DISSOLVED ORGANIC CARBON CONCENTRATION, PATTERNS AND QUALITY AT A RECLAIMED AND TWO NATURAL WETLANDS, FORT MCMURRAY, ALBERTA.

DISSOLVED ORGANIC CARBON CONCENTRATION, PATTERNS AND QUALITY AT A RECLAIMED AND TWO NATURAL WETLANDS, FORT MCMURRAY, ALBERTA.

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Title: Dissolved organic carbon concentration, patterns and quality at a reclaimed and two natural wetlands, Fort McMurray, Alberta.

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ABSTRACT

The oil sands extraction process in Northern Alberta is very extensive, as it requires the removal of vegetation and overburden materials from the landscape surface. By law, mining companies are required to restore the land to its previous capability once operations have ceased. To achieve this, reclamation practices have been initiated; however, limited research has focused on upland-wetland systems in the oil sands region. In 2012, Syncrude Canada Ltd. (SCL) constructed a 52-hectare wetland, known as Sandhill Fen Watershed (SFW). SFW is a highly managed system that is composed of a water storage and outlet pond, underdrains, hummocks and perched and lowland fens. DOC is a major source of carbon and plays an important role in wetland biogeochemical and ecological functions. In disturbed landscapes, it is unclear as to how the quantity and quality of DOC compare with natural analogies. The objective of this thesis is to determine the spatial and temporal patterns of dissolved organic carbon (DOC) quality and quantity of SFW and compare these findings with those from two natural wetlands near Fort McMurray, AB. In 2014 and 2015, water samples were collected and analyzed for DOC concentration and optical properties. To assess DOC composition, four fluorescence indices were used: Fluorescence Index (FI), Freshness Index (β/α), Humification Index (HIX) and Specific Ultraviolet Absorbance at 254nm ($SUVA_{254}$). Results indicate that there is significant difference between SFW and the natural fens for all fluorescence indices and DOC concentration. More specifically, DOC concentrations and composition at SFW are greater and more variable than at the natural wetlands - Pauciflora (PC) and Poplar fen (PP). Additionally, DOC concentrations at SFW appear to be primarily controlled by water table (WT), sodium (Na^+) concentration and electrical conductivity (EC), whereas PC and PP are influenced by additional variables such as peat depth and vegetation. At SFW, fluorescence indices and a 3-component Parallel Factor Analysis (PARAFAC) model suggest that the carbon changes at a "transition zone" located at the boundary between the lowlands and margins from terrestrially-derived, old with high humification, aromaticity and molecular weight to microbially-derived, recently produced with low humification, aromaticity and molecular weight. Results from this research will help guide reclamation efforts through the characterization of carbon cycling processes and their relation to undisturbed systems.

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LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	Analysis of Variance
B1	Boardwalk 1
B2	Boardwalk 2
B3	Boardwalk 3
bgs	Below Ground Surface
$CaSO_4 \cdot 2H_2O$	Gypsum
CF	Constructed Fen
CH_4	Methane
CHWE	Clark Hot Water Extraction
CO_2	Carbon Dioxide
CT	Composite Tailings
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DS	Downstream
EC	Electrical Conductivity
EEM	Excitation-Emission Matrix
EIP	East-In-Pit
ET	Evapotranspiration
fDOM	Fluorescence Dissolved Organic Matter
FI	Fluorescence Index
GHG	Greenhouse Gas
Gt	Gigatonne
HCl	Hydrochloric Acid
HDPE	High-density Polyethylene
HIX	Humification Index
HSD	Honestly Significant Difference
IFE	Inner Filter Effects
LFH	Litter, Fibric and Humic
LTC	Level, Temperature, Conductivity
Na^+	Sodium Ion
NaOH	Caustic Hot Water
NPP	Net Primary Productivity
OP	Outlet
OSPW	Oil Sands Processed Water
P	Precipitation
PARAFAC	Parallel Factor Analysis
PC	Pauciflora Fen
Peak A	UVC Humic-like
Peak B	Protein-like Tyrosine-like
Peak M	UVA Marine Humic-like

PET	Potential Evapotranspiration
PF	Poor Fen
PP	Poplar Fen
QS	Quinine Sulfate
RF	Rich Fen
RS	Raman Signal
SCL	Syncrude Canada Limited
SF	Saline Fen
SFW	Sandhill Fen Watershed
SH	Sandhill
SMA	Surface Minable Area
SOM	Soil Organic Matter
$SUVA_{254}$	Specific Ultraviolet Absorbance at 254 nm
T1	Transect 1
T2	Transect 2
T3	Transect 3
TOC	Total Organic Carbon
TR	Margin
UP	Upland
UV	Ultraviolet
UVA	UV Absorbance of a Sample in Absorbance Units
WBP	Western Boreal Plains
WSP	Water Storage Pond
WT	Water Table
β/α	Freshness Index

SECTION 1: INTRODUCTON

1.1. Motivation

In Canada, approximately 1.1 million km^2 of the landscape (~12%) is occupied by peatlands, in which these peatlands contain roughly 147 Gt of soil organic carbon, representing 56% of all organic carbon stored in Canadian soils (Tarnocai, 2006). Wetlands in the Boreal Plains of Northeastern Alberta account for 50% of the landscape and of these, more than 65% are fen-peatlands (Vitt et al., 2000; Price et al., 2010). One of the most important components of Boreal wetlands are their carbon balance because these ecosystems store a large volume of the global carbon (Vitt et al., 2000). The carbon cycle in natural wetlands influences several ecosystem processes. For example, carbon is exchanged as carbon dioxide (CO_2) between plants and the atmosphere via photosynthesis and respiration, microorganisms decompose organic carbon from dead plant material accumulated in soil and very old carbon can become buried in deep geological sediments and turn into coal, oil and natural gas deposits (Archer, 2010). However, natural and anthropogenic activities can negatively disturb the natural landscape, which will subsequently affect the carbon balance of wetlands. Natural (e.g. forest fires) and anthropogenic (e.g. oil sands mining) activities in the Boreal region can cause sequestered carbon in plants or sediments to be released into the atmosphere, which will amplify global atmospheric CO_2 content (Schlesinger and Andrews, 2000; Limpens et al., 2008; Heimann, 2013). Additionally, organic carbon in the aqueous phase maybe hydrologically redistributed throughout the system, which will affect carbon availability for vegetation and microorganisms (Limpens et al., 2008).

The Alberta Oil Sands is the third largest oil sands deposit in the world, in which the Athabasca, Cold Lake and Peace River Oil Sands occupy approximately 142,200 km^2 of the total 381,000 km^2 area of the Alberta Boreal Forest (Alberta Government, 2009). There are two methods to extract bitumen in the Athabasca Oil Sands: open-pit surface mining, where deposits are less than 75 m in depth from the ground surface, and in-situ techniques that are used to extract deeper deposits (Alberta Government, 2009). Surface mining is only conducted in the Athabasca Oil Sands and accounts for 3.4% of the total surface mineable area (SMA) in Alberta. The open-pit surface mining process to extract bitumen is very extensive and has disrupted approximately 900 km^2 of the SMA (Alberta Government, 2016). Prior to extraction, all vegetation is removed and overburden material stripped from the surface and then open-pits and tailings ponds are created (Meier and Barbour, 2002; Elshorbagy et al., 2005; Alberta Government, 2009). Additionally, peat material is the stockpiled and undergoes an oxidation reaction, in which carbon is oxidized and carbon dioxide is produced under aerobic conditions (Turetsky et al., 2002). The removal of vegetation and soil organic matter (SOM) diminishes a systems ability to accumulate and store carbon and leads to an increase in carbon greenhouse gas (GHG) emissions. The overall carbon balance of the system subsequently shifts from a carbon sink to a carbon source, which may limit the availability of carbon for plants and microorganisms (Kelly et al., 1997; St. Louis et al., 2000; Turetsky et al., 2002).

The Alberta Environmental Protection and Enhancement Act states that by law, mining companies are required to restore the land to its previous habitable state once mining activities have ceased (Alberta, 2014; Vitt and Bhatti, 2012). To achieve this, reclamation efforts in the oil sands region have been initiated with a shift in focus from upland-forested systems to peatland-wetland systems. However, there are many difficulties associated with wetland construction in this region. For example, the climate of the Boreal Plains is sub-humid, in which potential evapotranspiration (PET) exceeds precipitation (P) and natural peatlands can take upwards of thousands of years to fully develop (Price et al., 2010). Additionally, these areas are prone to high levels salinity in the soil water due to tailings material (Trites and Bayley, 2009). However, despite potential challenges, Syncrude Canada Limited (SCL) constructed its first peatland-wetland system, a 52-hectare fen known as Sandhill Fen Watershed (SFW).

