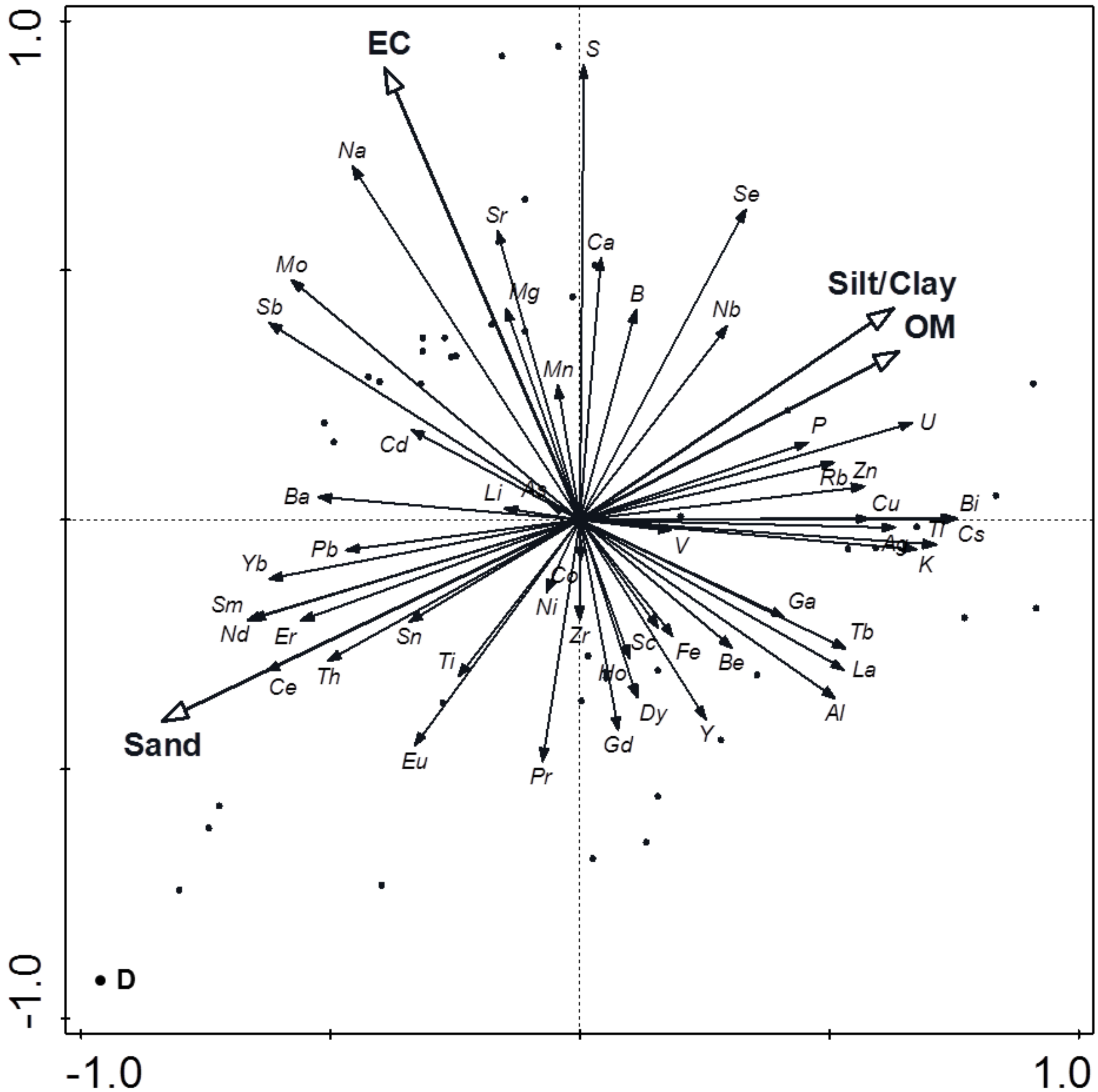

Figure 3.13. Ordination plot of RDA of element concentrations in DF to 1m depth constrained by environmental variables (in bold): Sand = %, EC = Electrical Conductivity, OM = Organic Matter, and Silt/Sand = %. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

with reduced iron (Fe^{2+}). Pyrite when exposed to aerobic conditions during dry periods becomes oxidized to SO^{2-}_4-S. During wet and dry climatic cycles, oxidation of pyrite is likely to be responsible for sulfur as sulfate which is able to move in and out of the wetland system (Lamers, et al., 1998, Bailey Boomer and Bedford, 2008, Vasilas, et al., 2010, Cowdery and Brigham, 2011, Demers, et al., 2013).

Table 3.4. Pearson Correlation coefficients of select soil physical properties and the highest correlated soil chemical elements in fringe to 1m depth. (p<0.001). In the PPR, elements in bold (Ni) are uncommon elements and elements underlined (Na, S, Mg) are common in wetland of the region.

	------------------------------------ Elemental Correlation (r^2) ------------------------------------				
	-- Combined Fringe Data --				
Depth	OM (-0.660)	BD (0.631)	Se (-0.628)	**Ni (0.607)**	*Mg (0.509)*
pH	Sr (0.720)	*Mg (0.710)*	Se (-0.628)	U (0.463)	EC (0.445)
Clay	Cr (0.696)	Al (0.691)	Fe (0.651)	Zn (0.607)	Rb (0.606
EC	*Na (0.721)*	*S (0.715)*	Sr (.605)	B (0.524)	Pr (-0.491)
	----------------------------------- Undisturbed Fringe (UF) -----------------------------------				
Sand	Silt (-0.756)	Al (-0.741)	Rb (-0.737)	Zn (-0.728)	Cu (-0.709)
EC	OM (0.505)	*S (0.499)*	*Na (0.469)*	Ag (0.494)	U (0.454)
Depth	**Ni (0.738)**	BD (0.721)	Se (-0.705)	OM (-0.684)	*Mg (0.670)*
Silt	BD (-0.761)	Sand (-0.756)	Cd (0.656)	OM (0.615)	*Mg (-0.591)*
Clay	Ga (0.844)	Al (0.843)	Cr (0.798)	Sc (0.782)	Th (0.758)
pH	Sr (0.748)	*Mg (0.661)*	BD (0.554)	Se (-0.531)	U (0.502)
	--Disturbed Fringe (DF) -----------------------------------				
Sand	Silt (-0.752)	U (-0.668)	Nd (0.664)	Sm (0.652)	Yb (0.627)
EC	*S (0.803)*	*Na (0.798)*	Sr (0.711)	B (0.664)	Al (-0.632)
OM	Th (-0.690)	Se (0.657)	Depth (-0.648)	BD (-0.612)	Yb (-0.605)
Silt	Sand (-0.752)	Yb (-0.658)	Nd (-0.638)	Sm (-0.637)	Ce (-0.616)
Clay	Zn (0.613)	Cu (0.568)	Cr (0.527)	K (0.519)	Fe (0.486)

Naturally found in the PPR soil parent materials, Na and Mg salts have variable concentrations related to the composition and original concentrations levels of the glacial soil parent materials (Bluemle, 1980). Higher concentrations of these salts can be found in soils in poor quality wetland and fringe sites due to the lateral subsurface water movement into the wetlands occurring from percolation through the surrounding landscapes transporting Na and Mg as salts. These salts naturally accumulate as ions within the wetland system are readily soluble, and influence the EC of wetland soils (Timpson, et al., 1986, Richardson and Arndt, 1989, Seelig, 2010).

Sediments eroded from the surrounding landscapes can contribute to higher concentration of phosphorus deposited within the wetland (Bailey Boomer and Bedford, 2008). This, in part, could also be a result of fertilizer additions to the surrounding landscapes or depositions of windblown sediments during wind erosion events. Dissolved and particulate P readily moves into wetlands through sediments that are that elevated in phosphorus and move through runoff during heavy precipitation or dust events (van der Valk, et al., 1978, Woltemade, 2000, Lamers, et al., 2006, Cowdery and Brigham, 2011, Jacob, et al., 2013). However, P solubility is readily influenced by pH and presences of soluble Al^{3+}, Fe^{3+}, and Ca^{2+}ions.

An increase in nickel concentration within the soil may be associated with anthropogenic influences such as fertilizer or urban manufacturing infrastructure. However, this area is far from urban infrastructure and is not likely influenced by industrial sources (Holmgren, et al., 1993, Hupp, et al., 1993, Mortvedt, 1996, Beck and Sneddon, 2000). As seen in Table 3.3 and 6 however, nickel shows a positive correlation with depth for the combined wetland and fringe and UF and DF data in addition to the combined UW and UF as well as UF. There is negative correlation with OM for the combined wetland and fringe. Organic matter usually is higher within the topsoil and decreases with depth within the soil profile. This correlation indicates that as OM decreases, Ni increases with depth in soil. However, this trend was not identified for wetlands alone (Table 2.2).

Organic matter is one of the main EV factors that influence the multi-element chemistry of both DW (Table 3.1 and 3.2) as well as the combined data. As seen in Figure 3.6 within the surface OM layer, the UW and UF have higher OM as compared to DW and DF (Martin and Hartman, 1987a). In Figures 3.8 and 3.10, OM and depth plus OM and BD are inversely related and negatively correlated (vectors point in opposite direction). Organic matter influences soil aggregation and structure which generally reduces BD. Organic matter appears to be positively correlated with S and negatively correlated with Ni in the RDA ordination plots and confirmed by the Pearson correlation (Figure 3.8, Table 3.3). This could be due to the ion exchange properties of OM because S and Ni can be influenced by the chemical charge properties of the OM. Sulfur is a component of OM found as amino acids and other structural components and is a common ion as $SO^{=}_4$ or $S^{=}$ in ground water in these glacial systems (Brady and Weil, 2002, Schaetzl and Anderson, 2005).

Sodium (Na) and S are correlated with EC; the vectors point in similar direction (Figure 3.8, 3.9, 3.10 and Table 3.3 and 3.4). This occurs because EC is a measure of ions such as Na and S (as SO_4^{-2}) and salts in solution are common in surface and ground water of this PPR region (Sparks, 1996). Salts easily move within the soil profile with changes in water flows and can be readily transported through erosion and water movement during evapotranspiration (Malo, et al., 1974, Mikac, et al., 2011, Kissoon, et al., 2015, Yellick, et al., 2016). In addition, due to the calcareous nature and mineralogy of the geologic materials in this region's parent material, magnesium salts tend to be higher in this region, resulting in Mg being positively correlated with soil pH (Bluemle, 1980, Schaetzl and Anderson, 2005). In Figure 3.2, DW and DF shows higher EC starting at the mineral surface throughout the soil profile as well. Site and EC vectors are directed in opposite directions showing an inverse relationship with each other (Figure 3.8, 3.10). This is likely related to anthropogenic disturbances on the DW landscapes since EC in the DW and DF RDA models is the highest variance explained (Table 1). The Na and S reflect the characteristics of groundwater which is impacted by the soil's glacial till parent material which is derived from marine deposits (Pierre shale) in this region of the PPR (Bluemle, 1980).

Magnesium (Mg) has a positive relationship with pH, which may relate to Mg forming salts in the wetland (Table 3.3 and 3.4). Disturbed wetlands (DW) and DF have a higher pH than UW and UF (Figure 3.1) which is likely related to the higher salts in the DW and DF (Figure 3.2) and from the deposition sediments within the wetland from the surrounding landscape. Altered hydrology, due to uniform crop growth characteristic (i.e., corn, wheat) not utilizing as much water as native vegetation, influences salt movement in the PPR soils (Arndt and Richardson, 1988). In general, soil hydrology related to runoff, precipitation, and subsurface water movement affects the chemical properties (salt) in these soils. A trend not seen previously in the wetland RDA analysis and Pearson correlation coefficient is a positive correlation of depth and Mg for the UW, UF and for the combined data. Perhaps an association is present within the landscape and sample location, which could play a role within soil chemical multi-elements. In addition, the glacially derived parent material could influence the UW and UF (Kantrud, et al., 1989).

The large number of elements in the upper left quadrant of the RDA plot appears to be directly related to soil pH (Figure 3.1) in UW and UF (Figure 3.9). Soil P appears to have an inverse relationship with soil pH in both UW and UF (Figure 3.9 and Table 3.3). Both of these trends were also seen previously with RDA UW plot (Figure 10). Phosphorus only appears to be positively correlated with OM for the DW. Perhaps this is a result of the addition of P containing fertilizers on the surrounding tilled landscape and the accumulation in the biomass of wetland plants (Khan and Brush, 1994, Freeland, et al., 1999). Also, waterfowl naturally inhabit these wetlands in the PPR as well as use these wetlands during migration periods and can be significant P contributors (Guntenspergen, et al., 2002).

Bulk density (BD) is an EV factor in DW and DF (Figure 3.9 and Table 3.3). This is likely due to periodic disturbance of the disturbed sites through tillage and other anthropogenic activity as illustrated in Figure 3.7. Often, tillage is directly imposed on the DW and DF during dry periods, which can increase BD due to breaking down OM through oxidation, soil structure disturbance, and mechanical compaction. However, in the short-term tillage can reduce BD due to a loosening effect on the soil. Sediments from cultivated fields would likely be lower in OM in the DW and DF. However, the most likely cause of BD increase is due to the deposition of erosional soil sediments lower in organic matter in the wetlands and fringe caused by tillage and low surface cover in the surrounding uplands (Figure 3.7) (Brubaker, et al., 1993, Freeland, et al., 1999, Skagen, et al., 2016). Sediments deposited in wetlands are single grained and lack structure which is presented as a soil mass with low porosity due to lack of structure. Deposition of erosion sediments on the soil surface of the wetland and fringe will result in averaged of values of the wetland soils to be biased by the chemistry of the depositional sediments. Organic matter reduction is due to differences in biomass production between the two types of wetlands and fringe as well as occasional mechanical disturbances of the DW and DF contributing to oxidation and decline of OM.

3.5. Summary and Conclusions

Within the Missouri Coteau, wetland sites were selected in a similar broad scale topographical setting in order to reduce the variability between locations. But, these are natural landscapes and the heterogeneity of the underlying glacial till sediments as well as soil series/type can change in a matter of a few feet (Soil Survey Staff, 2010). The calcareous parent material, which creates chemical and physical characteristics that are unique to the PPR, plays a role in the multi-element distribution for such elements as P, Mg, Na, Ni, and S (Arndt and Richardson, 1989, Richardson and Arndt, 1989). The site EVs reflect the anthropogenic influence on the surrounding landscape for the DWs and DFs.

Multi-element chemistry of the wetlands reflects the wetland and fringe quality and the EV’s that relate to and affect the quality. Disturbed wetland margin areas with a fringe have a different chemical signature vs. undisturbed wetland fringes as seen by the RDA ordination plots. Differences in EV (such as OM, BD, EC, pH, depth, and texture) between DW, DF, UW, and UF confirm the common understanding of the differences between cultivated and undisturbed landscapes (Brinson, 1993a, Parkin, 1993, Bedford, et al., 1999, Gwin, et al., 1999, Jolley, et al., 2010, Paradeis, et al., 2010). Based on the RDA models, there does not appear to be any placement trend or grouping with DW, DF, UW, and UF in relation EV and multi-elements. Pearson correlation coefficients identified that with wetland and fringe landscape positions Ni plays a role in the UW, UF and combined data with EVs depth and OM. This is different from what was previously seen with the Pearson correlation coefficients for wetlands, which showed that Se and Nb play a role with EV's BD, OM, and depth. A larger sampling scheme is suggested to further determine the broad scale impacts by EV. This research generates the potential that sampling in the fringes instead of the wetlands, when the wetlands are flooded creating problematic sampling, is suitable in many cases and will yield data from which to generate conclusions that can be valid as long as the relationships between the wetlands and their surrounding landscapes are understood.