To assess the success of reclamation of Boreal peatlands, it is important to investigate key ecosystem processes. Furthermore, it is crucial to understand how these processes are interconnected and influence the overall function of the system, such as the relationship between the water and carbon balances. Carbon allocation and dynamics is historically assessed by analyzing carbon stocks and currently, is investigated using Eddy Covariance towers, which accurately measure atmospheric fluxes. However, a large volume of carbon is lost in the aqueous phase as dissolved organic carbon (DOC) from natural wetland systems (J Pastor et al., 2003). DOC is produced by the partial decomposition of organic matter followed by its dissolution in pore water. It is a complex and heterogeneous mixture of organic molecules that vary in molecular structure and weight and differ in optical properties (Koprivnjak and Moore, 1992; Thurman, 1985). DOC influences biological, chemical and physical processes. For example, in surface and near-surface waters, DOC provides a substrate for microbial activity, affects nutrient cycling and availability, impacts the mobility and toxicity of metals and contaminants, as well as attenuates UV light absorption (Eimers et al., 2008; Moore and Dalva, 2001; Pace and Cole, 2002; Peacock et al., 2014; Xenopoulos et al., 2003). Boreal peatlands contain a large volume of organic matter characterized by poor adsorption, in which they supply the majority of terrestrial DOC to downstream aquatic ecosystems, thus suggesting a significant redistribution of terrestrial organic carbon throughout the system (Dalva and Moore, 1991; J Pastor et al., 2003). Multiple studies (Dalva and Moore, 1991; Koprivnjak and Moore, 1992; Xenopoulos et al., 2003) have reported that the size of a wetland relative to the rest of a catchment is related to DOC concentrations, in which high concentrations is associated with a higher percentage of wetland coverage. DOC concentrations in peatlands are typically high due to increases in primary productivity or slow microbial decomposition of organic matter (Freeman et al., 2004; Moore and Dalva, 2001; Strohmeier et al., 2013; Xenopoulos et al., 2003). However, since Boreal peatlands are a large reservoir of organic carbon, landscape alterations can change the distribution of DOC throughout the system and negatively impact important biogeochemical processes associated with the carbon balance (Pace and Cole, 2002). In the oil sands region, the DOC of a constructed wetland may be susceptible to changes in concentration and composition due to the removal of vegetation and peat material and the addition of tailings in the wetland construction process. The loss of vegetation and peat alters hydrological flow paths throughout the system and as previously mentioned, stockpiled peat may be oxidized under aerobic conditions, thus releasing carbon (Waddington and Roulet, 1997; Turetsky et al., 2002). The tailings material is associated with high salinity levels and the presence of oil sand process-affected water (OSPW), which can be toxic to vegetative and microbial communities commonly found in freshwater wetlands, therefore leading to an overall decline in carbon accumulation (Trites and Bayley, 2009).

The composition and concentration of DOC is highly variable within a reclaimed wetland due to the influence of peat and tailings material present, as well as the young age of the system itself. To characterize DOC within these systems and to see if the carbon present is similar to observations in natural wetlands, techniques such as fluorescence spectroscopy have been used (e.g. Khadka et al., 2016). Fluorescence spectroscopy is a rapid and precise technique used to interpret DOC composition among various ecosystems (e.g. Coble et al., 1990; Coble, 1996; McKnight et al., 2001; Jaffé et al., 2008). When a molecule absorbs light, it moves from a ground state to an excited state. It subsequently falls back to its ground state, and it is when this occurs that light is emitted through fluorescence (Aiken, 2014). Fluorescence spectroscopy produces an excitation-emission matrix (EEM), which is a collection of excitation spectra and the emission wavelengths that fluorescence is observed at (Coble, 1996; Baker, 2001; Stedmon et al., 2003; Cory and McKnight, 2005). To analyze EEMs, fluorescence indices and Parallel Factor Analysis (PARAFAC) have been used widely in previous research (Stedmon et al., 2003; Cory and McKnight, 2005; Yamashita et al., 2008; Fellman et al., 2011; Olefeldt et al., 2013). There are several fluorescence indices that characterize DOC composition, in which they can classify the carbon source, either terrestrially- or microbially-derived (McKnight et al., 2001; Cory and McKnight, 2005), age (Parlanti et al., 2000; Wilson and Xenopoulos, 2009), degree of humification (Ohno, 2002) and molecular structure. PARAFAC is a multivariate analysis tool that has also been used widely to analyze DOC composition, in which it decomposes EEMs into individual fluorescent components (Bro, 1997; Stedmon and Bro, 2008; Coble et al., 2014). Several components have been reported in the literature for diverse ecosystems and infer different characteristics of the carbon composition (Coble et al., 1998, 1990; Parlanti et al., 2000).

1.2. Research Objectives

The overall goal of wetland reclamation post-oil sands mining is to construct a self-sustaining, carbon accumulating system that is resilient to natural environmental stresses and allows for the successful establishment of vegetative species (Price et al., 2010; CEMA, 2014). The majority of research on the carbon balance of Boreal systems has focused on surface-atmospheric exchanges; however, the aqueous portion strongly influences carbon accumulation in this region. Therefore, investigating DOC quantity and quality is helpful to determine if a reclaimed wetland is functioning similarly to natural wetlands in the oil sands region from an aqueous carbon balance perspective. The objective of this research is to characterize DOC quantity and quality of a reclaimed wetland using fluorescence spectroscopy and EEM-PARAFAC analysis and compare DOC patterns to those observed in natural wetlands in the Fort McMurray area. To achieve this, DOC concentration and fluorescent measurements will be used to 1) classify the source, age and structure of carbon, and 2) identify spatial and temporal patterns of DOC within and among wetlands. Results from this study will provide enhanced understanding of aqueous carbon cycling and characteristics of a reclaimed wetland in relation to natural wetlands within the area. It will provide scientists, engineers and mine closure personnel with knowledgeable information for future wetland reclamation efforts in the oil sands region. Characterizing DOC compositional patterns within a reclaimed wetland and comparing it to those observed in natural systems in the area will describe how oil sands mining and reclamation techniques have influenced carbon dynamics of these wetlands.

SECTION 2: BACKGROUND

2.1. The Western Boreal Plains (WBP)

2.1.1. Characteristics of the WBP

Canada's Western Boreal Plains are primarily located in Alberta and extend eastward into Saskatchewan and Manitoba and consist of a mosaic of forest and wetland ecosystems (Agriculture and Agri-Food Canada, 2013). The climate of the WBP is described as sub-humid, in which potential evapotranspiration is greater than precipitation (Ferone and Devito, 2004; Smerdon et al., 2005; Devito et al., 2012). The majority of precipitation (approximately 65-75%) is received during the growing season (May to September); however, at this time, evapotranspiration (ET) demands are the greatest. Therefore, the synchronization of high P and ET demand further enhance net moisture deficit of the WBP (Devito et al., 2005; Devito et al 2012). Additionally, the WBP are characterized by season and decadal wet and dry cycles, in which wet conditions reduce water storage and increase runoff, whereas dry conditions provide a large water storage and decrease runoff potential. However, the water storage capacity is rarely exceeded and surface runoff is limited, especially during high ET demands (Devito et al., 2012a).

The geological profile of the WBP is complex and variable, in which the deep glacial till deposits are heterogeneous in material and depth and range in storage capability (Ferone and Devito, 2004; Devito et al., 2005; Devito et al., 2012). The glacial till deposits are either fine- or coarse-textured. Fine-textured deposits are composed of silt or clay materials and limit infiltration and lateral flow in the subsurface due to the fine composition of the sediments. These fine sediments poorly transfer water through the catchment and are generally only connected to local groundwater flow systems (Devito et al., 2005b; Devito et al., 2012). In contrast, coarse-textured sediments are generally consist of sand and gravel outwash and enhance infiltration and lateral groundwater flow in the subsurface because of the higher hydraulic conductivity, relative to fine-textured sediments. Therefore, water is more easily transferred throughout the system and can be connected to local, intermediate or regional groundwater flow systems (Devito et al., 2005b; Devito et al., 2012).

In this region, there are complex interactions between the climate and geology that influence the overall hydrology and connectivity within an ecosystem. Connectivity among landscapes is very important in the WBP. For example, during dry conditions, lowland areas supply water inputs to forested uplands to maintain vegetative growth, whereas in wet conditions, groundwater flow reversals occur, in which water is discharged to the peatland (Ferone and Devito, 2004; Brown et al., 2009).

2.1.2. Naturally-occurring wetlands of the WBP

Naturally occurring wetlands are defined by a water table at, below or above the ground surface and promote vey wet soils, hydrophilic vegetation and biological activity (National Wetlands Working Group, 1997). In Canada, wetlands are either classified as mineral soil wetlands or peatlands (National Wetlands Working Group, 1997; Price and Waddington, 2000). Mineral soil wetlands consist of marshes, shallow water and some swamps and produce minimal to no peat. In contrast, bogs, fens and some swamps are classified as peatlands, in which the depth of peat accumulation is greater than or equal to 40 cm (National Wetlands Working Group, 1997). Bogs are ombotrophic, in which precipitation is the only source of water input. Additionally, bogs have a water table that generally remains below the surface and are characterized by the dominance of sphagnum mosses, low availability of nutrients and acidic pH (Bedford et al., 2014). In contrast, fens are described as generally having a water table at or below the surface and are minerotrophic, in which they receive water inputs from surface and groundwater, as well as precipitation (National Wetlands Working Group, 1997). Nutrient poor fens have relatively similar characteristics to bogs, whereas nutrient rich fens are dominated by brown mosses and sedges and have a neutral pH (Bedford et al., 2014). This classification method is a guideline used to describe wetland systems; however, it is possible to observe multiple types of wetlands within a single system. For example, within a wetland, half of the wetland may be described as a poor fen, whereas the other half may be characterized as bog-like. In WBP peatlands, net primary productivity (NPP) rates are greater than decomposition rates, which subsequently leads to the accumulation of organic matter under anoxic conditions below the ground surface (National Wetlands Working Group, 1997). The large accumulation of organic matter contributes to the carbon sink of the WBP and is an important component of the global carbon cycle.