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4. FOOTSLOPE AND BACKSLOPE LANDSCAPE POSITION IN RELATION TO SOIL MULTI-ELEMENT COMPOSITION AND ENVIRONMENTAL VARIABLES AT DEPTH

4.1. Abstract

In the Prairie Pothole Region (PPR), the impact of surrounding landscapes on wetland ecosystems has been recognized but there is limited understanding of how soils on landscapes influence the multi-element chemistry concentrations of wetlands at depth. Knowledge of multi-element chemistry composition is needed to aid in understanding soils and soil development and their relationship within the wetland ecosystem. This would aid in wetland and landscape restoration and provide information for future guidelines on wetland management within their landscape settings. The objectives of this study were to: 1) identify differences or similarities in biogeochemical characteristics of footslope (FS) and backslope (BS) soils in PPR wetland ecosystems; 2) assess the vertical variation in the chemical composition of FS and BS soils; and 3) interpret the soil chemistry reflected by undisturbed footslope UFS and undisturbed backslope (UBS) (good quality; prairie vegetation) and disturbed footslope (DFS) and disturbed backslope (DBS) (poor quality; cultivated) emphasizing differences between the landscape positions and linking to our findings in our previous work. A field study was conducted on six DFS, DBS, and six UFS, UBS adjacent to North Dakota (ND) PRR wetlands. Using redundancy analysis (RDA), resulting environmental variables (EV) models of element concentrations to a 1m depth in DFS, DBS, UFS, and UBS were generated. The RDA ordination plots of element concentrations in UFS to depth of 1m was constrained by one set of variables (sand, pH, depth, site, bulk density (BD)) while in DFS, a different set of variables (site, pH, EC) provided constraint. This is also seen for UBS (sand, pH, depth, BD, silt/clay) while DBS has a different set of variables (site, EC, depth, organic matter (OM), pH). Pearson correlation coefficients of select soil physical properties correlated with the five most prominent soil elements differed between the DFS, DBS, UFS, and UBS. This research indicates that anthropogenic impacts on landscapes in the DFS and DBS likely influenced their subsurface hydrology but differed in physical and chemical properties from the UFS and UBS. These differences appear to be influenced by the unique chemical and physical characteristics of the underlying calcareous parent material. Thus, the "site" EV reflects the anthropogenic influences on the surrounding landscape for the DFS and DBS.

4.2. Introduction

Understanding the relationship between a wetland ecosystem and the surrounding landscape is not always clear although wetlands are known to be linked with the properties of the landscape (Bedford and Preston, 1988, Bedford, 1996). The entire wetland ecosystem including the landscape improves water quality, recharges existing aquifers, enriches biological diversity, and provides flood control within the regions where they exist (Woltemade, 2000, Brady and Weil, 2002, Lamers, et al., 2006, Oki and Kanae, 2006, Gleason, et al., 2008, Hussain, et al., 2012). The PPR, glacially created ~10,000 - 12,000 years ago with varying, irregular and undulating deposition of glacial till parent material and characterized by closed hydrological system, is located in Montana, North Dakota (ND), South Dakota, Minnesota, Iowa, and the Canadian Provinces (Bluemle, 1980, Berkas, 1996, Dahl, 2014). Since 1780, 50% (2,000,000 acres or 893,000 hectares) of ND PPR has disappeared due to land conversion (tillage, drainage, grazing, construction) (Tiner, 1984, Martin and Hartman, 1987b, Winter, 1988, Dahl, 1990, Berkas, 1996, DeKeyser, et al., 2003). In ND, the remaining wetlands, are to some extent, protected from anthropogenic conversion due federal, state, local, and tribal agencies (Leitch and Baltezore, 1992). Today, relatively undisturbed prairie pothole wetlands with intact undisturbed landscape can only be found in grazed native grassland landscapes (DeKeyser, et al., 2003, Mita, et al., 2007, Hargiss, et al., 2008, Paradeis, et al., 2010).

A link between wetlands and their landscapes can be tied to the mineralogical composition of the parent material that was deposited ~12000 years ago as over time soil formation and development has occurred influencing the hydrology of the area (Bluemle, 1980, Bedford, 1999). The function of the wetland position within the landscape correlates with the salinity and soil chemistry (i.e., plant available nutrients) of the PPR due to a ground-water hydrological flow system and surface topographical relief (Kantrud, et al., 1989, Richardson, et al., 1994, Bedford, 1999, Bedford, et al., 1999). Over time, landscape transitions affect the biogeochemical functions of wetlands through sediment deposition and nutrient movement (i.e., erosion and disturbance) (Brinson, 1993a).

Management of surrounding landscapes impacts soil erosion intensity resulting in sedimentation in the wetland and creating wetland degradation (Byrdand Kelly, 2006). From 1997-2009, PPR wetland quantity has declined by 39% due to anthropogenic impact on the surrounding landscape (Dahl, 2014).

When established perennial vegetation (i.e., native grasses) occurs on the landscape, the vegetation surrounding the wetland on the landscape can reduce the runoff water impact and can catch/retain sediment outside of the wetland (Dahl, 2014). However, as sediment is deposited within the wetland this process can, in time, alter the vegetation present within the wetland (DeKeyser, et al., 2009). When a landscape is tilled, the amount and composition of plant cover is reduced resulting in the vegetation to be actively growing only for a few months during the growing season affecting water movement within the system (Euliss and Mushet, 1996). A grassland landscape has vegetation able to catch and utilize the water allowing it to percolate naturally through the soil into the wetland instead of flowing across the landscape (Euliss and Mushet, 1996). Since the water level has greater fluctuation in a tilled landscape wetland with increased sedimentation, the wetland vegetation present is impacted (DeKeyser, et al., 2003).

There is a need to understand the broader perspective of how the landscape is managed and the landscape impacts on the wetland ecosystem (Euliss, et al., 2010). Multi-element analysis can be an effective tool in studying soil chemistry due to advances in analytical technology and enables examination of detailed landscape chemistry in an efficient manner. But wetland and landscape chemistry correlated with ecosystem functions can be confusing. There is still limited understanding of different ecosystem functions that may occur in natural, restored, or created wetlands and the impacts that wetlands and landscapes have on these functions (Mitsch, et al., 2012). Thus, the relationship between wetland ecosystems and the surrounding landscape linkages need to be better defined (Bedford and Preston, 1988).

Wetland and landscape functions can be categorized through biogeochemistry, hydrology, vegetation, and environment (Brinson, 1993b). Use of biogeochemistry in studying these functions aides in a better understanding of how the element concentrations vary within a landscape attached to a wetland (Glazovskaya, 1968). The soil element content analysis is a potential technique to distinguish between different levels of disturbance on the landscapes. Knowing the identifying “fingerprints” within the pothole watershed can show the impact that landscapes can have on the wetlands (Martin and Hartman, 1987a, Bedford, 1999, Beckand Sneddon, 2000, Wilson, et al., 2008, Mikac, et al., 2011, Zhuang and McBride, 2013, Werkmeister, et al., 2018).

To study wetland landscape chemistry, sound sample data collection procedures as well as maintaining sampling consistency throughout the study by taking multiple sampling points to gather a representative picture of the wetland are needed (Yang and Rose, 2003, Dahlin, et al., 2012). Studies involving sampling in two different landscape management systems (i.e., cultivated vs grassland), can generate results relating to soil profile development of the A (surface) horizon to plant nutrients or OM level in both the wetland and landscape positions. In addition, depending on sampling location and deposition within the landscape, the landscape can show past and current landscape uses and practices (Freeland, et al., 1999). Studying geochemistry in the landscapes helps us to understand how elements migrate within the landscape and developing an understanding of the relationship in the geochemistry of the wetlands and landscapes (Glazovskaya, 1968). This aids in the understanding of how elements and landscape components (i.e., parent material, vegetation, climate, and organisms) interact with each other as one entity (Glazovskaya, 1968).

This research evaluates how the landscape positions impact the selected wetlands and their fringes and assesses the relationships between the wetlands and their surrounding landscapes. This study compares untilled undisturbed soil footslopes (UFS) with tilled disturbed soil footslopes (DFS) along with representative undisturbed backslopes (UBS) and disturbed backslopes (DBS) areas by looking at soil biogeochemistry and element concentrations at various depths in the footslope (FS) and backslope (BS) landscape positions. The quality of the wetland sites were identified by previous research and used the Index of Plant Community Integrity (IPCI) (DeKeyser, et al., 2003).

The objectives of this study were to: 1) identify differences or similarities in biogeochemical characteristics of footslope and backslope soil in the PPR; 2) assess the vertical variation in the chemical composition of FS and BS soils; and 3) interpret the soil chemistry reflected by UFS and UBS (good quality; prairie vegetation) and DFS and DBS (poor quality; cultivated) emphasizing differences between the landscape positions and linking to our findings in our previous work. In this study, we hypothesize the following: 1) DFS, DBS, UFS and UBS will have distinctly different concentrations of multi-elements related to anthropogenic activity, and 2) at depth, there will be chemistry differences between the two groups of landscape positions related to disturbances and topography.

4.3. Materials and Methods

4.3.1. Field and Lab Analysis

A field study conducted in the PPR evaluated the BS and FS landscape positions surrounding wetlands within the North Dakota Missouri Coteau region. This region of the PPR, contains small, shallow glacial basins and zone specific plant communities which influence the characteristics of wetlands in the area (Stewart and Kantrud, 1971). The landscape samples (FS, BS) were taken at twelve ND PPR wetland locations to support in the explanation of the differences between UW and DW. The wetlands, latitude 47.3^{o} to 47.9^{o} and longitude -100.5^{o} to -101.1^{o}, were evaluated in Burleigh, McLean, Sheridan, and Ward counties. The sites were selected from wetlands in this region previously assessed for quality using the Index of Plant Community Integrity (IPCI) (DeKeyser, et al., 2003), where the soils and landscapes have developed from similar glacially derived parent materials, including lacustrine and palustrine sediments (Kantrud, et al., 1989). The ND soils have a mesic soil temperature regime (8^{o}C to 15^{o}C mean annual soil temperature) and a ustic moisture regime (plant-available moisture limited at times during the growing season) (Soil Survey Staff, 2014). Six wetlands were classified as disturbed wetlands (DW) and six wetlands were classified undisturbed wetlands (UW) by IPCI as either very poor (VP), or very good (VG) respectively (DeKeyser, et al., 2003). In 2012, after a period of relatively low rainfall, most seasonal wetlands as well as landscapes were dry and allowed vehicles. Sampling of the wetland has been previously reported by Werkmeister et al. (2018). In addition to samples with within the wetland, a total of six cores, 3 in FS and 3 in BS, up to 1 m depth were collected using a truck mounted hydraulic soil probe as a transect from the wetland center across the most typical aspect of the associated landscape. All six cores were used for pH and EC determination but subsequently, one of the cores were used for multi-element analysis and BD, and one core for soil characterization and textural analysis (Figure 2.1). Footslope and BS landscape positions were identified by this topography (Figure 4.1). The FS and BS positions were chosen based upon impact to the wetland biogeochemistry (Brinson, 1993a, Soil Survey Staff, 2014). The soil cores were encased in acetate (metal free) liners to prevent moisture loss and contamination, sealed, and labeled, and stored in a cold room (2^{o}C) until processed. For soil sampling, the soil cores were segmented in 10 cm increments from the mineral surface to a depth of 30 cm, and then at 15 cm increments to a depth of 1 m (Figure 4.1). The soil samples were air-dried, hand crushed and passed through a 2 mm stainless steel sieve to prevent trace metal contamination which often occurs from standard brass sieves and mechanical grinders (Thompson and Bankston, 1970, Hickson and Juras, 1986). Subsamples were analyzed for pH and electrical conductivity (EC) on 1:1 (soil:water) basis (Watson and Brown, 1998, Whitney, 1998). Bulk density (BD) analysis followed the abbreviated core method of Blake and Hartge (1986). Organic matter was determined by loss of weight on ignition (Combs and Nathan, 1998). Particle-size analysis was obtained by the hydrometer method of Gee and Bauder (1986). A subsample was milled using carborundum media to <180 μm for aqua regia digest and analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Ultra Trace 2 method) for multiple elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Ge, Gd, Hf, Hg, 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, Zr) (Act Labs, 2016). In a few instances, if FS and BS had an organic matter layer (O horizon) on the surface, the layer was separated from the mineral surface and sampled in a manner similar to the mineral surface. The organic material (O horizon) in the footslope and backslope was air-dried, hand crushed with mortar and pestle with the aid of liquid nitrogen to <180

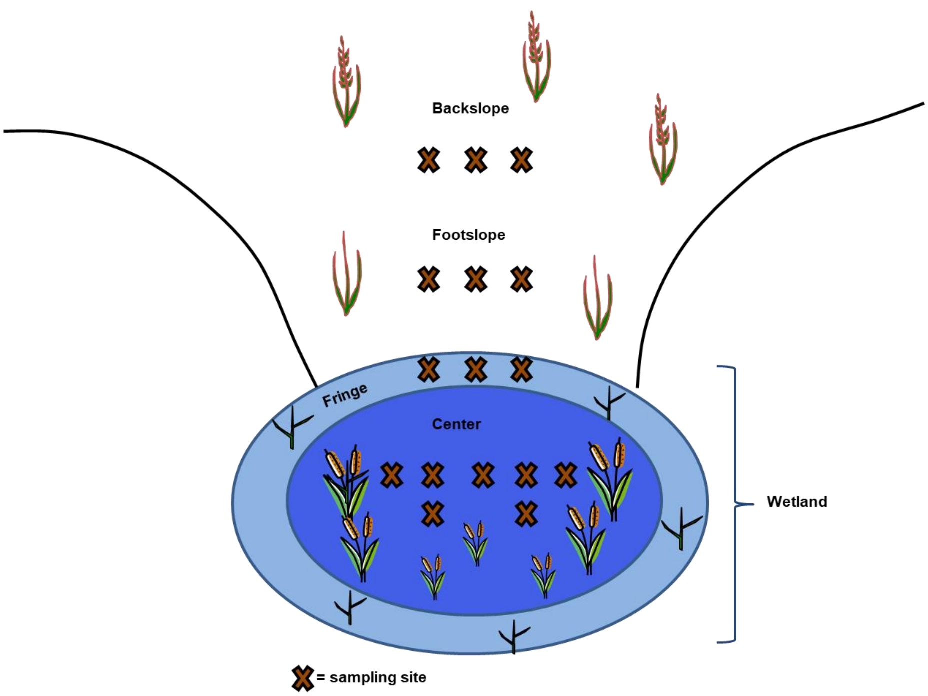

Figure 4.1. Schematic representation of W, F, FS, and BS landscape sampling locations.

μm for digestion and analyzed by ICP-MS (Act Labs, 2016). However, for this chapter, O horizon will not be addressed due to O horizon lacking in most landscapes and there were not enough values to test differences between FS and BS.