2.2. Oil sands mining and reclamation practices

2.2.1. Oil sands surface mining

Oil sands surface mining only occurs in the Athabasca Oil Sands region and completely destroys the ecological and hydrological functions of the natural landscape (Alberta Government, 2009). All overburden material must be stripped from the landscape prior to bitumen extraction including the vegetation, surficial glacial-till deposit and peat material (Alberta Government, 2009). The Cretaceous Clearwater and McMurray geological formations are located beneath the glacial-till deposits, in which the Clearwater consists of loose shale and silt stone and the McMurray layer contains the majority of bitumen resources (Hackbarth and Nastasa, 1979). Additionally, these formations overlie a thick Devonian layer, which consists of limestone and shale (Hackbarth and Nastasa, 1979).

The bitumen extraction process results in the creation of large, open-pits up to approximately 80 m in depth (Alberta Government, 2009). Bitumen can be described as a thick, black mixture of hydrocarbons that does not flow unless it is headed or diluted by lighter hydrocarbons (Alberta Government, 2009). To obtain the bitumen from the oil sands at SCL, a process known as the Clark Hot Water Extraction (CHWE) process is used. Caustic hot water (NaOH) is added to the oil-sand ore to decrease the molecule's structural integrity which produces wet tailings (Chalaturnyk et al., 2002). Then, gypsum ($CaSO_4 \bullet 2H_2O$) is added to the tailings, in which it becomes a non-segregating mixture in the ponds and produces composite tailings (CT) (Chalaturnyk et al., 2002). Bitumen extraction requires the use of large volumes of water, which subsequently becomes saline due to the addition of NaOH and $CaSO_4 \bullet 2H_2O$ during the treatment process to form tailings (Trites and Bayley, 2009).

2.2.2. Wetland reclamation

According to the Alberta Environmental Protection and Enhancement Act, mining companies are required to reclaim the disturbed landscape back to equal pre-mining ecosystem function after mining operations are complete (Alberta, 2014). The overall objective of reclamation is to reconstruct a watershed with a hydrological design that will support biogeochemical and ecological processes (Alberta Government, 2009). Minimal research has been conducted on wetland reclamation in the oil sands region, although wetlands cover more than 50% of the landscape (Rooney et al., 2012). Recently, there has been a shift in reclamation efforts from forested-upland systems (Elshorbagy et al., 2005; Carey, 2008; Lilles et al., 2010; Sorenson et al., 2011; Huang et al., 2015) to peatland-wetland systems (Trites and Bayley, 2009; Price et al., 2010; Rooney et al., 2012). However, there are multiple challenges associated with wetland reclamation such as the sub-humid climate of the WBP (Devito et al., 2012a), peatlands can take upwards of thousands of years to develop and the potential for salts to enter the system due to underlying estuarine and marine sediment deposits and deep saline aquifers (Trites and Bayley, 2009). The reclamation process involves filling the large pits with left over sand, consolidated tailings and overburden, re-contouring the placed material into a functioning landscape, introduction of vegetative species and multiple years of intensive monitoring (Alberta Government, 2009). Reclamation ends with certification, which is issued once a system functions at same efficiency prior to mining (Alberta Government, 2009). In the oil sands region, there are currently two ongoing wetland reclamation projects: Suncor's Nikanotee Fen (Price et al., 2010; Daly et al., 2012) and Syncrude's Sandhill Fen (Wytrykush et al., 2012) . These reclamation projects will serve as the baseline for future wetland reclamation projects in the oil sands region.

2.3. The Carbon Balance

The largest pool of terrestrially derived organic carbon is located within peatlands which account for approximately one third of the world's soil carbon (Gorham, 1991; Waddington and Roulet, 1997). The majority of Canadian peatlands are located in the Boreal and Subarctic Regions and occupy approximately 64% and 33% respectively, where they store about 56% of the organic carbon found in all of Canadian soils (Tarnocai, 2006). The most widely studied components of the peatland carbon balances are atmospheric CO_2 (Moore et al., 1998; Waddington et al., 1998), methane (CH_4) (Moore et al., 1998; Strack et al., 2004) and aqueous DOC fluxes (Moore et al., 1998; Pastor et al., 2003; Khadka et al., 2016). CO_2 and CH_4 are naturally occurring GHG's and are released during the decomposition process of organic matter (Moore et al., 1998; Moore and Dalva, 2001). However, natural (i.e. droughts, wildfires, climate change) and anthropogenic (i.e. agriculture, mining) disturbances will enhance CO_2 and CH_4

emissions into the atmosphere and loss of DOC in aquatic ecosystems, thereby shifting the system from a carbon sink to a carbon source (Hogg et al., 2005; Tarnocai, 2006; Bhatti and Tarnocai, 2009). In Boreal peatlands, the majority of research conducted on the carbon balance has focused on surface-atmospheric processes, in which CO_2 exchange in the past was analyzed using carbon stocks and currently is determined via eddy covariance towers (e.g. Carey, 2008; Huang et al., 2015; Nicholls et al., 2016). However, there is less research focused on assessing carbon loss and composition as DOC in the WBP (e.g. Khadka et al., 2016).

2.3.1. Dissolved Organic Carbon (DOC)

DOC represents an important component of the aqueous carbon balance and is a complex and heterogeneous mixture of organic molecules that range from low to high molecular weight organic compounds (i.e. humic acids) (Thurman, 1985; Koprivnjak and Moore, 1992; Moore et al., 1998; Olefeldt and Roulet, 2012). It is produced by the partial decomposition of terrestrial organic matter by microbial communities, followed by its dissolution in pore water. In Boreal systems, DOC accumulation is high as primary productivity rates exceed decomposition rates (Moore et al., 1998). DOC influences several ecosystem processes such as microbial activity, mobility and availability of nutrients, metals and contaminants and attenuates ultraviolet (UV) light in surface waters (Moore and Dalva, 2001; Pace and Cole, 2002; Xenopoulos et al., 2003; Eimers et al., 2008; Strohmeier et al., 2013; Peacock et al., 2014). Boreal peatlands supply the majority of DOC entering aquatic ecosystems such as lakes and streams and therefore, represent a significant redistribution of terrestrial organic carbon throughout the system (Dalva and Moore, 1991; Pastor et al., 2003). Multiple studies have observed that hydrologic flow paths are the primary control on DOC production, distribution and export in peatland and adjacent upland systems (Moore, 1987; Urban, 1989; Waddington and Roulet, 1997; Pastor et al., 2003; Eimers et al., 2008; Waddington et al., 2008; Laudon et al., 2011). DOC has been observed to vary greatly both spatially and temporally within peatlands (Moore, 1987; Waddington and Roulet, 1997;Agren et al., 2014). For example, Boothroyd et al. (2015) investigated DOC concentrations at different peatland hillslope positions and observed a decrease in concentration downslope. Eimers et al. (2008) observed a temporal pattern of DOC concentration, in which maximum concentrations were observed in late summer and early fall, then subsequently declined through the fall and remained relatively constant throughout the winter months. Waddington and Roulet (1997) suggested that DOC concentrations in peatlands are generally higher in the summer months due to high ET and decomposition rates. Additionally, significant hydrological events can result in variable temporal concentration patterns.

Several factors have been reported in the literature that influence changes in DOC concentrations. Moore and Dalva (2001) reported an increase in peatland DOC production was associated with slow decomposition rates of plant material by microbial communities under anoxic soil conditions, whereas, Freeman et al. (2004) observed high DOC concentrations due to enhanced primary productivity in peatlands. Furthermore, DOC concentrations were found to increase as the size of the peatland-wetland within a catchment increased (Eimers et al., 2008; Koprivnjak and Moore, 1992; Laudon et al., 2011). Natural peatlands are carbon sinks; however, natural and anthropogenic disturbances that result in the removal of vegetation and peat material, will lead to a loss of accumulated carbon, and thus, a potential shift in the carbon balance from a sink to source. Therefore, it is important to assess DOC to provide information on factors that influence carbon cycling and transport patterns and carbon characteristics in peatlands.