4.3.2. Data and Statistical Analysis

Element data received from the laboratory was presented in different concentrations (ppm, ppb) and converted to one standard unit (μmol g^{-1}). If the data was not normally distributed, it was either $\log_{10}$ or Johnson transformed to obtain normal distribution with Minitab statistical software (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018). For the element concentration data in the data set: 1) if more than half of the samples had concentrations below the detection limit of that element, these were deemed non-detectable and not included in analysis; or, 2) if less than half of the element concentrations in the samples were below the detection limit but the remainder of the values were within detection limits, then the values below detection were replaced with half the detection limit and included in the analysis (Farnham, et al., 2002). Due to a large database and for logistical reasons, the multi-element data concentrations were averaged for each depth at each landscape position (FS, BS) and then averaged by wetland quality (very poor/disturbed i.e., tilled, or, very good/ undisturbed i.e., native grassland).

The environmental variables (EVs) were selected based on their quantifiability in the soils and landscapes. The EVs evaluated in this study were electrical conductivity (EC), pH, sampling depth (0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105+ cm), soil texture (sand, silt, clay), site location, organic matter (OM), and bulk density (BD). Generally, for each depth, samples from 3 cores (Werkmeister, et al., 2018) in the FS and samples from 3 cores in the BS (n=6) were used for EC, pH, BD, OM, while 1core each for FS or BS (n=2) for multi-element analysis except when the sample was not adequate (e.g., a core could not be collected to a 1m depth). In some cases, due to very dry soil conditions, difficulty sampling below 60 cm was experienced. However, in all cases, all sample cores extended well into the soil parent material (C horizon) due to the thinned A and B horizons. Samples from one core each in both FS and BS was used to determine soil texture due to limited sample quantity (e.g., textural analysis requires a large sample size). The strength of the relationships between the EV and multi-element concentration were assessed using redundancy analysis (RDA) (Yellick, et al., 2016) using

Canoco 5 (ter Braak and Smilauer, 2012). The RDA model results of element concentrations using EV was determined by manual forward selection procedure with Monte Carlo permutation tests (ter Braak and Smilauer, 2002). The ordination plot of RDA for element concentrations is displayed as two-dimensional for the purpose of this paper, but it is actually three-dimensional within X, Y, and Z planes. A Pearson correlation of the five most strongest related soil elements and select soil physical properties in DFS, UFS, DBS, and UBS to 1m depth ($p<0.001$) was conducted with PROC CORR in SAS (SAS Institute, 2008).

4.4. Results and Discussion

The management of the surrounding landscape (i.e., anthropogenic influence) affects the wetland (Gustafson and Wang, 2002). A tilled landscape when compared to a grassland landscape has an increase in sediment deposition at the bottom of the landscape from soil erosion (Gleason and Euliss, 1998, Gustafsona nd Wang, 2002). Water movement through the landscape into the wetland is due to extensive hydrology network links the landscape together creating unique soil characteristics (Hubbard, et al., 1988, Godwin, et al., 2002, Guntenspergen, et al., 2002). The soil type, climate, parent material, and landscape all play a role in how the multi-elements are presented within the landscape (Gustavsson, et al., 2001). Differences in pH values between DFS, DBS, UFS, and UBS were observed throughout the soil profile to a depth of 90cm (Figure 4.2). The almost vertical linear pH lines of DFS and DBS likely show the tillage influence by creating a homogeneous profile (Figure 4.2). The UFS and UBS had lower pH throughout the soil profile to a depth of 90cm when compared to DFS and DBS. There was a significant difference in pH between the UFS vs DFS and UBS vs DBS, to a depth of 20cm where the DFS and DBS were more than a ½ pH unit higher than the UFS and UBS. As seen in Figure 4.2, the DFS and DBS had similar pH to a depth of 30cm perhaps due to the erosion of higher pH subsurface soil material on the landscape (i.e., eroded calcareous glacial till) and the blending of sediment by soil tillage, hence, creating uniformity within the top layers (Papiernik, et al., 2007).

When an area has been disturbed by tillage, the vegetation cover is changed from a permanent vegetative cover to an annual seasonal crop cover that does not utilize all of the precipitation that occurs over the effective plant-growing season (April – October). Thus, perennial vegetation on UFS and UBS utilizes moisture from precipitation throughout the growing season resulting in reduced deep percolation of water in the soil profile keeping the salts uniform through the profile. The topsoil EC is similar between the UBS and DBS while there is an increase in EC concentration at the UFS and DFS which are also similar to each other (Figure 4.3). There is also a significant difference (p<0.10) between the FS and BS landscape positions. The UFS and UBS have vertically similar lines throughout the soil profile perhaps due to 1) lack of the tillage disturbance; 2) constant movement of water through the profile; or 3) perhaps the system is in an equilibrium state relative to water. The UFS and UBS overall have uniform EC concentrations at depth which in part could be due to the vegetation effect and equalization of salt concentrations by diffusion within a constant aqueous environment. In the BS position, the excess water percolation moves the salts downward in the soil profile. In the FS, water moves to a shallower subsurface water table which contains dissolved salts. The capillary rise of the water brings the salts to the surface. The EC concentration increase at this position results from salt laden water winding up in the FS area and the salts are left behind as the water evaporates (i.e., capillary rise).

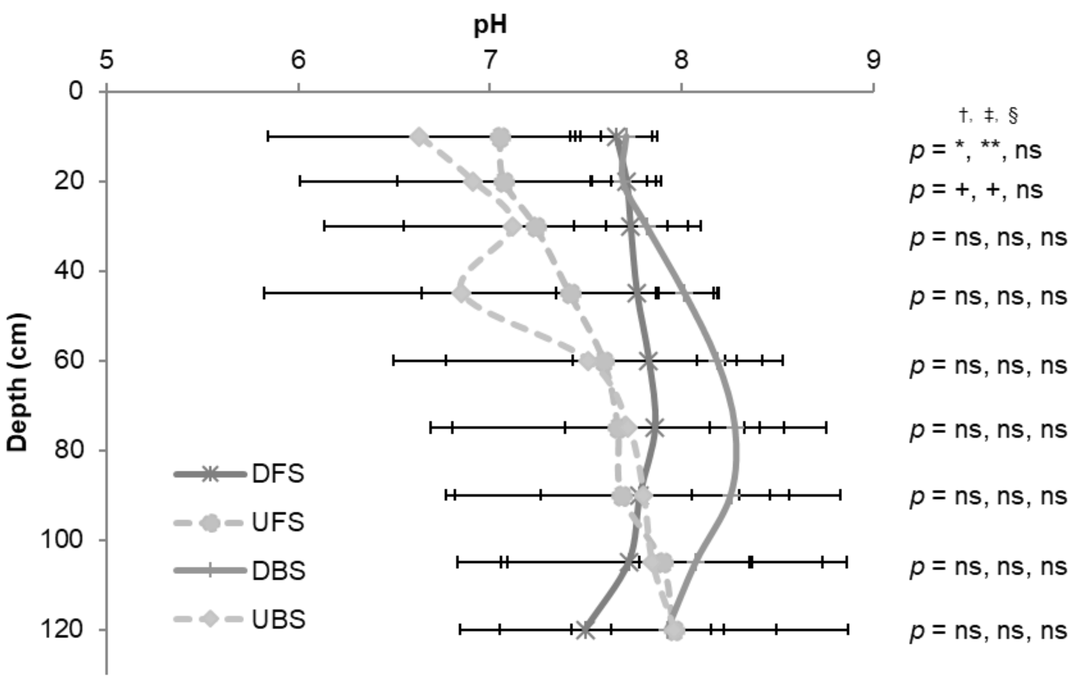

Figure 4.2. A comparison of averaged pH for DFS, DBS, UFS, and UBS at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

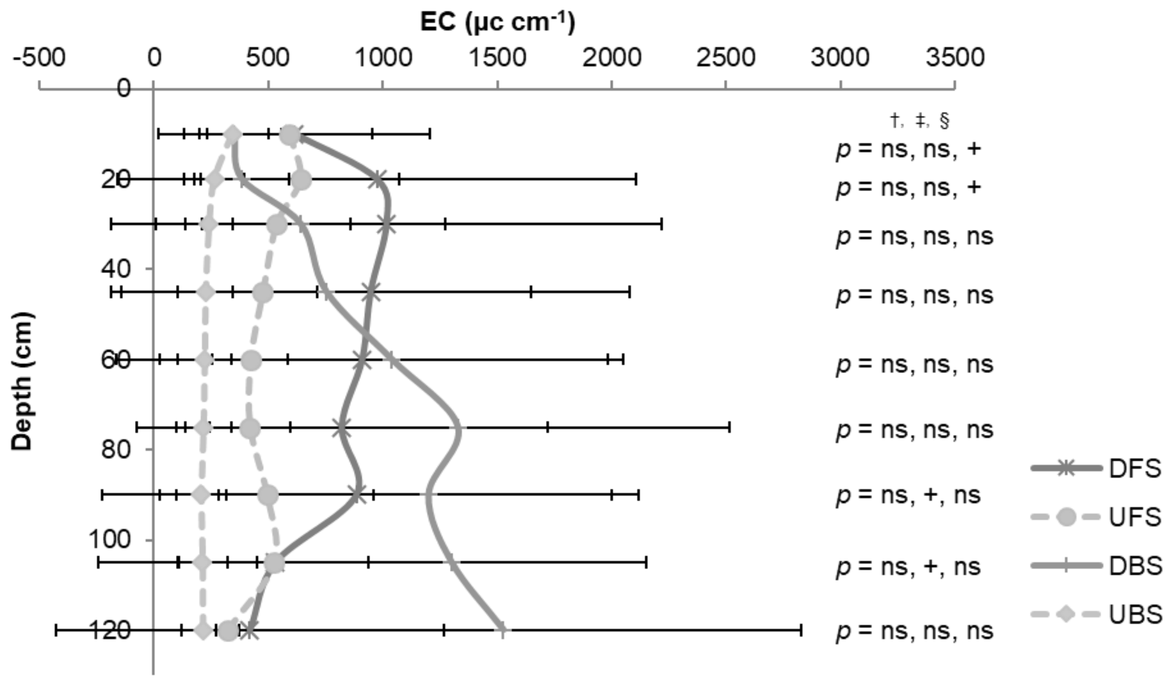

Figure 4.3. A comparison of averaged EC for DFS, DBS, UFS, and UBS at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

Overall, the texture of the FS and BS does not show differences between disturbed vs undisturbed landscape except for the UFS (Figures 4.4, 4.5, and 4.6). The two best indicators of cultivation on a landscape are sand and clay distribution and deposition in a wetland. The UFS, perhaps, is showing the minimal impact of erosion while as DFS, DBS and UBS are impacted (Arndtand Richardson, 1988). It has been previously shown that the landscape position affects the percent sand within the landscape (Arndt and Richardson, 1988, Brubaker, et al., 1993, Byrd and Kelly, 2006). The UFS does have textural differences which can be clearly seen with sand and silt from the topsoil to 45cm depth (Figure 4.4 and 4.5). There are significant differences in sand between UFS and DFS in upper profile as well as FS and BS across disturbance levels. However, no significant soil differences between UBS and DBS were observed. Perhaps the glacial till parent material was laid down relatively uniformly in this area by the glaciers and this is being reflected by the UBS, DFS, and DBS.

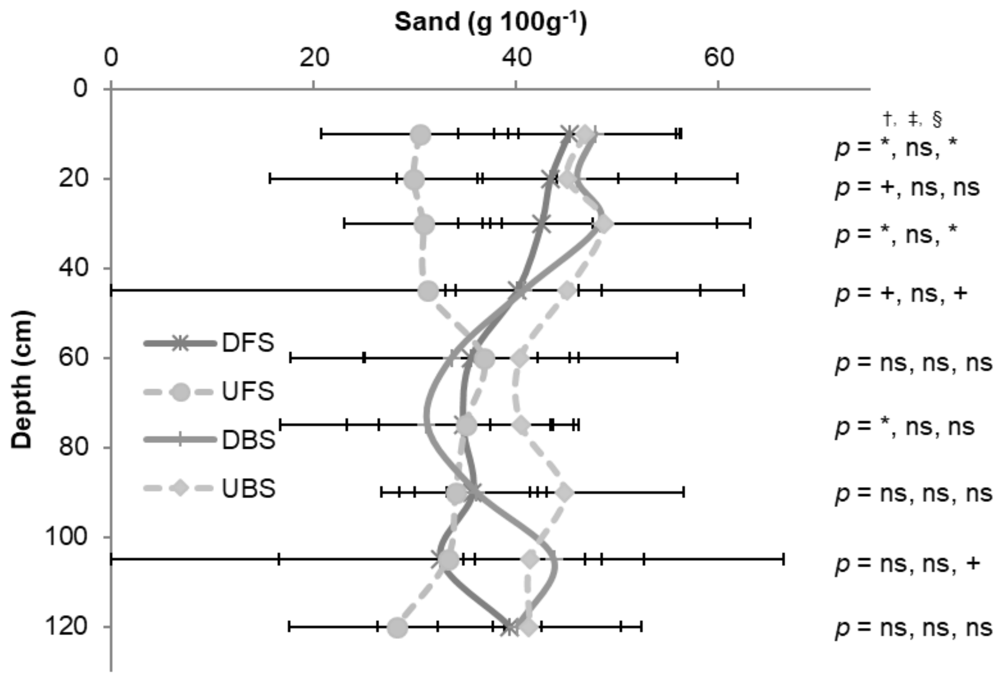

Figure 4.4. A comparison of averaged sand percent for DFS, DBS, UFS, and UBS at depth for the mineral horizons. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

Silt, however, shows differences between the landscape positions with significantly more silt in DFS than DBS which is likely due to erosion caused by tillage erosion (Figure 4.5). However, there are also significant differences across both situations between FS and BS with the presence or absence of disturbance. This likely due to erosion process of anthropogenic tillage.

Clay which would normally have differences in the wetland and marsh locations does not show anything of permanent significance throughout the soil profile in the footslope and backslope positions. The comparisons are nonsignificant between DFS, DBS, UFS, and UBS except at deeper depths between BS and FS (Figure 4.6). Clay shows up as an EV with higher explained variance in the RDA model for BS when UBS and DBS are combined (Figure 4.13 and Table 4.3).

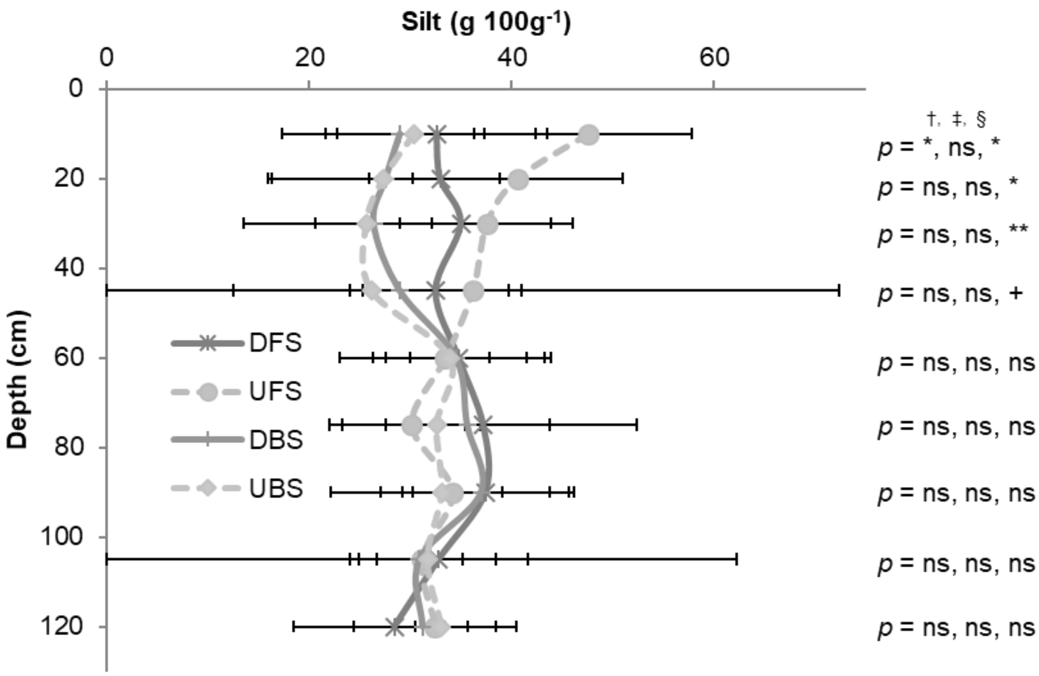

Figure 4.5. A comparison of averaged silt percent for DFS, DBS, UFS, and UBS at depth for the mineral horizons. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

Organic matter is a key influencer of soil quality within a landscape system (Bedford, 1999). When the upper landscape is impacted anthropogenically, erosion is significantly increased resulting from the loss of OM which affects soil structure and soil particle cohesion resulting in soil moving more readily within the landscape (Byrd and Kelly, 2006). As seen in Figure 4.7, the UFS and UBS have significantly higher OM soil to a 30cm depth. In addition, the OM concentration is significantly different (p value <0.0) from 0-10cm depth for UFS vs DFS and UBS and DBS (Table 4.2). This trend is also followed to the 10-20cm depth (Table 4.2) where the UFS had higher OM throughout the soil profile. The difference between the UFS and UBS throughout the soil profile is that the BS has higher erosion potential due to the slope and also the relationships between moisture and plant growth. The FS would have higher level of water availability due to runoff from higher landscape positions and potential capillary rise from the water table which in turn would allow ample vegetation growth when compared the BS position. Also, to note that

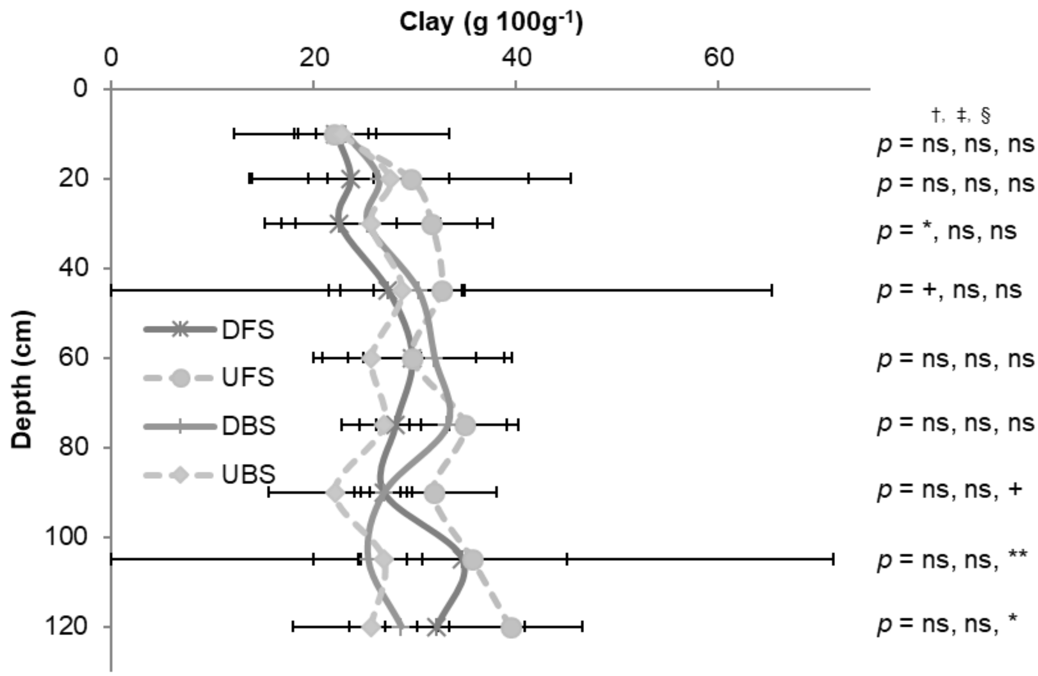

Figure 4.6. A comparison of averaged clay percent for DFS, DBS, UFS, and UBS at depth for the mineral horizons. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The p-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

there was significant difference between 10cm-60cm for the OM between the FS and BS landscape positions (Table 4.2). This is also likely due to natural soil formation processes where footslope positions tend to be moister. This better supports greater plant growth and greater biomass production which influence greater soil OM accumulations in the soil near the surface.

Within the soil to 30cm depth, the UFS and UBS have lower BD when compared to DFS and DBS. Bulk density shows a similar trend as seen with the OM (Figure 4.7 and 4.8). This trend could be explained by the depth of tillage disturbance. Most tillage occurs in the surface 0-20cm of the soil in this region. In addition, tillage processes can also cause compaction in the 20-30cm depth zone. Tillage destroys soil structure and when soil structure is destroyed, bulk density is increased resulting in DFS and DBS having higher bulk density within the topsoil.

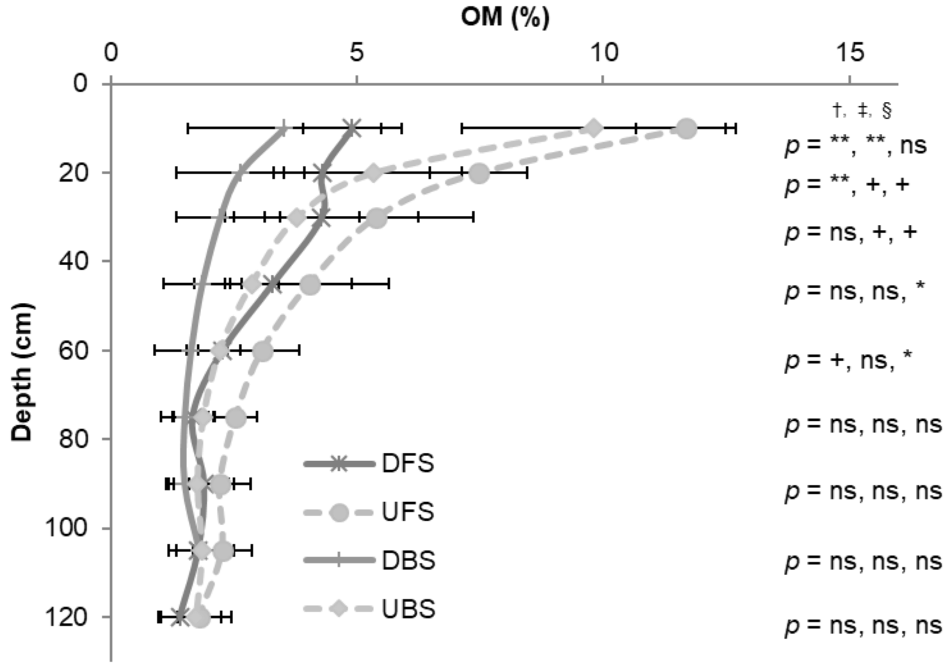

Figure 4.7. A comparison of averaged organic matter (OM) for DFS, DBS, UFS, and UBS at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

The RDA model of element concentrations for the combined DFS, DBS, UFS, and UBS to 1m depth identifies the primary environmental variables (EVs) EC, OM, sand, pH, and site (Figure 4.9 and Table 4.1). The EVs explaining the highest percent of variance for individual RDA mode are determined for the combined data for DFS, DBS, UFS, and UBS are shown in Table 4.1. The same logic for only footslope EVs (Figure 4.10) for combined DFS and UFS data are shown Table 4.2. Although the EVs ($p<0.01$) have high probability values for the data, only the substantial EVs are identified (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018). As seen in Table 4.3, 4.4, and 4.5, the EVs (EC, pH, site) are the same when the data for both the footslope and backslope and the footslope plus backslope are combined. A switch in explained variances was observed indicating site which is the topography location plays a role in the soil biogeochemistry (Table 4.2 and 4.3). Site as an EV for wetlands have previously been shown to relate to element concentration but the other landscape positions in the past have not been closely evaluated (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018). Site appears to be a critical EV illustrating the importance of site quality (e.g., with or without disturbance) in multi-element concentrations. As one moves up the landscape the slope potential increases and the topography changes from footslope to backslope which has a higher chance for erosion. Erosion can displace soil components downslope in the landscape position hence impacting the EV factors within each system.

In Table 4.4, the chemical elements that are most highly correlated with the underlying EVs in the footslope and backslope to a 1m depth are identified using Pearson correlation coefficients as well as in Table 4.5 for EVs in the footslope and Table 4.6 for backslope. The soil properties making up the main EVs are EC, depth, clay, sand, silt, site, OM, pH, BD and IPCI. Table 4.4 shows how these correlations are similar or different between the combined of footslope and backslope data and data specific to DFS, DBS, UFS, and UBS while Table 4.5 shows the correlation to the footslope and Table 4.6 correlations for backslope.

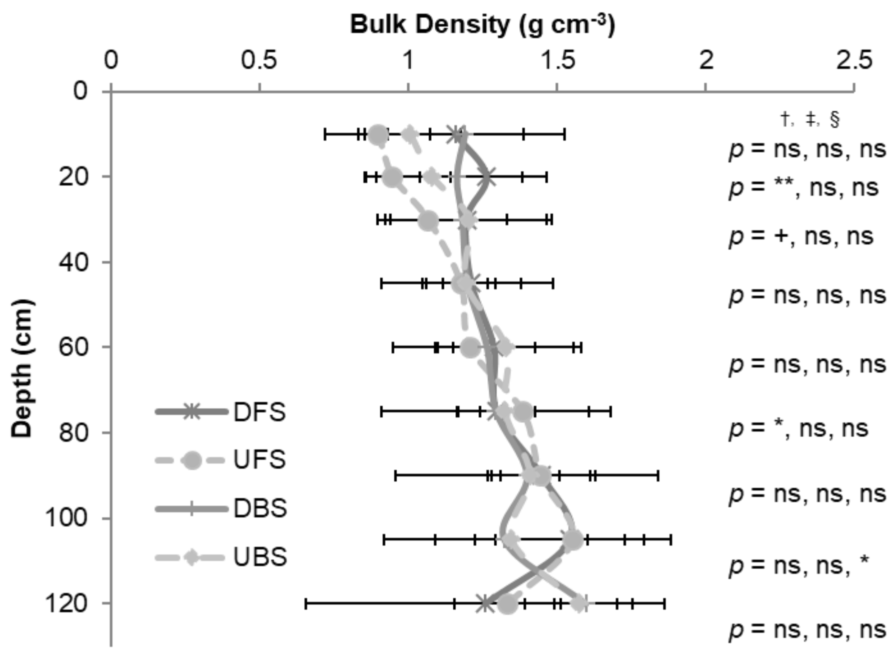

Figure 4.8. A comparison of averaged bulk density (BD) for DFS, DBS, UBS, and UBS at depth. Bars indicate the standard deviation of data for the profile depth. The values for the mineral layers are plotted at the flowing depth on the graph, 0-10cm plotted at 10cm, 10-20cm plotted at 20cm, 20-30cm plotted at 30cm, 30-45cm plotted at 45cm, 45-60cm plotted at 60cm, 60-75cm plotted at 75cm, 75-90cm plotted at 90cm, 90-105cm plotted at 105cm, and 105cm+ plotted at 120cm. Difference between † = DFS and UFS, ‡ = DBS and UBS, § = FS and BS at each depth were tested by One-way ANOVA in SAS. The *p*-values were categorized by <0.01= **, 0.01-0.05 = *, 0.05-0.10 = +, >0.1 = not significant (ns).

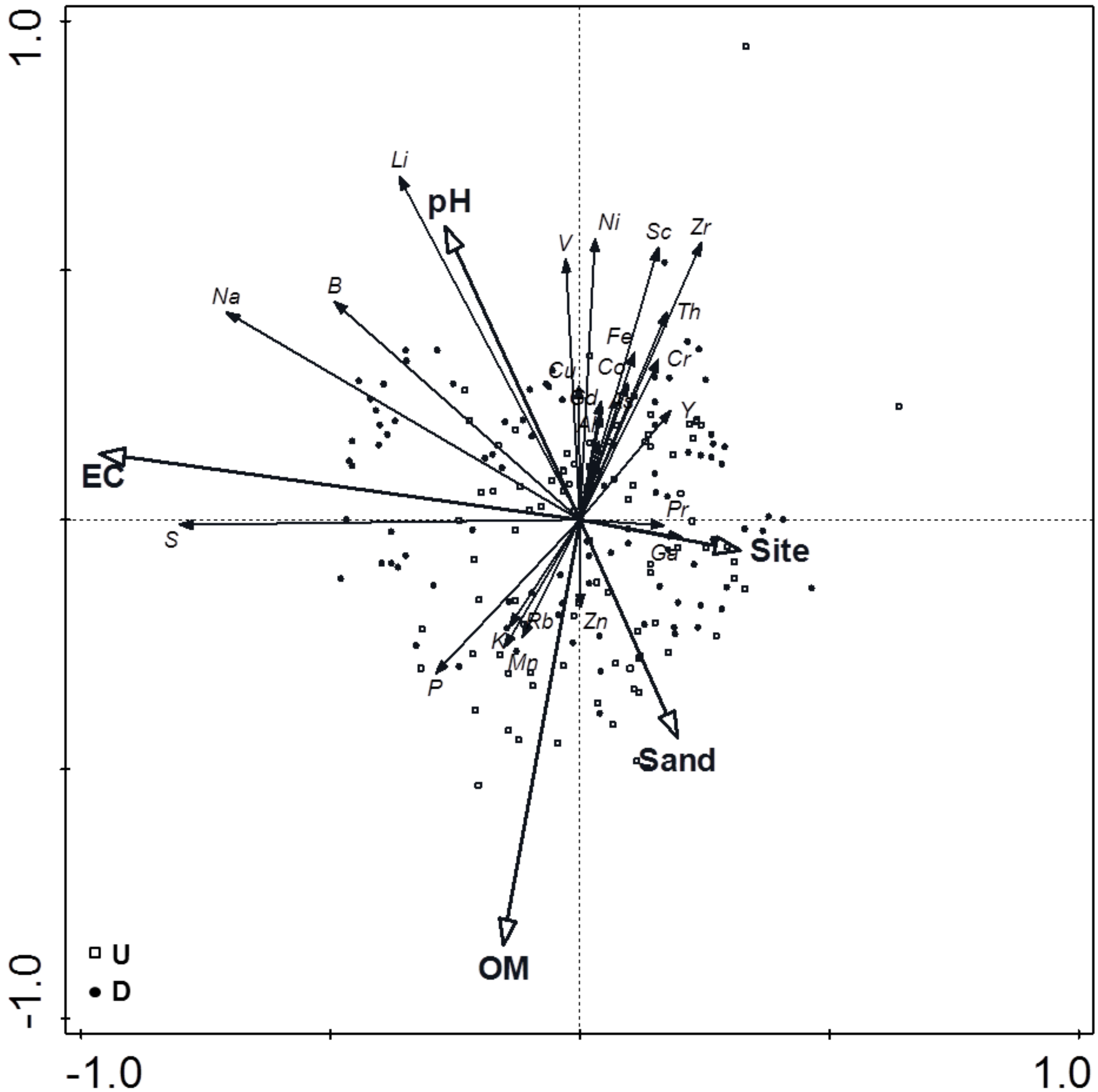

Figure 4.9. Ordination plot of RDA of element concentrations for combined data DFS, DBS, UFS, and UBS to 1m depth constrained by environmental variables (in bold): EC = Electrical Conductivity, OM = Organic Matter, Sand = Sand %, pH, Site = 12 sites. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

The element Ni in Table 3.5, 3.6, 4.6, 4.7, and 4.8 was noted within wetland and fringe soil systems as well as seen now in the footslope and backslope combined landscape as well as the footslope position but not in the DBS landscape system. The elements sodium (Na), sulfur (S), phosphorus (P), and magnesium (Mg) are commonly observed in PPR soils (Werkmeister, et al., 2018). The presence of Ni may be related to the composition of the glacial parent materials in this region of the

Table 4.1. Results of RDA model of element concentrations in FS and BS to 1m depth using environmental variables, determined by manual forward selection procedure with Monte Carlo permutation tests according to ter Braak and Šmilauer (2002) ($p<0.05$). EC = Electrical Conductivity, Depth = 1 m (0-105+ cm), Sand = Sand%, Clay = Clay %, Site = 12 sites FS or BS, OM = Organic Matter, pH, and BD = Bulk Density.