2.4. Fluorescence Spectroscopy

2.4.1. Absorption and fluorescence

Absorption of light in the UV-visible spectrum (i.e. 190 nm to 780 nm) occurs when the electrons present in a chemical bond are excited and move from a ground energy state to an excited energy state (Valeur, 2001). A chromophore is the region of the molecule that absorbs incoming light and the wavelength that it absorbs light at is dependent on the energy difference between the ground and excited states and the molecular structure of the chromophore (Aiken, 2014). For example, single bonded molecules, such as alkanes and carbohydrates, absorb light at shorter wavelengths (i.e. higher energy) that do not fall within the UV-visible light spectrum. In contrast, conjugated structures, such as alkene and aromatic molecules, absorb light at longer wavelengths (i.e. lower energy) within the UV-visible spectrum, in which aromatic molecules generally have the greatest absorption of UV-visible light (Aiken, 2014).

Fluorescence is observed through the direct emission of light when electrons return to ground state from an excited state (Valeur, 2001). The group of compounds that emit light after excitation is referred to as a fluorophore. The fluorescence of a molecule is due to the loss of energy upon arrival at the ground state through competing pathways and similarly to chromophores, is influenced by the molecular structure (Schulman, 1985; Aiken, 2014). Schulman (1985) stated that the molecular structure determines the intensity and location that fluorescence is observed at. For example, aromatic molecules generally fluoresce more intensely than other organic molecules (Aiken, 2014). However, aromatic molecules that contain functional groups fluoresce at even longer wavelengths because energy is lost through the functional groups (Valeur, 2001). Therefore, the molecular structure of organic molecules is very important in both absorption and fluorescence processes and is essential to DOC analysis.

2.4.2. Fluorescence spectroscopy of Dissolved Organic Matter (DOM)

Fluorescence spectroscopy is a rapid and precise technique used to identify and interpret the composition of dissolved organic matter and presents data in the form of excitation-emission matrices, which are a collection of excitation and emission wavelengths of the UV-visible light spectrum for an individual sample (Coble, 1996; Coble, 2007). In DOM fluorescence, EEMs have a broad excitation and emission spectrum between 250 – 400 nm and 350 – 500 nm respectively (Stedmon and Bro, 2008). These EEMs vary extensively among ecosystems and the maximum fluorescence of a sample is greatly dependent on the fluorophores present, in which each individual fluorophore corresponds to a specific range of maximum excitation and emission wavelengths.

There is a general assumption made when using fluorescence spectroscopy on DOM samples, in which the compounds that make up DOM behave similarly to the pure compound present in solution (Aiken, 2014). This implies that changes in fluorescence parameters such as efficiency, intensity, peak width and maximum fluorescence of fluorophores are due to instrumental (e.g. Inner Filter Effects (IFEs), Raman or Rayleigh scattering) and environmental (e.g. pH or temperature) variations (Stedmon and Bro, 2008; Aiken, 2014). Therefore, instrument calibration and correction are essential to produce the most accurate results; however, it is almost impossible to remove all error (Stedmon and Bro, 2008). Instrument specific corrections are applied to fluorescence measurements to account for any instrument biases. In DOM fluorescence, it is necessary to calibrate the signal intensity to compare fluorescence measurements among studies. The two approaches used in the literature to calibrate the signal intensity are Quinine Sulfate (QS) and Raman Signal (RS). The Quinine Sulfate is measured using an excitation and emission at 350 nm and 450 nm respectively, whereas the Raman Signal is from pure water. Additionally, spectral corrections account for deviations in the light source output. In relatively new fluorescence spectrometers, a reference detector is used to correct for any changes and remove any spectral error from the light source (Stedmon and Bro, 2008). Furthermore, IFEs, Raman and Rayleigh scattering must also be corrected. IFE's in DOM samples are primarily due to the absorption of incoming excitation light, rather than the absorption of emission light (Ohno, 2002; Stedmon and Bro, 2008). Raman scattering is removed in fluorescence spectroscopy by the subtraction of the pure water spectrum from the sample spectrum, whereas correcting for Rayleigh scattering involves the removal of areas within an EEM that do not contain any data (Stedmon and Bro, 2008).

Fluorescence spectroscopy has been used to characterize DOM for over a century (Hartley, 1893); however, in the past decades, several scientists have used this method to assess DOM composition in a variety of ecosystems such as marine waters (Coble, 1996), lakes and estuaries (Cory and McKnight, 2005; Stedmon et al., 2003), wetlands (Olefeldt et al., 2013; Khadka et al., 2016) and waste water treatment plants (Baker, 2001; Hudson et al., 2007). Recent advances in fluorescence spectroscopy provide new approaches for characterizing spatial and temporal DOM patterns in a range of aquatic and terrestrial ecosystems.

2.4.3. Common organic fluorophores

The majority of organic fluorophores in DOM analysis are conjugated aromatic molecules that contain polar functional groups and are commonly classified by the central conjugated group such as indoles and phenols (Aiken, 2014). The location of excitation and emission maxima of individual fluorophores aids in identifying and interpreting complex DOM characteristics in a variety of ecosystems (Aiken, 2014). In DOM analysis, there are two general fluorescence groups that represent the DOM pool: protein-like and humic-like substances. The term "like" is generally associated with these groups in previous research (e.g. Coble, 1996;

Coble, 2007) to suggest that the observed fluorophore has a chemical composition similar to reference fluorophores, however, it is not a pure fluorophore (Stedmon et al., 2003). Protein-like substances are typically amino acids, free or bound to proteins, associated with biological activity and higher-molecular-weight DOM (Coble, 1996; Fellman et al., 2010). Humic-like substances comprise the majority of fluorescence observed in natural waters and typically fluoresce at longer emission wavelengths (Coble, 1996). The most common fluorophores observed in DOM analysis are summarized in Table 2.1.

2.4.4. Fluorescence Indices

Fluorescence indices are broadly utilized to interpret and characterize DOM in a range of ecosystems. These indices use the excitation and emission spectra collected from an individual sample to identify its characteristics, such the precursor material (Cory and McKnight, 2005; McKnight et al., 2001b), age (Parlanti et al., 2000; Wilson and Xenopoulos, 2009), degree of humification (Zsolnay et al., 1999; Ohno, 2002), aromaticity and molecular structure (Karanfil et al., 2002; Weishaar et al., 2003; Ågren et al., 2008; Olefeldt et al., 2013).

2.4.4.1. Fluorescence Index (FI)

The fluorescence index is a widely used 2-D technique to infer the source of carbon, either terrestrially-derived from higher plant material (i.e. living plant species) or microbially-derived from decomposed dead organic matter (McKnight et al., 2001; Cory and McKnight, 2005). The FI was originally calculated as the ratio of emission 450 nm to emission 500 nm at an excitation of 370 nm, until it was modified for instrument-corrected spectra to the ratio of emission 470 nm to emission 520 nm at an excitation of 370 nm (McKnight et al., 2001; Cory and McKnight, 2005). McKnight et al. (2001) used microbially- and terrestrially-derived end members to determine the fluorescence index of lakes and rivers in Antarctica and the United

States. Within the lakes of Antarctica, terrestrial vegetation is very limited and the majority of DOM is produced by microbial and algal material. In contrast, the DOM observed in the lakes of United States catchments were dominated by terrestrial plants and SOM. When the FI was applied to the data, lakes and rivers with microbially-derived end members had a value of approximately 1.9, whereas those with terrestrially-derived end members had a value of approximately 1.4. Additionally, McKnight et al. (2001) observed differences between the EEMs of microbial and terrestrial end-members, in which microbially-derived DOM had a maximum emission fluorescence at lower wavelengths and terrestrially-derived DOM had a maximum emission fluorescence at higher wavelengths. This trend was very similar to the differences observed between marine and freshwater samples in a study conducted by Coble (1996b).

2.4.4.2. Freshness Index (β/α)

The freshness index is used to determine the age of organic matter within a system, in which β refers to the amount of recently produced organic matter and α refers to older and more decomposed organic matter (Parlanti et al., 2000; Wilson and Xenopoulos, 2009). The freshness index was originally determined using the ratio of β/α peaks. The β peak was the ratio between the maximum intensity within excitation 310 to 320 nm to maximum intensity within emission 380 to 420 nm, whereas the α peak was the ratio between maximum intensity within excitation 330 to 350 nm to maximum intensity within emission 420 to 480 nm (Parlanti et al., 2000). Parlanti et al. (2000) observed a spectral band with the β component due to the presence of protein-like fluorophores, in which the compounds are associated with recently-produced organic matter by microbes. It was concluded that biological activity is one of the main factors that influence the β component of DOM. Wilson and Xenopoulos (2009) modified the β/α ratio used by Parlanti et al. (2000) to a ratio of two known fluorophores, where the intensity at emission wavelength 380 nm was divided by the maximum intensity between emission 420 to 435 nm at an excitation of 310 nm. When applied to the dataset, Wilson and Xenopoulos (2009) observed an increase in β/α with an increase in autochthonous carbon production, which indicated the relative contribution of recently produced DOM within the system. Additionally, the β/α increased greatly as the proportion of cropland increased, further suggesting recently produced DOM by microbial activity (Wilson and Xenopoulos, 2009).