Environmental Variables	Explained Variance	*p*-value
	----%----	
-------------- Combined Footslope & Backslope Data --------------		
EC	27.45	0.001
OM	12.31	0.001
Sand	5.14	0.001
pH	2.05	0.001
Site	0.95	0.001
Total	47.90	
------- Undisturbed Footslope (UFS) & Backslope (UBS) ------		
Depth	24.96	0.001
EC	13.96	0.001
Sand	9.64	0.001
pH	2.45	0.001
Site	1.09	0.001
Total	52.10	
-------- Disturbed Footslope (DFS) & Backslope (DBS) --------		
EC	35.80	0.001
OM	14.14	0.001
Site	2.76	0.001
Clay	1.87	0.002
pH	0.93	0.003
Total	55.50	

PPR. There is a difference between the wetland (Figure 2.8), the wetland and fringe (Table 3.3 and 3.4) and footslope and backslope where Se were found as an important factor within the wetland and now in the backslope position. This in part perhaps due to the glacial parent material as well.

Sulfur is a common element found in PPR soils and occurs as variable sulfur concentrations (Table 4.4, 4.5, and 4.6) (Bluemle, 1980). Unable to determine S species by the analytical methods used in this study, the S levels reported here represent total S within the soils. To further understand the occurrence of S in the landscape, background knowledge of S transformations is needed. Pyrite when

Table 4.2. Results of RDA model of element concentrations in FS to 1m depth using environmental variables, determined by manual forward selection procedure with Monte Carlo permutation tests according to ter Braak and Šmilauer (2002) ($p<0.05$). EC = Electrical Conductivity, Depth = 1 m (0-105+ cm), Sand = Sand%, Site = 12 sites FS, pH, and BD = Bulk Density.

Environmental Variables	Explained Variance	*p*-value
	----%----	
	------------- Combined Data -------------	
Site	19.74	0.001
Sand	6.22	0.008
pH	2.78	0.004
EC	2.22	0.026
BD	0.44	0.029
Total	31.40	
	------- Undisturbed Footslope (UFS) ------	
Sand	44.92	0.001
pH	8.72	0.001
Depth	4.27	0.001
Site	1.24	0.002
BD	0.75	0.013
Total	59.90	
	-------- Disturbed Footslope (DFS) --------	
Site	46.34	0.001
pH	7.43	0.001
EC	1.77	0.003
Total	55.54	

exposed to aerobic conditions during dry periods becomes oxidized to SO^{2-}_4-S. During wet and dry climatic cycles, oxidation of pyrite is likely to be responsible for sulfur as sulfate which is able to move in and out of the wetland system (Lamers, et al., 1998, Bailey Boomer and Bedford, 2008, Vasilas, et al., 2010, Cowdery and Brigham, 2011, Demers, et al., 2013).

Naturally found in the PPR soil parent materials, Na and Mg salts have variable levels related to the composition and original levels of the glacial soil parent materials (Table 4.4, 4.5, and 4.6) (Bluemle, 1980). Higher concentrations of these salts can be found in soils in footslope landscape position. Due to the lateral subsurface water movement into the wetlands occurring from percolation through the

Table 4.3. Results of RDA model of element concentrations in BS to 1m depth using environmental variables, determined by manual forward selection procedure with Monte Carlo permutation tests according to ter Braak and Šmilauer (2002) ($p<0.05$). EC = Electrical Conductivity, Depth = 1 m (0-105+ cm), Sand = Sand %, Silt = Silt %, Clay = Clay %, Site = 12 sites BS, pH, BD = Bulk Density, OM = Organic Matter, and IPCI = Index of Plant Community Integrity (very good or very poor).

Environmental Variables	Explained Variance	*p*-value
	----%----	
	-------------- Combined Data --------------	
Site	27.90	0.001
Clay	7.40	0.001
IPCI	3.27	0.001
pH	0.59	0.004
EC	0.34	0.009
Total	39.50	
	------- Undisturbed Backslope (UBS) ------	
Sand	35.49	0.001
pH	15.87	0.001
Depth	5.95	0.004
BD	2.22	0.001
Silt/Clay	0.97	0.014
Total	60.50	
	-------- Disturbed Backslope (DBS) --------	
Site	48.14	0.001
EC	5.67	0.007
Depth	3.46	0.020
OM	1.33	0.003
pH	0.70	0.003
Total	59.30	

surrounding landscapes this transports Mg from the backslope into the footslope position (Table 4.5 and 4.6). These salts naturally accumulated as ions within the wetland system are readily soluble, and influence the EC of wetland soils (Timpson, et al., 1986, Richardson and Arndt, 1989, Seelig, 2010).

Sediments eroded from the surrounding landscapes can contribute to higher concentrations of phosphorus deposited within the wetland (Bailey Boomer and Bedford, 2008). This, in part, could also be a result of fertilizer additions to the surrounding landscapes. Dissolved and particulate P readily moves

Table 4.4. Pearson Correlation coefficients of select soil physical properties and the highest correlated soil chemical elements in footslope and backslope to 1m depth. ($p<0.001$). In the PPR, elements in bold (Ni) are uncommon elements and elements underlined (Na, S, P) are common.

	----------------------------------- Elemental Correlation (r^2) -----------------------------------				
	----------------------- Combined Footslope & Backslope Data ---------------------				
EC	*S (0.690)*	*Na (0.686)*	B (0.438)	Li (0.365)	IPCl (-0.324)
OM	Depth (-0.636)	BD (-0.574)	*P (0.564)*	Rb (0.452)	pH (-0.444)
Sand	Silt (-0.737)	Cu (-0.577)	Clay (-0.574)	Al (-0.545)	Rb (-0.471)
pH	Li (0.640)	B (0.550)	*Na (0.505)*	Rb (-0.504)	Mn (-0.494)
Site	B (-0.401)	V (-0.281)	EC (-0.270)	**Ni (-0.256)**	Th (0.256)
	----------------- Undisturbed Footslope & Backslope (UFS,UBS) -----------------				
Depth	BD (0.740)	OM (-0.720)	Zr (0.639)	Th (0.612)	**Ni (0.566)**
EC	*Na (0.666)*	*S (0.610)*	Pr (-0.426)	Gd (-0.421)	Fe (-0.419)
Sand	Silt (-0.706)	Cu (-0.621)	Zn (-0.565)	Clay (-0.567)	Al (-0.548)
pH	Li (0.752)	Mn (-0.648)	B (0.586)	*Na (0.581)*	Rb (-0.519)
Site	B (-0.574)	Silt (0.311)	V (-0.274)	*P (-0.242)*	Th (0.247)
	------------ Distrubed Footslope & Disturbed Backslope (DFS, DBS) ----------				
EC	*S (0.751)*	*Na (0.743)*	B (0.573)	Li (0.429)	V (0.344)
OM	Depth (-0.705)	Zr (-0.636)	Sc (-0.593)	Li (-0.589)	**Ni (-0.507)**
Site	BD (0.368)	Gd (-0.366)	**Ni (-0.348)**	V (-0.337)	Cu (-0.275)
Clay	Fe (0.595)	**Ni (0.592)**	Sand (-0.580)	V (0.575)	Sc (0.551)
pH	Li (0.650)	*Na (0.540)*	B (0.484)	OM (-0.426)	Zn (-0.422)

into wetlands through sediments that are that elevated in phosphorus and move through runoff during heavy precipitation events (van der Valk, et al., 1978, Woltemade, 2000, Lamers, et al., 2006, Cowdery and Brigham, 2011, Jacob, et al., 2013). However, P solubility is readily influenced by pH and presences of soluble Al^{3+}, Fe^{3+}, and Ca^{2+}ions.

An increase in nickel concentration within the soil may be associated with anthropogenic influences such as fertilizer or deposited from the atmosphere through air pollution (Holmgren, et al., 1993, Hupp, et al., 1993, Mortvedt, 1996, Beck and Sneddon, 2000). As seen in Table 4.4 and 4.5, nickel shows a negative correlation with site and OM but a positive correlation in Table 4.4, 4.5 and 4.6 with depth, clay, and BD. Organic matter usually is higher within the topsoil and decreases with depth within the soil profile. This correlation indicates that as OM decreases, Ni increases with depth in soil this trend was as seen in Table 3.5. However, this trend was not identified for wetlands alone (Table 2.2).

Table 4.5. Pearson Correlation coefficients of select soil physical properties and the highest correlated soil chemical elements footslope to 1m depth. ($p<0.05$). In the PPR, elements in bold (Ni) are uncommon elements and elements underlined (Na, S, P, Mg) are common.

	----------------------------------- Elemental Correlation (r^2) -----------------------------------				
	-- Combined Footslope Data --				
Site	As (-0.347)	Th (0.346)	B (-0.343)	EC (-0.295)	Zn (0.289)
Sand	Silt (-0.704)	Al (-0.597)	Clay (-0.516)	Cu (-0.486)	Ga (-0.463)
pH	Rb (0.728)	*<u>Mg (0.693)</u>*	Li (0.642)	*<u>Na (0.493)</u>*	Mn (-0.418)
EC	*<u>S (0.736)</u>*	*<u>Na (0.721)</u>*	B (0.443)	Li (0.338)	Sb (0.366)
BD	OM (-0.700)	Depth (0.681)	Zr (0.483)	*<u>P (-0.480)</u>*	V (-0.481)
	---------------------------------- Undisturbed Footslope (UFS) ----------------------------------				
Sand	Al (-0.686)	Silt (-0.665)	Cu (-0.571)	Zn (-0.550)	Ga (-0.515)
pH	Rb (0.870)	Li (0.793)	*<u>Mg (0.784)</u>*	*<u>Na (0.770)</u>*	Mn (-0.558)
Depth	BD (0.782)	OM (-0.742)	V (0.683)	**Ni (0.652)**	Zr (0.546)
Site	B (-0.563)	Cr (0.501)	Th (0.490)	*<u>S (-0.463)</u>*	Ga (0.440)
BD	Depth (0.782)	OM (-0.746)	*<u>P (-0.555)</u>*	Silt (-0.526)	**Ni (0.525)**
	---------------------------------------Disturbed Footslope (DFS) ----------------------------------				
Site	Gd (-0.495)	**Ni (-0.489)**	V (-0.455)	As (-0.396)	Mn (-0.370)
pH	*<u>Mg (0.822)</u>*	Rb (0.796)	Sb (0.700)	Li (0.691)	B (0.577)
EC	*<u>S (0.849)</u>*	*<u>Na (0.837)</u>*	Sb (0.695)	B (0.590)	Rb (0.472)

Site disturbance as an EV for DW or UW have previously been shown to relate to element concentration in the DW and UW but the footslope and backslope positions have not been closely evaluated in the past (Kissoon, et al., 2015, Yellick, et al., 2016, Werkmeister, et al., 2018). The combined data RDA analysis for both footslope and backslope types in this study (Figure 4.9) showed that site was an important factor influencing the distribution of element data. Site appears as a critical EV which illustrates the importance of site quality (e.g., with or without anthropogenic disturbance) in multi-element concentrations within the footslope and backslope. The RDA ordination plots of element concentrations for disturbed sites and undisturbed sites show quality differences. The importance of site has been shown in Table 2.4, 4.3, 4.4, and 4.5. However, site explains <1% of the EVs for the combined data and >19% of the EV for FS and BS (Table 4.1, 4.2 and 4.3) with trend as shown in Table 2.1.

Figure 4.16 shows the RDA plot identifying different EVs and percent explained variance for UFS and UBS combined. The main EVs (depth, EC, sand, pH, site) explaining the variance of element

Table 4.6. Pearson Correlation coefficients of select soil physical properties and the highest correlated soil chemical elements in backslope to 1m depth. ($p<0.05$). In the PPR, elements in bold (Ni) are uncommon elements and elements underlined (Na, S, Se) are common.

	------------------------------------ Elemental Correlation (r^2) ------------------------------------				
	-- Combined Backslope Data --				
Site	Ag (-0.478)	*Se (-0.439)*	B (-0.437)	Sc (-0.388)	La (-0.384)
Clay	Sand (-0.613)	Li (0.513)	**Ni (0.482)**	B (0.744)	V (0.406)
IPCl	*Na (-0.505)*	Ag (-0.467)	*S (-0.455)*	EC (-0.431)	pH (-0.390)
pH	B (0.695)	Li (0.654)	Rb (-0.558)	*Na (0.550)*	OM (-0.538)
EC	*Na (0.643)*	*S (0.631)*	IPCl (-0.431)	B (0.425)	Li (0.395)
	---------------------------------- Undisturbed Backslope (UBS) ----------------------------------				
Sand	Cu (-0.676)	Silt (-0.676)	Li (-0.559)	Clay (-0.522)	La (0.402)
pH	B (0.788)	Li (0.754)	Mn (-0.749)	Zr (0.660)	Rb (-0.595)
Depth	*S (-0.820)*	Th (0.781)	Zr (0.768)	OM (-0.750)	BD (0.702)
BD	Depth (0.702)	OM (-0.698)	*S (-0.612)*	K (-0.584)	Rb (-0.556)
Silt	Sand (-0.675)	Cu (0.458)	Site (0.410)	Zn (0.391)	Ag (-0.284)
Clay	Li (0.593)	Sand (-0.522)	B (0.504)	**Ni (0.432)**	V (0.407)
	---------------------------------------Disturbed Backslope (DBS) ----------------------------------				
Site	Ag (-0.549)	La (-0.513)	*Se (-0.504)*	Dy (-0.441)	Gd (-0.336)
EC	*Na (0.669)*	*S (0.657)*	V (0.544)	B (0.524)	Rb (0.488)
Depth	*Na (0.727)*	OM (-0.700)	Li (0.658)	pH (0.602)	B (0.582)
OM	Li (-0.711)	pH (-0.702)	Depth (-0.700)	*Na (-0.667)*	Zr (-0.634)
pH	OM (-0.702)	Depth (0.602)	Li (0.551)	*Na (0.535)*	Zr (0.455)

distribution for the correlated data in the UFS and UBS are shown in Table 4.1. As seen, depth makes up >24% explained variance for UW and UF while depth is not an EV for DFS and DBS (Table 4.1). As natural soil development occurs on surrounding landscapes, a Bt horizon develops in the landscape soil profile. Then due to natural or accelerated erosion, sand, silt, and clay are moved and deposited in the wetland. In the landscapes surrounding the disturbed wetland, most of the A horizon has been reworked and mixed with subsurface (B horizon) soil materials and likely eroded. Now sediments from the Bt are being deposited in the wetland (Figure 4.4, 4.5, 4.6). It is not clear whether the apparent Bt in the wetland is due to soil formation in place marking the natural soil profile of the landscape before anthropogenic influence for DFS, DBS, and UBS. Overall, however, this shows the role soil development in soil formation and development in the two landscape positions. The UBS, DFS, and DBS have been

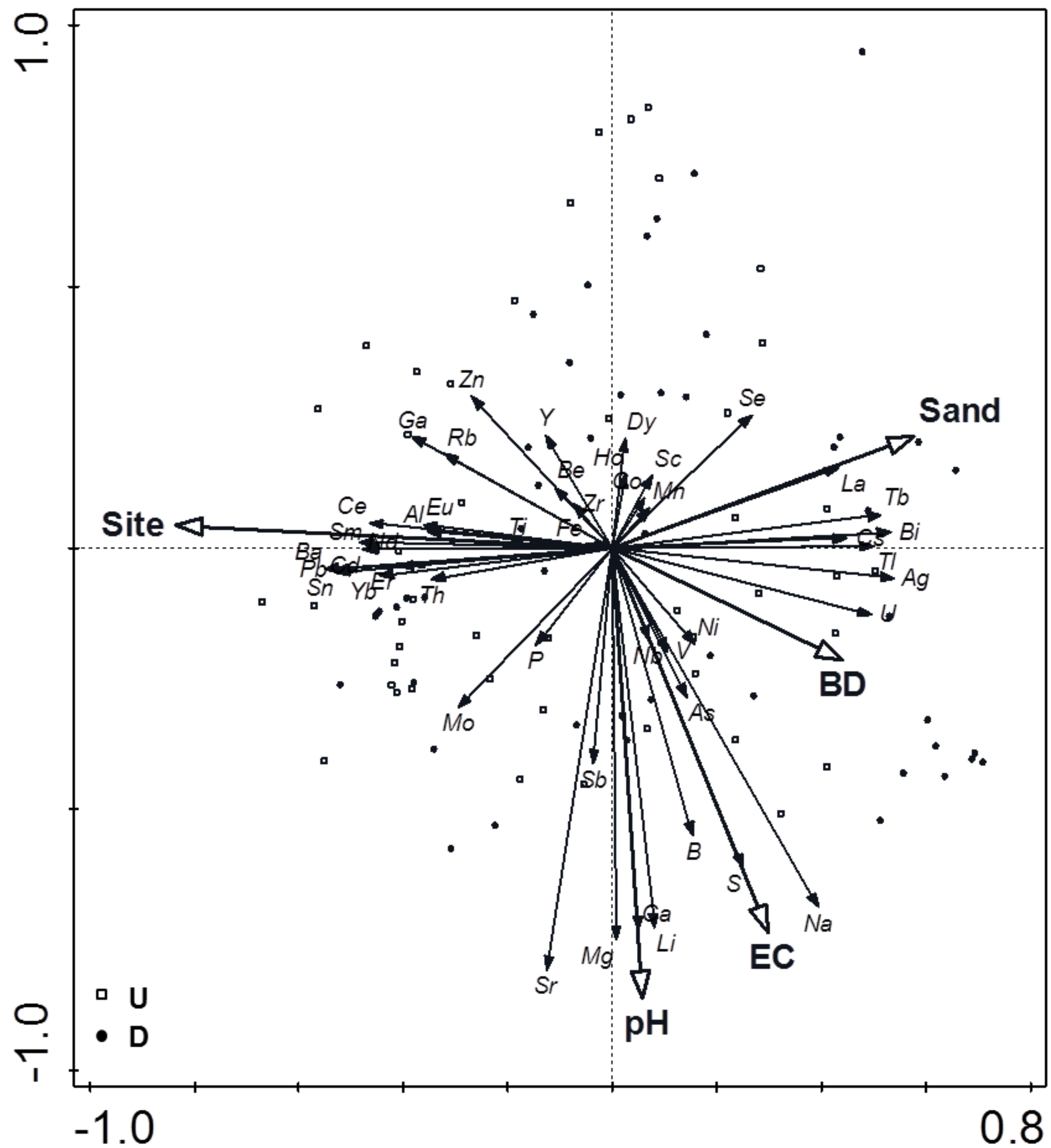

Figure 4.10. Ordination plot of RDA of element concentrations in UFS and DFS to 1m depth constrained by environmental variables (in bold): Site = 12 sites, Sand = Sand %, pH, EC = Electrical Conductivity, and BD = Bulk Density. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

influenced by erosion. The characteristics of the UBS are due to the topography but the DFS and DBS characteristics are due to anthropogenic influences. In addition, EC is a main EV for DFS and DBS, and as well as with DW and DF alone (Chapter 3) and contributes >35% of explained variance while for UFS and UBS it is >13% of the explained variance, illustrating, the role EC plays in the biogeochemistry in the disturbed sites (Table 4.1). The EC reflects anthropogenic disturbances (e.g., cultivation) which not only

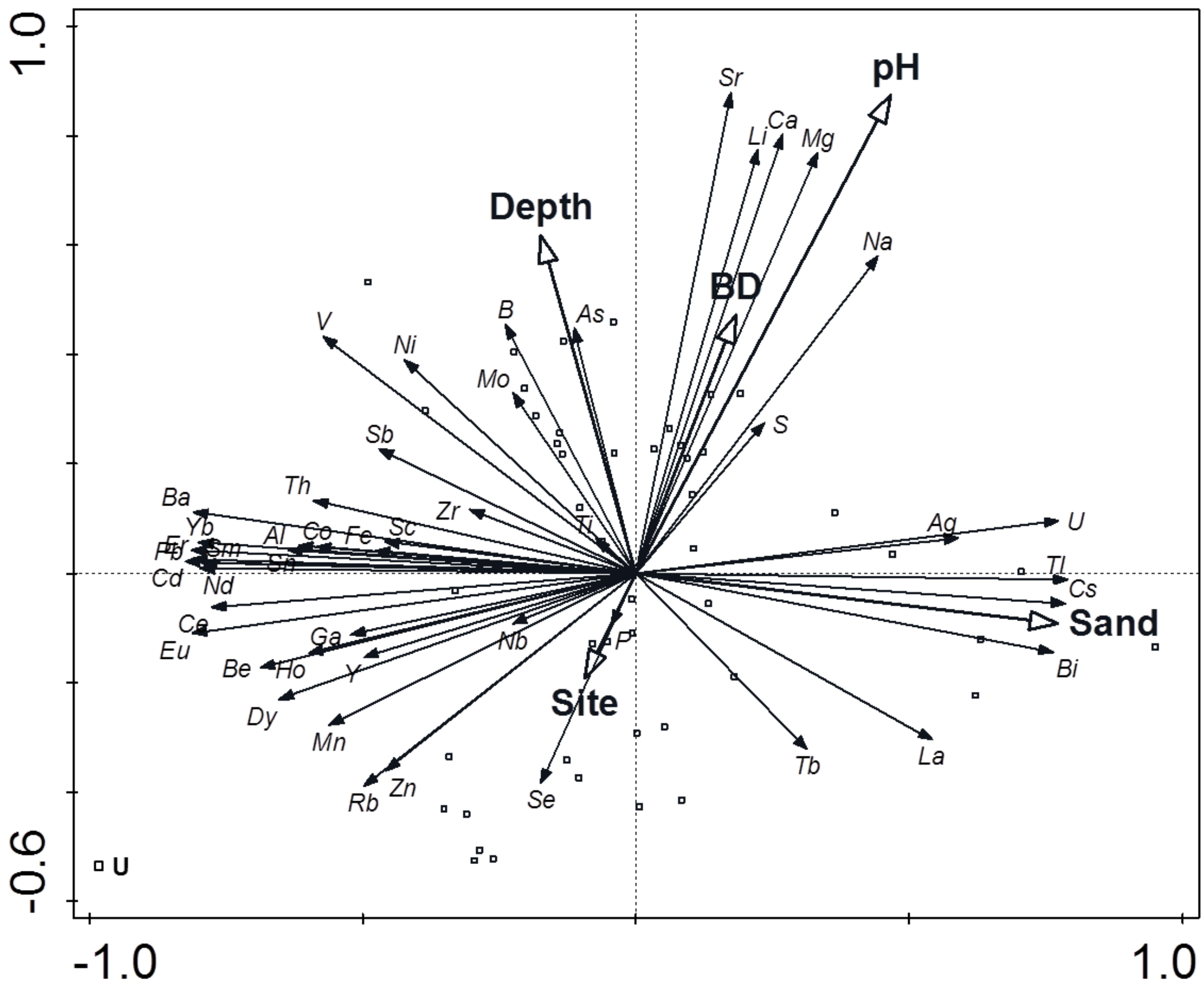

Figure 4.11. Ordination plot of RDA of element concentrations in UFS to 1m depth constrained by environmental variables (in bold): Sand = Sand %, pH, Depth = 1 m (0-105+ cm), Site = 12 sites, and BD = Bulk Density. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

accelerates erosion and sedimentation within the landscape but also alters subsurface hydrology and enhances movement of soluble soil components (salts) (Stewart and Kantrud, 1971, Parkin, 1993, Seelig, 2010).

The ordination plot of RDA of element concentrations in UFS and DFS had site as the main EV (Figure 4.10 and Table 4.2). This identifies that there is a difference between UFS and DFS at the footslope position. This in part is due to the depositional nature of the of the landscape position (i.e., sediment is being deposited from the upper positions in part due to erosion). In addition, the difference

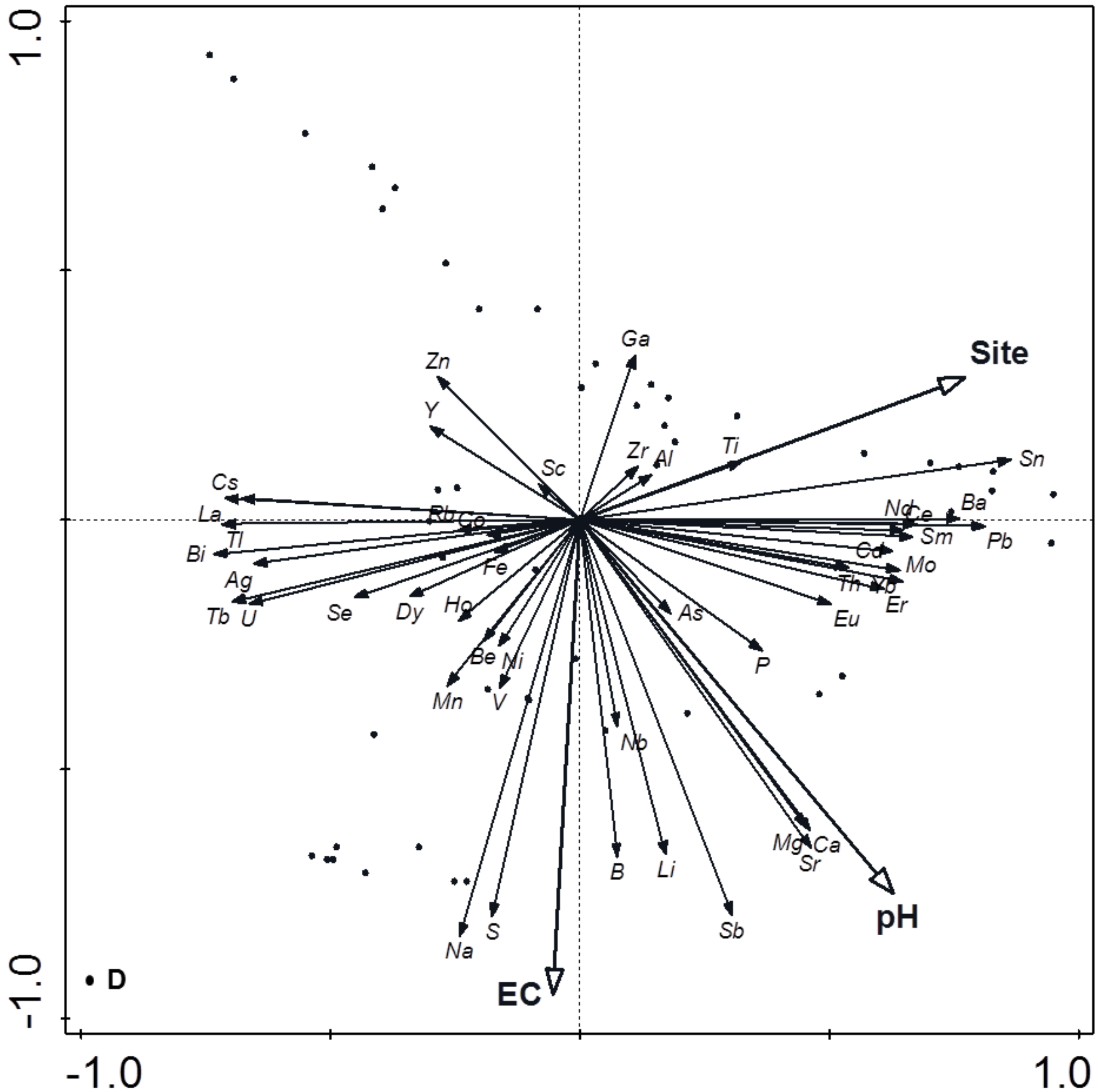

Figure 4.12. Ordination plot of RDA of element concentrations in DFS to 1m depth constrained by environmental variables (in bold): Site = 12 sites, pH, and EC = Electrical Conductivity. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

between the combined UFS and DFS vs UFS shows similar EVs except for EC and depth (Figure 4.10 and 4.11, and Table 4.2). The UFS has depth as an EV partly due to the soil profile development while DFS does not have depth as an EV (Figure 4.10, 4.11, 4.12, and Table 4.2). The reason for this is a homogeneity that has been created by the anthropogenic influence of tillage. Tillage mixes or