2.4.4.3. Humification Index (HIX)

The humification index indicates the degree of humification of organic matter and an increase in humification is associated with a decrease in the ratio of H/C, and subsequently a shift to longer emission wavelengths (Zsolnay et al., 1999; Gabor et al., 2014). The HIX was originally calculated at an excitation of 254 nm, as the area under a peak from emission wavelengths 435 to 480 nm divided by the area under a peak from emission wavelengths 300 to 345 nm (Zsolnay et al., 1999). The two sources of DOM in soils are SOM, which are generally humified, and freshly introduced material (i.e. from cell lysis), which is not humified. In the experiment designed by Zsolnay et al. (1999), the effect of drying on the HIX of soils was interpreted for two methods: 1) air drying and 2) oven drying. The soil that was air-dried had a minor shift into the humified spectral region and resulted in an increase in humification. In contrast, the oven-dried soil had a strong shift into the non-humified spectral region and decreased in humification. Zsolnay et al. (1999) concluded that the DOM source for humified soil was due to the extract of SOM, whereas the DOM source for the non-humified soil was due to decomposition of biomass; however, the researchers did advise that caution be used when interpreting the results.

Despite the results from Zsolnay et al. (1999), Ohno (2002) wanted to eliminate the potential for IFEs for concentrated samples and modified the HIX equation to a ratio of the area under emission from 435 to 480 nm divided by the sum of the area under emission 300 to 345 nm and 435 to 480 nm, in which the HIX ranges from 0 to 1. In addition to modifying the equation to calculate HIX, Ohno (2002) also recommended that all samples should be diluted to a fixed absorbance (<0.3 cm^{-1}).

2.4.4.4. Specific Ultraviolet Absorbance at 254 nm (SUVA$_{254}$)

SUVA$_{254}$ is defined as the ratio of UV absorbance at a desired wavelength (generally at excitation 254 nm) to DOC concentration in mg/L-m. SUVA$_{254}$ infers the aromatic carbon and molecular weight, in which a high SUVA$_{254}$ correlates to a higher aromatic carbon content and higher molecular weight (Weishaar et al., 2003; Olefeldt et al., 2013). Peatland DOC has been found to have generally higher aromatic contents and greater molecular weights and observed to influence bioavailability of DOM (Ågren et al., 2008; Olefeldt et al., 2013). Weishaar et al. (2003) confirmed that SUVA$_{254}$ was a good indicator for aromaticity and molecular weight by comparing results to those observed using Nuclear Magnetic Resonance (NMR) spectroscopy. Additionally, Karanfil et al. (2002) suggested that SUVA$_{254}$ values ≥ 4 mg/L-m generally have greater aromatic content and higher molecular weight, whereas SUVA$_{254}$ values ≤ 3 mg/L-m generally have lower aromatic content and molecular weight. SUVA$_{254}$ has also been observed to correlated with DOM reactivity and disinfection by-products (DBP), in which coagulation can remove the humic fraction of DOC during chlorination in water treatment processes (Karanfil et al., 2002).

2.4.5. Parallel Factor Analysis (PARAFAC)

PARAFAC analysis is multivariate analysis model that is commonly used to further interpret DOM composition by decomposing EEMs into individual fluorescent components that most accurately describe a given dataset. The advantage of PARAFAC analysis is that it provides both a qualitative and quantitative model of the data (Stedmon and Bro, 2008).

In fluorescence spectroscopy, the fluorescence of a sample is dependent on the wavelength at which light is absorbed (i.e. excitation) and the wavelength at which fluorescence is observed at (i.e. emission) (Stedmon and Bro, 2008). Therefore, combining the excitation and emission spectra of multiple samples produces a three-way dataset (Stedmon and Bro, 2008). Using a series of samples, PARAFAC models are described by the following equation (1):

$$x_{ijk} = \Sigma\, a_{if} b_{jf} c_{kf} + \varepsilon_{ijk}\ ,\ i=1,.,I;\ j= =1,.,J;\ k=1,.,K; \qquad (1)$$

where x_{ijk} is the fluorescence intensity of sample I measured at emission wavelength j and excitation wavelength k, ε_{ijk} refers to unexplained signals, a, b and c are the model parameters and represent concentration, emission spectra and excitation spectra of fluorophores respectively (Stedmon and Bro, 2008). In PARAFAC modeling, it is assumed that a change in concentration results in a change fluorescence intensity and does not affect the shape of the excitation and emission spectra (Stedmon and Bro, 2008).

Stedmon and Bro (2008) thoroughly describe each stage of modeling, and summarizes the process into four main stages: 1) Data collection and pre-processing, 2) Outlier analysis (initial models), 3) Model validation and 4) Model interpretation. Stedmon and Bro (2008) recommend that a minimum of 20 to 100 samples be used to create a PARAFAC model due to the complexity of DOC; however, they recommend using more than 100 samples to make the modeling and validation processes easier. A reasonable fit for fluorescence EEM data is normally above 99% variance explained (Stedmon and Bro, 2008). The objective of model validation is to determine the appropriate number of components to represent the data using model validation techniques: 1) residual analysis, 2) examination of spectral properties, 3) random initialization and 4) split half analysis, in which method 4 is the most commonly used (Stedmon and Bro, 2008). Split half analysis involves splitting the dataset into two halves and modeling each half independently. If both of the models are identical, it can be concluded that the model is robust (Stedmon and Bro, 2008). The final stage of PARAFAC modeling is to interpret the model components; in which individual components are compared to those previously identified in the literature based on their excitation and emission maximums (Coble et al., 1990; Coble, 1996; Coble et al., 1998; Stedmon et al., 2003; Gabor et al., 2014). The five most common fluorescent components reported in the literature are summarized in Table 2.2.

SECTION 3: SITE DESCRIPTION, MATERIALS AND METHODOLOGY

3.1. Site description

3.1.1. Sandhill Fen

Sandhill fen ($57^{o}2'22.31''$N, $111^{o}25'20.40''$W) is a 52 hectare reclaimed watershed containing an upland (35 hectare) and wetland (17 hectare), located approximately 40 km north of Fort McMurray, Alberta (Figure 3.1). SFW is the first instrumented and monitored fen-wetland to be constructed on SCL property and is located in the northwest portion of the mine, previously known as East-In-Pit (EIP), which was mined from 1977 to 1999. EIP was filled with a 35 m layer of inter-bedded CT and tailings sand and then was capped with 10 m of tailings sand. In 2008, reclamation efforts began to construct SFW. The design plan for SFW included upland hills (also known as hummocks), vegetated swales, woody berms, a water storage pond, a fen-wetland, an underdrain system and two perched fens. There are 7 upland hummocks that vary in size throughout the fen and were designed to create an upland recharge area to supply water to the lowlands. Additionally, the long axis of the hummocks are aligned parallel to the lowland to maximize the seepage face of the lowland to ensure long-term flushing of salts within the system (Wytrykush et al., 2012). The majority of the hummocks are 3-4 m high and approximately 180x60 m; however, hummock 7 is approximately 8 m tall and about 350x100m. Additionally, there are two isolated perched fens within SFW designed to mimic natural perched fens that are common within the WBP. The purpose of the perched fen was to determine if these systems could be sustained with only precipitation inputs. Furthermore, boardwalks, dirt roads, a weir building and a sump at the outlet were to be added to the construction plan for SFW (Wytrykush et al., 2012) (Figure 3.2).

On top of the previously placed 35 m of CT and tailings sand layer, 0.5 m of clay-till (finely-grained) was added in the wetland area only. The function of the clay-till layer is to create a mineral-based soil and to limit the upward diffusion of tailings water to the surface of the fen. An additional 0.5 m layer of recently recovered peatland material was added on top of the clay-till to function as the organic soil layer. At five of the seven hummocks, approximately 0.1-0.5 m of fluvial sand (Pf sand) and 0.1-0.2 m of harvested litter, fibric and humic material (LFH) from the forest floor of a jack pine ecosystem was added to the existing substrate material. The remaining two hummocks, as well as the swales, had 0.3-0.4 m of clay-till subsoil and 0.1-0.2 m of LFH material from the forest floor of an aspen/white spruce ecosystem (Wytrykush et al., 2012) (Figure 3.3).

In this study, five locations were selected for analysis and include the lowland, margin, outlet, upland and WSP. The lowland (Figure 3.4a) refers to the wetland portion of the SFW and is the only section of SFW to contain the peat material. The margin position (Figure 3.4b) is located in between the upland (hummocks) and the lowland-wetland. It represents the transition from the lowlands to the upland areas and acts as a boundary between the lowlands and uplands (although this “boundary” is not strictly bound). The outlet (Figure 3.4c) is located at the west end of the fen and is where the surface, near-surface and groundwater from SFW are collected before they are removed from the wetland. The upland hummocks (Figure 3.4d) were designed to establish an upland recharge area, in which sufficient water would be supplied to the lowlands (Wytrykush et al., 2012). All seven hummocks account for a total volume of approximately 825,000 m^3. (Wytrykush et al., 2012). The WSP (Figure 3.4e) is a highly managed water system that receives water from the Mildred Lake Reservoir (located north of SFW). The water is supplied through a pipe from Mildred Lake into the double clay-lined pond and is then diffused into the fen through a leaky gravel berm. The water will then flow east through the lowlands towards the fen outlet where the surface and near-surface water from the fen will flow through a v-notch weir and into the sump. Once the water has reached the sump, it is pumped out of SFW back into EIP (Wytrykush et al., 2012; Nicholls et al., 2016).

In 2012, vegetation was introduced to SFW. The vegetation at the upland include: *Populus tremuloides* (trembling aspen), *Pinus bamksiana* (jack pine), *Picea glauca* (white spruce) and a variety of shrubs, whereas the vegetation at the lowlands include: *Betula glandulosa* (bog birch) and *Carex spp.* (sedges).

3.1.2. Pauciflora Fen

Pauciflora Fen (56^{o}22’37.45”N, 111^{o}14’12.17”W) is a 22 km^2 natural wetland located approximately 40 km south of Fort McMurray and approximately 80 km south of SFW (Figure 3.1). PC is also known as the Poor Fen (PF) in other studies (Khadka et al., 2016) due to its nutrient poor status in the northern portion of the wetland and its bog-like characteristics in the south. The lowland is located within a local topographic depression and is surrounded by a relatively steep forested upland. The peat depth at the lowlands of Pauciflora is approximately 4 m on average (Khadka et al., 2016). The soil at Pauciflora is categorized as a peat-mineral mix; therefore, the organic matter content at this fen is relatively low (Thorne, 2015). The main vegetation species in the wetland are *Carex spp.* (sedge species), *Sphagnum spp.* (moss species), *Piecea mariana* (black spruce), *Betula pumila* (dwarf birch)*, Rubus chamgemorous* (cloudberry) and bog cranberry.

There are three transects (T1, T2 and T3) and a discharge outlet at PC (Figure 3.5). Each transect consists of a pair of sampling piezometers: one piezometer installed into the hummock, the other in a hollow. Additionally, Stony Mountain Road lies between transect 1 the discharge outlet.

3.1.3. Poplar Fen

The Poplar fen (56°56’25.24”N, 111°33’0.89”W) is a 25 km^2 natural wetland located approximately 20 km North of Fort McMurray and 10 km South of SFW (Figure 3.1). Poplar is categorized as a treed-moderate rich fen (RF), with a slight change in elevation between the lowland and upland hillslopes. The upland vegetation includes *Pinus banksiana* (Jack Pine), *Picea mariana* (black spruce), *Picea glauca* (white spruce) and *Equisteum* (horsetail), whereas the lowland-wetland vegetation includes *Larix laricana* (Tamarack), *Betula pumila* (dwarf birch), *Carex spp.* (sedges) and *Tomenthypnum nitens* (feather moss). Additionally, the upland soil is more of a sandy, silt mineral-based soil, whereas the lowland soil has a higher organic matter content with a peat thickness of approximately 1-1.5 m (Ketcheson, 2015; Thorne, 2015).

Similar to Pauciflora fen, there are three transects (T1, T2 and T3) and a discharge outlet at PP (Figure 3.6). Sampling piezometers were installed along each transect, with one piezometer in the hummock and the other in the hollow. Poplar is bordered by several dirt roads and contains seismic cutlines throughout the property (Khadka et al., 2016); however, these anthropogenic disturbances did not occur near the study area.

3.2. Materials and Methodology

3.2.1. Site identification

The sample identification used in this research indicates the location and type of sample taken. Firstly, the each sample name begins with “SH” to indicate then watershed name (Sandhill). The second portion of the sample identification refers to an abbreviated location name and includes the WSP, boardwalk 1 (B1), boardwalk 2 (B2), boardwalk 3 (B3), margin (TR), outlet (OP) and upland (UP). The final part of the name identification refers to either a numbered pore water (W#) or a numbered surface (S#) sample. For example, a pore water sample collected from margin area, well 3 at SFW would be labeled “SH-TR-W3” and surface sample collected from boardwalk three would be identified as “SH-B3-S1”.

At PC and PP, the site identification is similar to the method used at SFW. The first portion of the sample name refers to the watershed name (PC or PP); however, the final portion of the sample identification refers to the pore water or surface water sample taken. For example, a pore water sample collected at Pauciflora from well 5 would be labeled as “PC-W5”, whereas a surface sample from the outlet at Poplar would be identified as “PP-DS”, in which DS means downstream.

3.2.2. Site instrumentation

3.2.2.1. Sandhill Fen

A total of 33 near-surface wells were installed by 2014 throughout the SFW to measure water table depth and collect samples. Each well was a 1.60 m slotted PVC pipe that had been augured 0.48 m to 1.02 m below the ground surface. In 2014 and 2015, 27 Solinst Junior Edge Levelogger pressure transducers were placed into the wells and recorded temperature and water level measurements continuously every 15 minutes from May to October in both field years. Additionally, manual measurements of water level were taken using the Solinst TLC water level tape weekly. Water levels were also corrected annually for barometric pressure using a Solinst Barologger that was located on boardwalk 3.

Furthermore, a total of 10 Solinst LTC (level, temperature, conductivity) Levelogger Junior pressure transducers were instrumented down the major SFW drainage flow pathways (Biagi, 2015) in both 2014 and 2015 . These leveloggers were calibrated with 12,800 μS/cm conductivity solution prior to installation and were programmed to continuously record measurements every 15 minutes from May to October in 2014 and 2015.

Weekly surveys occurred in both study years to record discrete measurements of temperature, pH, dissolved oxygen (DO) and electrical conductivity (EC) in all near-surface wells and pooled water throughout SFW using the YSI Professional Plus Multi-parameter Handheld Instrument.

3.2.2.2. Pauciflora and Poplar Fens

In May 2012, a pair of piezometer nests were installed along 3 transects at both Pauciflora and Poplar, one if the hummock and the other in the hollow. Within each nest, there were 3 piezometers (at depths of 50 cm, 75 cm and 100 cm) and a sampling well. A hand auger was used to create holes, with the same diameter as the piezometer and well, through the peat profile at specified depths prior to installation. The piezometers and well were constructed of PVC pipes and were 1 m in length. Each piezometer was slotted with 5 mm holes over the 17 cm water intake to ensure the piezometer was centered at an ideal sampling depth (Khadka et al., 2016). Water samples were collected from the 50 cm piezometer at each transect and samples were collected from the discharge outlet at both wetlands.

3.2.3. Water sampling

At SFW, a total of 252 water samples were collected from May to October in 2014 and 2015. In 2014, 81 pore water and 47 surface water samples were collected biweekly, where as in 2015, 54 pore water and 63 surface water samples were collected monthly. At PC, 24 pore water and 4 surface water samples were collected from May to August in 2015, whereas at PP, 17 pore water and 2 surface samples were collected.

Prior to sample collection, all wells were purged to remove any stagnant water and were allowed to recharge. Water samples were collected using the Model 428 Biobailer and placed into a glass amber bottle after they had been environmentalized with three times. To prevent water contamination, a well cap was placed on each well. Additionally, surface water samples were collected in areas of pooled water and the WSP at SFW, as well as the outlet at SFW, PC and PP using a glass amber bottle after the bottle was environmentalized three times. In between sampling periods, the glass amber bottles were cleaned with Liquinox ®, bathed 5% HCl and baked at 200 ^{o}C for ~12 hours.

After collection, water samples were brought back to SCL's on site Environmental Research and Development laboratory where they were filtered using vacuum suction. Pore water samples were first filtered through a 47 mm, 0.45 µm filter to remove any large debris and then through a 25 mm, 0.07 µm filter. Surface water samples were only filtered through a 25 mm, 0.07 µm filter. Once filtered, samples were split and kept cool and in the dark for future analysis. For DOC concentration analysis, a 60 mL amber HDPE bottle was used. Additionally, a 40 mL amber glass bottle was used for fluorescence dissolved organic matter (fDOM) analysis.

DOC samples were analyzed by the Biogeochemical Analytical Service Laboratory at the University of Alberta using a Shimadzu 5000A TOC analyzer and concentrations were reported in units of mg/L.

3.2.4. Fluorescence spectroscopy

Fluorescence Dissolved Organic Carbon (fDOM) samples were analyzed at McMaster University on a Horiba-Jobin Yvon Aqualog Machine (Aqualog). The samples were kept out of the light and were allowed to reach room temperature prior to analysis. Quartz cuvettes were used to run the samples through the Aqualog. The cuvettes were first soaked in 50% nitric acid and bathed for 24 hours then thoroughly rinsed in deionized water prior to sample analysis. The cuvettes were environmentalized three times with the sample and were filled approximately two-thirds with the sample.