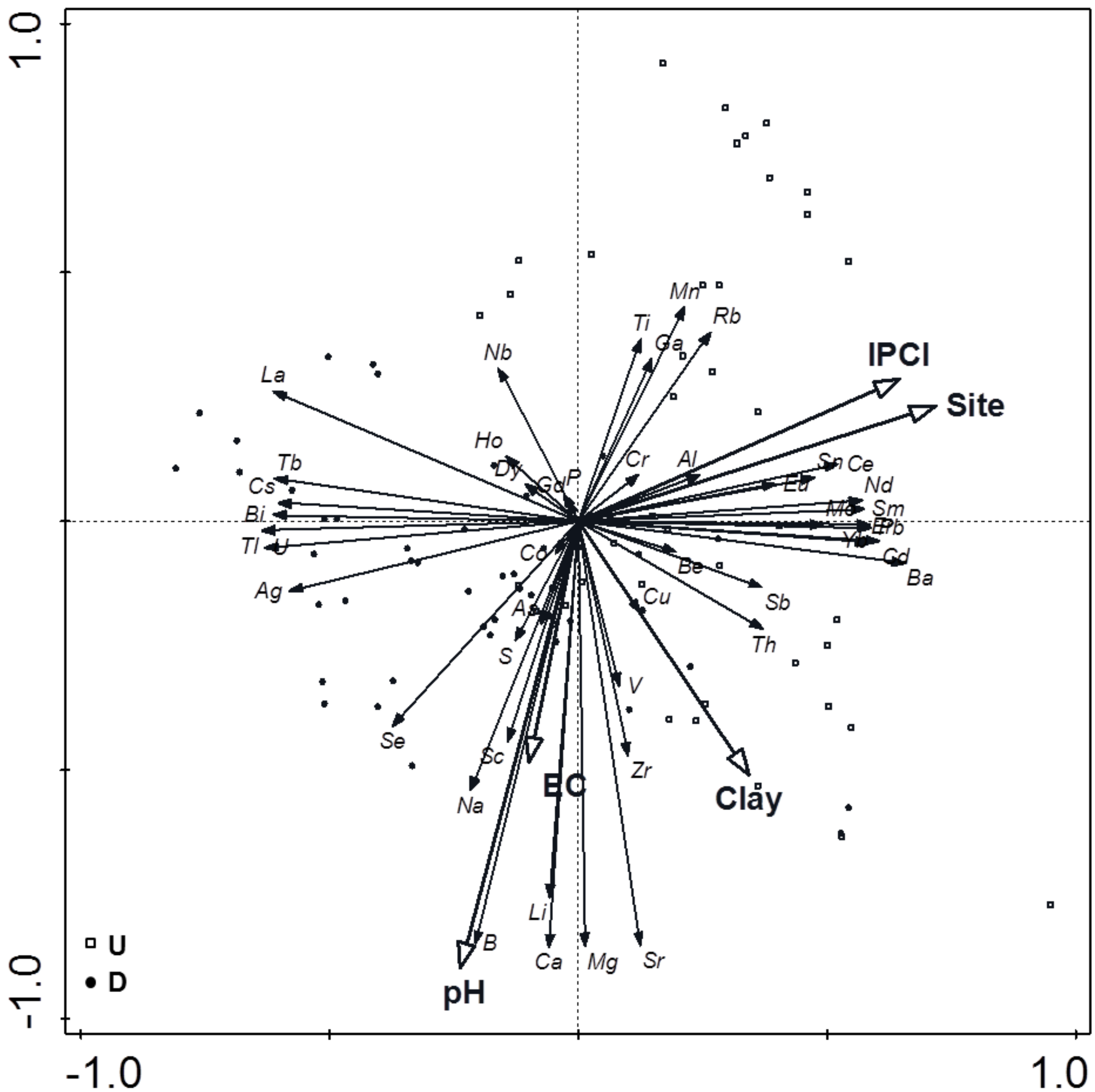

Figure 4.13. Ordination plot of RDA of element concentrations in UBS and DBS to 1m depth constrained by environmental variables (in bold): Site = 12 sites, Clay = Clay%, IPCI = Index of Plant Community Integrity (very good or very poor), pH, and EC = Electrical Conductivity. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

homogenizes the soil to a point where the soil profile development is eroded by the blending of the soil. These soil characteristics may also change with time as erosion removes the surface soil materials and subsequent tillage further blends the subsurface soil components creating a tillage zone. Site as an EV is notable when comparing UFS and DFS, especially where variance explained for UFS is 1.24% vs DFS at

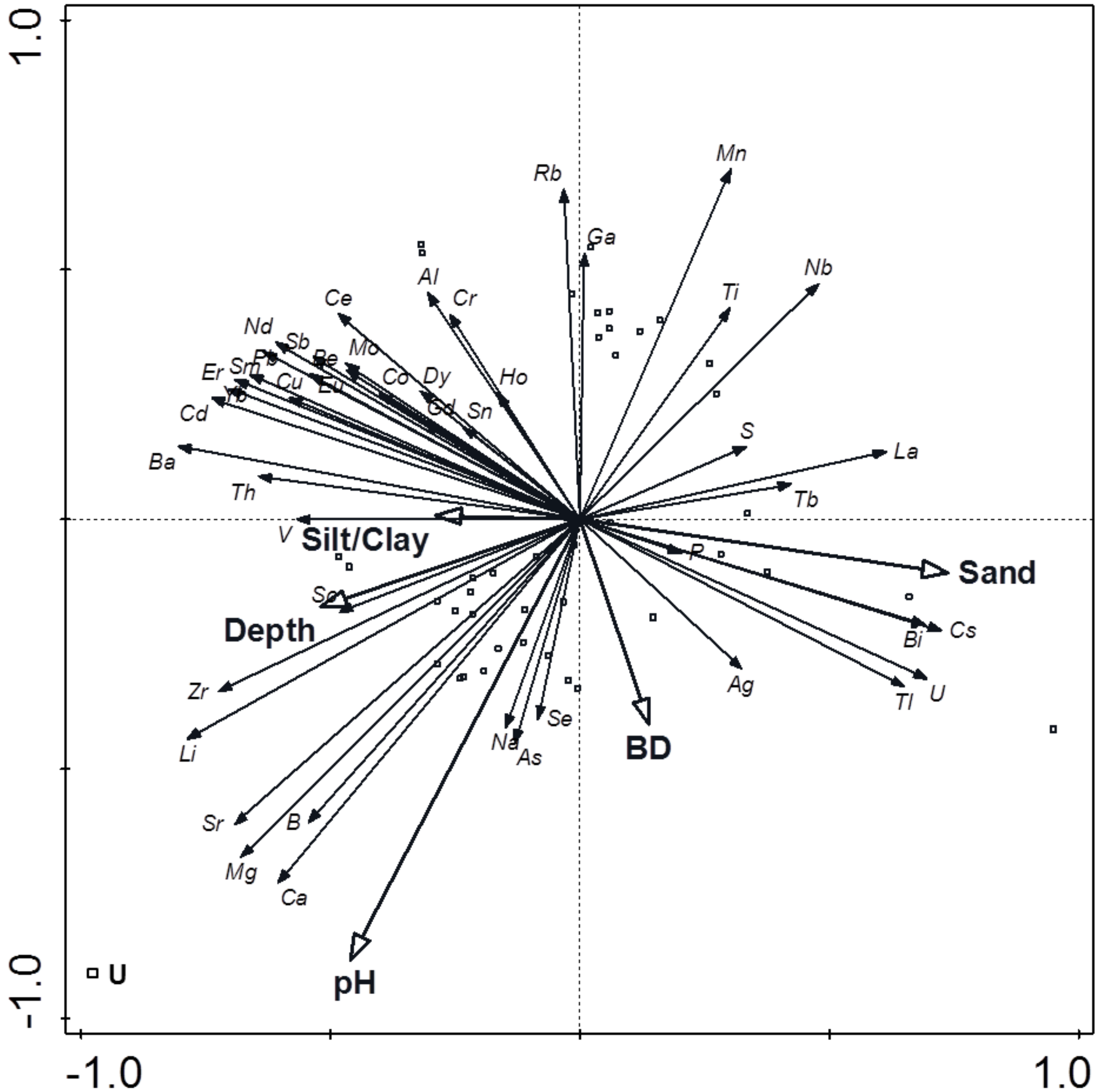

Figure 4.14. Ordination plot of RDA of element concentrations in UBS to 1m depth constrained by environmental variables (in bold): Sand = Sand %, pH, Depth = 1 m (0-105+ cm), BD = Bulk Density, Silt = Silt%, and Clay = Clay%. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

46.34% (Table 4.2). The EC is different for DFS which is not seen as an EV for UFS (Figure 4.10, 4.11, 4.12, and Table 4.2). The EC is influenced in the DFS because the soil structure has been disturbed/destroyed due to anthropogenic activity. When soil structure is disturbed, water infiltration into the soil is impeded which causes the water to pond at the surface. When the water evaporates then salts

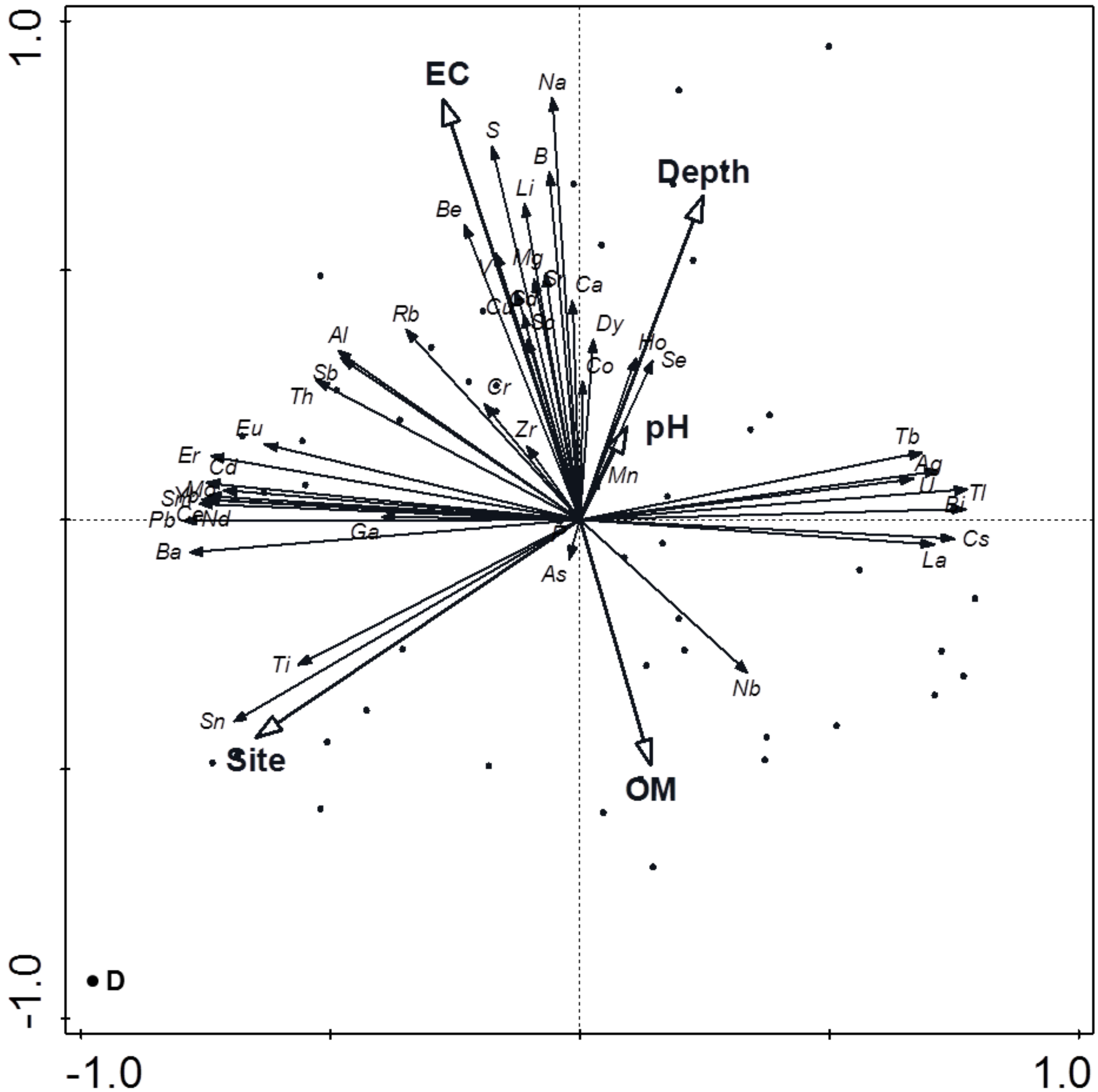

Figure 4.15. Ordination plot of RDA of element concentrations in DBS to 1m depth constrained by environmental variables (in bold): Site = 12 sites, EC = Electrical Conductivity, Depth = 1 m (0-105+ cm), OM = Organic Matter, and pH. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

are left behind hence, why EC as seen as an EV for DFS. Also, when water infiltrates into the soil, the local water table can be raised resulting in water closer to the surface allow for capillary wicking to occur (Table 4.2 and Figure 4.12).

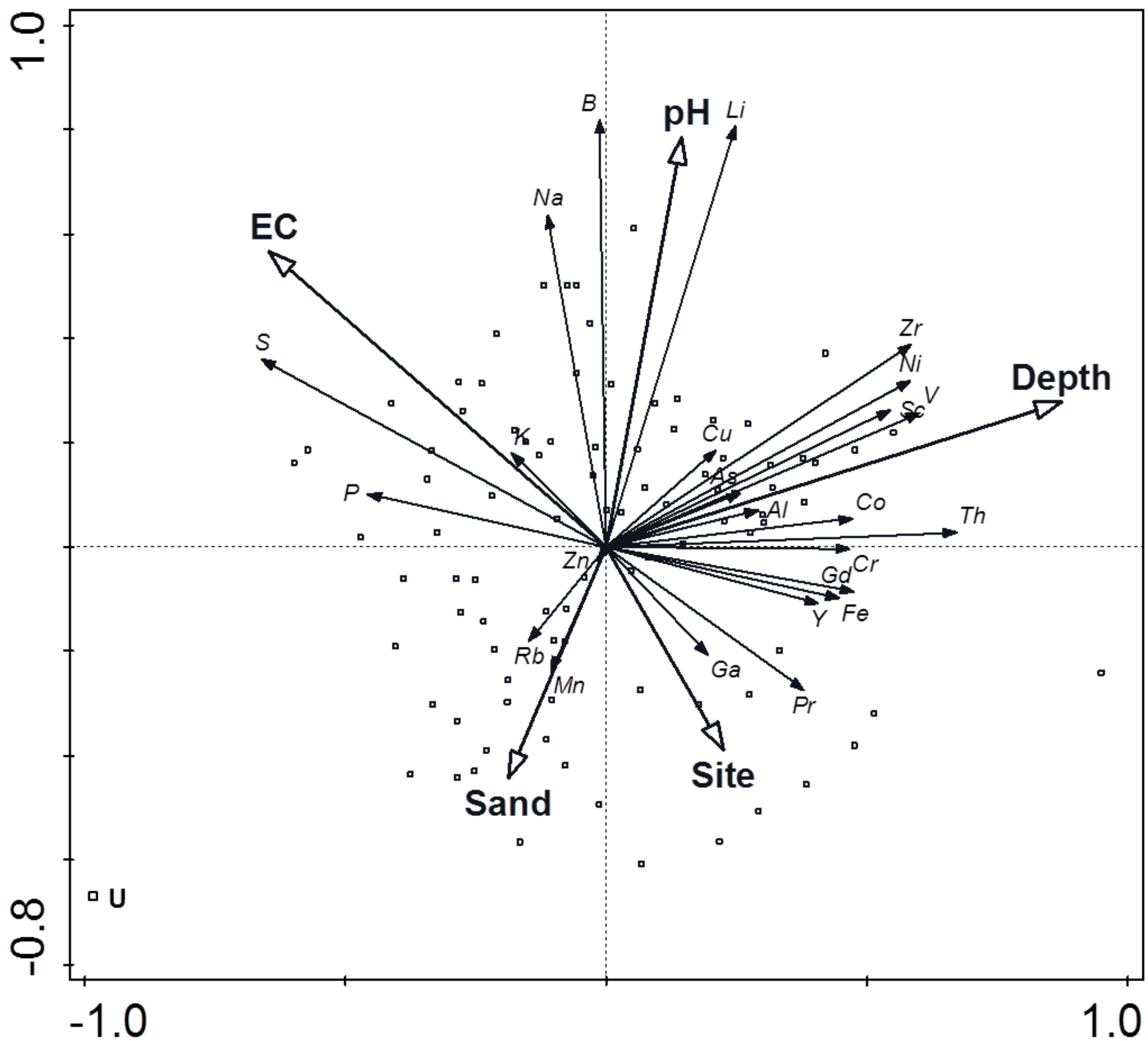

Figure 4.16. Ordination plot of RDA of element concentrations in UFS and UBS to 1m depth constrained by environmental variables (in bold): Depth = 1 m (0-105+ cm), EC = Electrical Conductivity, Sand = Sand %, pH, and Site = 12 sites. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

The same trend presents itself in that the combined RDA for UBS and DBS have site as the EV which tells that there are characteristic differences between UBS and DBS (Table 4.3 and Figure 4.13). The RDA of the UBS has all three soil textures (sand, silt, and clay) as EV which tells that the landscape position has natural pedogenesis occurring (Table 4.3 and Figure 4.14). Site comes as the dominant EV for DBS which in part could be due to the erosion and/or homogenization that is taking place due to the

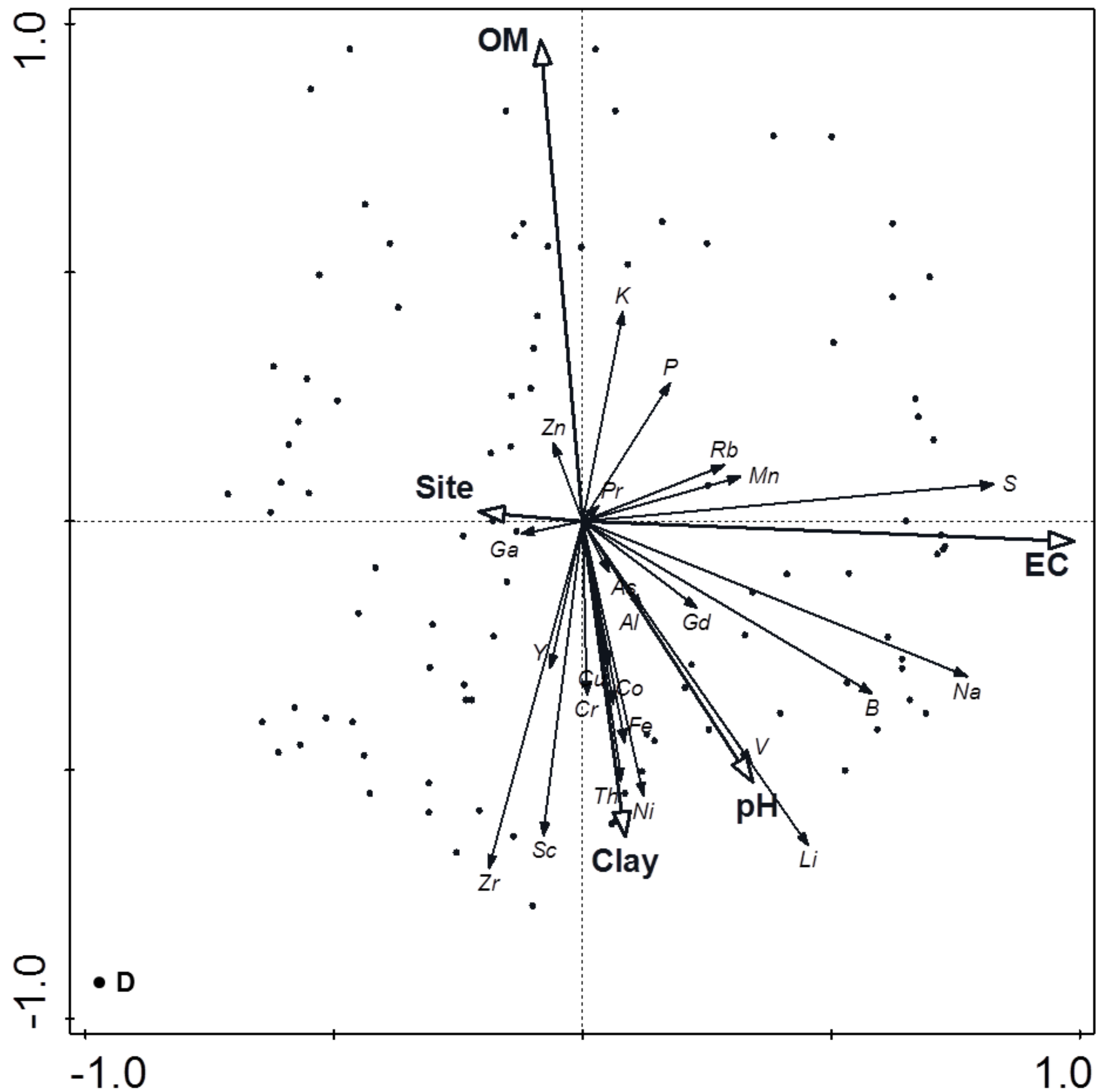

Figure 4.17. Ordination plot of RDA of element concentrations in DFS and DBS to 1m depth constrained by environmental variables (in bold): EC = Electrical Conductivity, OM = Organic Matter, Site = 12 sites, Clay = Clay%, and pH. Element data if not normal were log transformed and centered to normalize weights of data due to differences in orders of magnitude and ranges.

anthropogenic influence i.e., tillage (Table 4.3 and Figure 4.15). This can also explain why EC is also an EV for DBS while it is not an EV for UBS (Table 4.3 and Figure 4.14, 4.15).

4.5. Summary and Conclusions

In order to reduce the variability between locations, sample sites within the Missouri Coteau, which has calcareous parent material were selected based on a similar broad scale topographical setting.

Natural landscapes and the heterogeneity of the underlying glacial till sediments as well as soil series/type can change in a matter of a few feet and may impact the information gained (Soil Survey Staff, 2014). Influenced by the calcareous parent material chemical and physical characteristics that are unique to the PPR play a role in the multi-element distribution for such elements as P, Mg, Na, Ni, and S (Arndt and Richardson, 1989, Richardson and Arndt, 1989). The site EV reflects the anthropogenic influence on the surrounding landscape for the DFS and DBS.

Multi-element chemistry within the landscape reflects the FS and BS quality and the EV's that relate to and affect that quality. Disturbed FS and BS areas have different chemical signatures vs. UFS and UBS areas as seen by the RDA ordination plots. Differences in EV (such as EC, OM, texture, pH, and site) between DFS, DBS, UFS, and UBS illustrate and confirm the common understanding of the differences between cultivated and undisturbed landscapes (Brinson, 1993a, Parkin, 1993, Bedford, et al., 1999, Gwin, et al., 1999, Jolley, et al., 2010, Paradeis, et al., 2010). Based on the RDA models, there does not appear to be any placement trend or grouping with DFS, DBS, UFS, and UBS in relation EV and multi-elements. Pearson correlation coefficients identified that with footslope and backslope landscape positions Ni plays a role in the UFS, UBS and combined data with EV's depth, OM, BD, site, and clay texture (Table 4.6, 4.7, and 4.8). This is different from what was previously seen with the Pearson correlation coefficients for wetlands (Werkmeister, et al., 2018), which showed that Se and Nb play a role with EV's BD, OM, and depth as well as with the W and F data that showed that Ni was correlated with EV's depth and OM only (Table 3.4). A larger sampling scheme is suggested to further determine the broad scale impacts by EV. This research recognizes that landscape position impacts the movement of multi-elements (fingerprints) within the landscape position and helps to clarify the relationships between the wetlands, fringe, FS and BS and to understand the impact that is occurring.

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5. GENERAL DISCUSSION

The PPR of North America contains one of the largest expanses of wetlands in the continent resulting from extensive recent glaciation (~12,000-16,000 years ago) (Bluemle, 1980). This region is also highly suited for intensive agricultural production where many wetlands have been disturbed by crop production or drained. An area where wetlands still remain undisturbed are in a portion of the PPR containing a terminal glacial moraine known as the Missouri Coteau which is bounded to the south and west by the Missouri River in North Dakota (ND).

Within the Missouri Coteau portion of the PPR, wetlands and landscapes were selected in a similar broad scale topographical setting in order to reduce the variability between locations. These are natural landscapes and the underlying glacial till of the Missouri Coteau is composed of calcareous parent material sediments that can be highly variable, with topography and soil characteristics changing in a matter of a few feet (Soil Survey Staff, 2014). The calcareous parent material, which creates chemical and physical characteristics that are unique to the PPR, plays a role in the multi-element distribution for such elements as phosphorus (P), nickel (Ni), niobium (Nb) magnesium (Mg), sodium (Na), and sulfur (S) (Arndt and Richardson, 1989, Richardson and Arndt, 1989, Callaway et al., 1998, Pédrot, et al., 2008, Davranche, et al., 2011). Wetland soils typically show less horizonation due to slow, incremental soil sediment deposition compared to upland soils, (i.e. erosion or anthropogenic influence from tillage). Traditional methods of assessment of the impacts of disturbance (e.g. OM matter content, particle size distributions, pH, visual profile descriptions) are therefore limited in determining the depths to which soils are affected by disturbance in wetlands. However, examining element concentrations throughout the profile can show that disturbances lead to changes in element composition throughout the soil profile to a depth of at least one meter as seen in the wetland (Pédrot, et al., 2008, Davranche, et al., 2011, Werkmeister, et al., 2018).

Utilizing statistical techniques such as redundancy analysis (RDA), the site environmental variables (EV) reflect the anthropogenic influence on the surrounding landscape for the disturbed wetland (DW), disturbed fringe (DF), disturbed footslope (DFS) and disturbed backslope (DBS). Thus, multi-element chemistry of the wetlands surrounded by the landscape reflects the wetland and fringe quality related to the footslope and backslope quality and the EV's that relate to and affect that quality. Disturbed wetland and wetland fringe areas have a different chemical signature vs. undisturbed wetlands and wetland fringes. This trend is also seen with the disturbed FS and BS areas having a different chemical signature vs. UFS and UBS areas. This means that disturbance at the surface in the landscapes has consequences to greater depths than is generally acknowledged. These chemical signature trends can be observed by utilizing RDA ordination plots. Differences in EV (such as electrical conductivity (EC), organic matter (OM), bulk density (BD), pH, depth, site and texture) between DW, DF, undisturbed wetland (UW), and undisturbed fringe (UF) as well as DFS, DBS, undisturbed footslope (UFS) and undisturbed backslope (UBS) confirm and clarify the common understanding of the differences between cultivated and undisturbed landscapes (Brinson, 1993, Parkin, 1993, Bedford, et al., 1999, Gwin, et al., 1999, Jolley, et al., 2010, Paradeis, et al., 2010, Werkmeister, et al., 2018).

Pearson correlation coefficients identified that with wetland and fringe landscape positions Ni plays a role in the UW, UF and combined data with EV's depth and OM (Table 3.3 and 3.4, see Chapter 3). This development is also seen with the footslope and backslope landscape positions. Nickel plays a role in the UFS, UBS and combined data with EV's depth, OM, BD, site, and clay texture (Tables 4.4, 4.5 and 4.6 see Chapter 4). This is different from what was previously seen using Pearson correlation coefficients for wetlands alone, which showed that Se and Nb play a role with EV's BD, OM, and depth. Examining the wetland (W) and wetland and fringe (F) data together showed that Ni was correlated with EV's depth and OM only (Chapter 2 and 3). A larger and/or more detailed sampling scheme is suggested to further determine the impacts by EV. Such research would encompass a greater number research wetland sites used in the Index of Plant Community Integrity (IPCI) project (DeKeyser, 2000, Hargiss, et al., 2008, DeKeyser, et al., 2009).

According to Table 5.1, pH and EC are clearly impacted by disturbed landscape positions while the undisturbed landscape positions are not impacted in a detrimental manner. In addition, as one moves up the landscape clay is not removed from the undisturbed landscape but is removed from the disturbed landscape by accelerated erosion. Clay is transported from eroded landscape positions to depositional positions. In undisturbed wetlands, clay is the only factor moving by natural erosion. Clay movement in undisturbed landscapes may be due to aggregate movement rather than individual particle movement. This could be in related to erosion exposing more calcareous material is then being deposited in the wetlands. The fringe zone is a captive zone that catches sand due to its larger particle size. Starting at the footslope position, OM is impacted by the different management techniques. Erosion can transfer OM within the landscape and be deposited in the wetland due to the OM's potential solubility and low density. Bulk density is impacted by 3 out of the 4 landscape positions which can be tied to OM movement being transported and deposited as well.

Table 5.1. Environmental Variables (EV) of select soil physical properties compared between undisturbed (U) or disturbed (D) by describing as either lower (-), higher (+), or neutral (0). pH, EC = Electrical Conductivity, sand, silt, clay, OM = Organic Matter, and BD = Bulk Density.

EV	Wetland		Fringe		Footslope		Backslope	
	U	D	U	D	U	D	U	D
pH	-	+	-	+	-	+	-	+
EC	-	+	-	+	-	+	-	+
Sand	0	0	-	+	0	0	0	0
Silt	0	0	0	0	0	0	0	0
Clay	0	0	+	-	+	-	+	-
OM	0	0	0	0	+	-	+	-
BD	+	-	+	-	0	0	-	0

This research also indicates that there is potential of sampling in the fringes, which are a part of the wetland, instead of the wetland center, when the wetlands are underwater making sampling difficult. Fringe sampling would be suitable in many cases and could yield data from which can generate conclusions similar to those that can be obtained by sampling the wetlands as long as the relationships between the wetlands and their surrounding landscapes are clearly understood. Understanding the extent to which disturbances of soils in surrounding landscapes affect the soil profile in wetlands will help aid management and restoration efforts. This research recognizes that landscape position impacts the movement of multiple elements (fingerprints) within the landscapes and helps to clarify the relationships between the wetlands, fringe, FS and BS and to understand the impact that is occurring. It is also necessary to understand the larger abundance of key elements in the materials of soils surrounding wetlands

To develop a systematic understanding of the multi-element movement within the landscape, other landscape positions should be sampled. Sampling the shoulder and summit landscape positions would give a thorough examination of the landscape to accurately understand the anthropogenic impact. In addition, sampling the tillage ring's surrounding many of the disturbed wetlands would also aid the understanding of the tillage rings impact on the wetland. Tillage rings occur when soil sediments created due to tillage induce accelerated erosion on the landscape that move to the wetland edge. Vegetation surrounding the wetland and the wetland fringe slow the movement of the sediments causing them to accumulate around the edge of the wetland. Tillage rings have an elevation change that is added to the landscape by causing an anthropogenic hummocky ridge which can impact the surface flow of water as well as act as a means of sediment capture due to movement of soil within the landscape. This may impact the sediments reaching the wetland with effects on the ring that may perhaps influence the multi-element fingerprints. The tillage ring may also be an indicator of wetland quality. Expanding the radial sampling range in the wetland and fringe could aid in understanding the relationship between the source of the sediment from upper landscape positions.

This research generally reflects many of the observations reported in the literature regarding physical and chemical observations in both the DW and UW. However, because of the detailed geochemical analysis of the soils and sediments in this study some elements (e.g., Ni and Nb) appear to be potential significant element indicators of disturbance in this portion of the PPR. Further detailed research should be directed to elucidate these observations and their relationships with wetland disturbance. The findings of such research would be useful in refining techniques for wetland restoration.

5.1. References

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