Standard tests were conducted and normalization factors were recorded before samples were run on the Aqualog machine. The first standard test was the QS test with settings of: 8 pixel, medium CCD gain and ran at an integration time of 0.05 seconds. The second standard test was the RS test with settings of: 8 pixel, medium CCD gain and ran at an integration time of 10 seconds. Normalization factors for each standard test were conducted at 0.1, 0.25, 0.5, 0.75 and 1 second integration times. For the purposes of this research, the RS was used to normalize the data during sample analysis. Samples were run for an excitation range of 240 nm to 600 nm at 5 nm increments and an emission range of 212.5 nm to 621.38 nm at 3.27 nm increments. Additionally, IFE, Raman Scattering and Rayleigh Masking (1st order only) were corrected for, the CCD gain was set to medium and the sum of the slit widths was set as 12.

The first round of samples was used to determine the absorbance of each sample at 254 nm. This absorbance value would subsequently determine the approximate integration time for the sample. If samples had an absorbance value greater than 1.3, they were diluted using the following guide: 1.3 – 1.6 = 1:1; 1.61 – 1.75 = 1:2; 1.76 – 2.5 = 1:5; > 2.5 = 1:10. After samples were diluted, the absorbance at 254 nm was determined again for the newly diluted sample. A guide to determine the approximate integration time was used, in which samples with absorbance values greater than 1 generally were ran at an integration time of 0.1 seconds, whereas samples with absorbance's between 0.7 to 1 were typically ran at an integration time of 0.5 seconds. In contrast, samples with absorbance values less than 0.5 were typically run at a 1 second integration time. However, each individual sample was unique and this guideline did not always apply, in which samples with low a absorbance may have been ran at a high integration time (e.g. 0.1 seconds). Additionally, 0.25 second and 0.75 second integration times were also used for select samples. Sample counts ranged between 20,000 and 45,000; if less than or greater than the specified range, the sample was ran at a lower or higher integration time respectively. Samples that displayed unexplainable scattering were removed and not included in the final dataset. All data from the sample runs were collected in individual EEMs produced by the Aqualog.

3.2.4.1. Fluorescence indices

To interpret DOC composition, four fluorescence indices were used: Fluorescence Index (FI), Freshness Index (β/α), Humification Index (HIX) and Specific Ultraviolet Absorbance at 254 nm ($SUVA_{254}$). Fluorescence index tests were performed in R (Version 3.2.1) using a series of codes provided by Dr. Claire Oswald at Ryerson University. The excitation and emission dataset of each individual sample contained within an EEM was used to calculate each index.

The fluorescence index (Cory and McKnight, 2005) was used to determine if the dissolved organic matter was terrestrially- (<1.6) or microbially-derived (>1.6). The FI of a sample was calculated using equation 2:

$$\text{At an excitation of 370 nm:} \qquad \frac{\text{Emission at 470 nm}}{\text{Emission at 520 nm}} \qquad (2)$$

The freshness index (Wilson and Xenopoulos, 2009) was used to indicate the relative proportion of recently produced dissolved organic matter. The β/α for an individual sample can be summarized by equation 3:

$$\text{At an excitation of 310 nm:} \qquad \frac{\text{Emission at 380 nm}}{\begin{array}{c}\text{Maximum emission between}\\ \text{420 nm and 435 nm}\end{array}} \qquad (3)$$

The humification index (Ohno, 2002) suggested the degree of humification, in which a high HIX indicated more humified material. The HIX can be explained by equation 4:

$$\frac{\text{Sum of emission from 435 nm to 480 nm}}{(\text{Sum of emission from 300 nm to 345 nm}) + (\text{Sum of emission from 435 nm to 480 nm})} \quad (4)$$

$SUVA_{254}$ (Karanfil et al., 2002) was used to indicate the relative amount of aromatic carbon present, in which a high SUVA correlated to higher aromatic carbon. The $SUVA_{254}$ for a sample was calculated using equation 4:

$$\text{SUVA (L/mg-M)} = \frac{\text{UVA (cm}^{-1}\text{)}}{\text{DOC concentration (mg/L)}} \quad * \quad 100 \text{ (cm/M)} \quad (5)$$

In which, $UVA = \frac{A}{d}$ (5)

Where, *UVA* is the calculated UV absorbance of a sample in absorbance units (cm^{-1}), *A* is the measured UV absorbance of the sample at 254 nm and *d* is the path length of the quartz cell in cm (a path length of 1 cm was used in this study).

To calculate the $SUVA_{254}$ for a diluted sample, a dilution factor was needed prior to the final calculation. The equation to determine the dilution factor is represented by equation 6:

$$\text{Dilution Factor} = \frac{\text{Volume of diluted solution}}{\text{Aliquot of sample used in dilution}} \quad (6)$$

For example, if the dilution ratio used was 1:3 (1 mL of sample and 3 mL of DI), the total volume of diluted solution is 4 mL and the aliquot of sample used in the dilution is 1 mL. Therefore, the dilution factor is 4 mL/1 mL = 4. The dilution factor is then multiplied by the raw absorbance value at 254 nm and then the $SUVA_{254}$ calculation can proceed as normal.

3.2.4.2. Parallel Factor Analysis (PARAFAC)

The SOLO+MIA version 8.0 software created by Eigenvector Research Inc. was used to create a PARAFAC model for the Sandhill fen watershed. First, visual outliers, such as ones with abnormal scattering, were removed from the dataset. A leverage score plot was then created on Matlab using the steps outlined by Stedmon and Bro (2008) for the domFluor toolkit. A leverage score of 0.2 was selected, in which three additional outliers were identified and then subsequently removed from the dataset. A total of 200 samples from 2014 and 2015 were used for the SFW. The dataset was randomly split in two using the Kennard Stone method provided by SOLO+MIA, in which 100 samples were used to calibrate the model and 100 samples were used to validate the model. Additionally, a non-negatively constraint was applied to the dataset for all three modes as spectral parameters are typically non-negative. The model was tested for a two to five component model to determine the best number of components that described the dataset.

Once the model was built, the core consistency for both the calibration and validation datasets were analyzed to determine the appropriate number of components, where core consistency near 100% was ideal and suggested that the PARAFAC model was valid. Additionally, the percent variance for the model was also investigated to suggest how well the component model best described the dataset, in which a value greater than 99% indicated a robust model. To further validate the PARAFAC model, the data was split in half and modeled separately using the split half validation approach. If the two data splits produced the same results, the model can be assumed to be robust.

Once a PARAFAC model with the appropriate number of components was selected, the components were identified using the maximum excitation and emission wavelength (the peak excitation and emission). The peak excitation and emission for each component was then compared to the components commonly reported in the literature (Table 2.2).

3.2.5. Statistical analysis

All statistical analysis on all fluorescence indices and DOC concentration was performed in R (Version 3.2.1). Descriptive statistics including minimum, median, maximum, mean and standard deviation were calculated for all samples. A conceptual diagram of the steps taken to conduct statistical significance is summarized in Figure 3.7.

The dataset was first tested for normality using the Shapiro-Wilk test. The Shaprio-Wilk test was selected because it provides the best power for significance testing and is better at detecting a samples distribution (Steinskog et al., 2007; Thode, 2002). Additionally, kurtosis and skewness of the dataset was also conducted to assess normality (Thode, 2002). The dataset was then tested to see if the variances were homogenous. If samples were found to be normally distributed, Bartlett's Test was used, as it is more sensitive to departures from normality (Sokal and Rohlf, 1969). In contrast, if samples were not normally distributed, Levene's Test was selected because it is less sensitive to departures from normality (Levene, 1960; Gastwirth et al., 2009).

To test for statistical significance, an analysis of variance (ANOVA) was selected over multiple t-tests because it reduces the potential for an increase in type I errors. One-way ANOVAs are most commonly used to determine statistical significance in which the assumptions of normality, homogeneity and independence are met. When a dataset fails to meet the normality assumption, the one-way ANOVA is able to tolerate the violation with minimal influence on type I errors; however, if the dataset violates the assumption of homogenous variances, a one-way ANOVAs is not well suited to determine statistical significance and an alternative method, such as the Welch ANOVA, must be used. Therefore, if the dataset was normally distributed and homogeneous, the one-way ANOVA was selected. In contrast, if the dataset was either: 1) normally distributed and not homogeneous, 2) not normally distributed and homogeneous or 3) not normally distributed and not homogeneous, the Welch ANOVA was chosen. Tukey's Honestly Significant Difference (HSD) *post hoc* was chosen for samples that underwent a one-way ANOVA to determine which samples were significantly different from each other. Tukey's HSD was chosen because it is considered to be the best method for normal and homogenous datasets (Brophy, 1984). In contrast, the Games-Howell *post hoc* test was chosen for samples that had undergone a Welch ANOVA. The Games-Howell *post hoc* is often recommended when the dataset does not have homogeneous variances (Games and Howell, 1976; Toothaker, 1993; Ruxton and Beauchamp, 2008). The Welch ANOVA and subsequently the Games-Howell *post hoc*, with a confidence interval of 95% (significant if $p < 0.05$), was conducted on the entire dataset used in this study.

SECTION 4: RESULTS

4.1. Climate

The data collection period for this study was May to October in 2014 and 2015. Monthly average precipitation and air temperature for Fort McMurray, Alberta are provided in Table 4.1. Average precipitation from April to October was 353.3 mm and 221.9 mm in 2014 and 2015 respectively. Relative to the 30-year climate normal during these months (334.9 mm), 2014 was slightly wetter, whereas 2015 was considerably drier. The timing in which precipitation events occurred during the field season was different in 2014 and 2015 (Figure 4.1a). In 2014, there were three large rainfall events greater than 20 mm (May 29-41.3 mm, July 25-22.0 mm and September 26-35.7 mm) and six small rainfall events between 10 and 20 mm (May 26-16.6 mm, May 31-11.4 mm, June 21-15.1 mm, August 9-13.8 mm, August 30-10.3 mm and October 23-14.8mm). In contrast, there was only one large rainfall event (July 12-51.1 mm) and two small rainfall events (September 1-14.8 mm and September 3-12.3 mm) in 2015. Average air temperature during the study period was 10.6°C in 2014 and 11.4°C in 2015, both of which were warmer than the 30-year climate normal of 10.4°C (Table 4.1; Figure 4.1b).

4.2. Hydrologic Conditions

4.2.1. Water Table

Water table is reported as an "average" position, in which the position of each well in a location (e.g. the lowlands) was compiled as a list and the statistical average was taken.

4.2.1.1. Sandhill Fen Transects

In 2014, the highest to lowest average water table (WT) position from May to October was observed at the lowland (-0.02±0.13 m bgs), followed by the WSP (-0.44±0.15 m bgs), margin (-0.50±0.29 m bgs) and upland (-0.67±0.08 m bgs) (Table 4.2). The lowlands, margin and WSP followed the same temporal pattern, in which the WT was greatest in May and declined until August, followed by a slight increase again by October (Figure 4.2a). The upland position remained relatively constant from May to October and had minimal variation. Additionally, the margin, upland and WSP had a WT position below the ground surface (i.e. less than 0 m bgs) from May to October, whereas the lowland had an average water table position above the ground surface (i.e. greater than 0 m bgs) from May to July, then was below the ground surface from August to October (Figure 4.2a). The greatest variability was observed within the margin position, whereas the lowlands, upland and WSP had little variability.

In 2015, the highest WT was observed at the lowlands (0.01±0.14 m bgs), followed by the margin (-0.48±0.30 m bgs), WSP (-0.59±0.13 m bgs) and upland (-0.68±0.08 m bgs) (Table 4.2). All locations followed a similar trend, in which the water table was highest in May and declined until August and slightly increased by October (Figure 4.2b). Like 2014, the lowland was the only location to have a water table above the ground surface and was observed from May to July, whereas the margin, upland and WSP were all below the ground surface during the duration of the field season (Figure 4.2b).

Similar to 2014, the greatest variability in the WT was observed at the margin; however, comparing the margins between 2014 and 2015, there was less variability in 2015. Between 2014 and 2015, the lowlands consistently had the highest WT, whereas the uplands had the lowest WT. In 2015, the lowlands and margin had a slightly higher WT, whereas the upland and WSP had a slightly lower water table than what was observed in 2014.

4.2.1.2. Reclaimed and Natural Wetlands

SFW had the highest WT from May to August (0.07±0.15 m bgs), followed by PP (-0.21±0.18 m bgs) and PC (-0.22±0.08 m bgs) (Table 4.3). The WT at the reclaimed lowland was above the ground surface from May to July and was below the ground surface for the month of August. In contrast, the WT at the natural wetlands were all below the ground surface from May to August (Figure 4.3). The water table at SFW had the least variability, whereas PP had the greatest variability (Figure 4.3).

4.3. Dissolved Organic Carbon

4.3.1. Spatial and Temporal Patterns

4.3.1.1. Sandhill Fen

In 2014 and 2015, DOC concentrations varied spatially within SFW. During 2014, the highest average concentrations were observed at the lowlands, followed by the margin area, outlet and WSP (56.6±22.4 mg/L, 46.2±15.5 mg/L, 46.0±3.8 mg/L and 33.0±5.1 mg/L respectively (Table 4.4), in which the average DOC concentration at the WSP was significantly different from the DOC concentrations observed at the other positions (Figure 4.4a; Table 4.5; Table 4.6). The spatial pattern of DOC concentration in 2015 was similar to 2014; however, the average concentration at the WSP was greater than that found at the outlet. The average concentrations at the lowlands, margin, WSP and outlet were 44.8±14.6 mg/L, 42.7±19.6 mg/L, 34.9±19.4 mg/L and 29.6±4.5 mg/L respectively (Table 4.4). Unlike 2014, the DOC concentration at the lowland and outlet were significantly different from each other in 2015 (Figure 4.4b; Table 4.5; Table 4.6).

In 2014 and 2015, the same temporal patterns for DOC concentration were observed, as concentrations were lowest at the beginning of the growing season (May in 2015 and June in 2014) and then increased steadily by the end of the growing season (August). DOC concentrations continued to slowly increase by the fall (October); however, this increasing pattern was not observed in the lowlands, where concentrations decreased in October (Figure

4.5). At the beginning of the growing season, DOC concentration at the lowlands (eg. B2W3), outlet, margin (eg. TRW8) and WSP were 37.4 mg/L, 39.9 mg/L, 43.0 mg/L and 14.1 mg/L respectively in 2014, and 46.3 mg/L, 17.5 mg/L, 38.3 mg/L and 20.9 mg/L respectively in 2015 (Figure 4.5). In August, concentrations increased to 35.8 mg/L, 45.8 mg/L, 34.1 mg/L and 30.2 mg/L in 2014 and 93.2 mg/L, 32.4 mg/L, 64.9 mg/L and 35.7 mg/L in 2015 respectively (Figure 4.5). The final concentrations observed in both field seasons were 46.2 mg/L, 67.9 mg/L and 38.6 mg/L at the outlet, TRW8 and WSP in 2014 (no available October 2014 data for B3W2) and 42.9 mg/L, 34.8 mg/L, 65.4 mg/L and 62.0 mg/L in 2015 (Figure 4.5). The DOC concentration observed within the lowlands and outlet were significantly different between the 2014 and 2015 study years (Table 4.7).

4.3.1.2. Reclaimed vs. Natural Lowland-Wetlands

DOC concentrations in 2015 were significantly different among all three wetlands (Figure 4.6; Table 4.8; Table 4.9). Average DOC concentration for 2015 was greatest at the SFW lowland (44.8±14.6 mg/L), followed by PC lowland (39.6±9.7 mg/L) and lowest at the PP lowland (24.4±5.2 mg/L) (Table 4.10). Although the average concentration at each wetland was relatively similar, there was considerable spatial variation observed at the SFW lowland, unlike the more consistent pattern found at the natural lowlands (Figure 4.6; Table 4.10).

DOC concentrations at all wetlands were lowest at the beginning of the growing season and increased to a maximum by the end of the growing season (Figure 4.7). From May to August 2015, SFW increased from 23.7 mg/L to 93.2 mg/L, PC increased from 17.6 mg/L to 36.2 mg/L and PP increased from 17.6 mg/L to 36.2 mg/L.

4.4. Fluorescence Indices

4.4.1. Spatial and Temporal Pattern

4.4.1.1. Sandhill Fen

4.4.1.1.1. Fluorescence Index (FI)

Considerable variation in the FI was observed at the lowland and margin positions in 2014 and 2015, in which both positions had a combination of low and high FI values; however, the majority of the FI results in the transition area were higher than the lowland. All sampling wells in the lowlands had a FI less than 1.6 with the exception of B3W2, located at the south end of boardwalk 3 (Figure 3.2), in which FI values were greater than 1.6. The sampling wells in the margin position had a FI greater than 1.6; however, wells located near the lowlands (eg. TRW5) had a lower FI relative to wells near the uplands. In contrast, the outlet and WSP had little variation and consistently low FI for 2014 and 2015 (Figure 4.8a; Figure 4.8b).

The average FI for 2014 was greatest at the margin area (1.64 ±0.07), followed by the lowlands (1.52±0.06), outlet (1.51±0.03) and WSP (1.47±0.04). Furthermore, the FI at the margin position was significantly differently from the other positions in SFW (Figure 4.8a; Table 4.5; Table 4.6). The spatial variability among all four positions in 2015 was similar to that observed in 2014. The margins had the greatest average FI (1.63±0.06), followed by the lowlands (1.51±0.05), outlet (1.49±0.03) and WSP (1.44±0.02) (Table 4.4). In 2015, the transition sites and WSP were significantly different from each other, as were the lowlands and outlet (Figure 4.8b; Table 4.5; Table 4.6). There was no significant difference in the fluorescence index between 2014 and 2015 at any position (Table 4.6). Additionally, there was no temporal pattern change within a single study year (May to October) throughout SFW.

4.4.1.1.2. Freshness Index (β/α)

Similar to the FI spatial pattern, the β/α at the margin and lowland positions had the greatest variability in SFW, whereas the outlet and WSP had the lowest (Figure 4.8c; Figure

4.8d; Table 4.4). In 2014, the average β/α from greatest to least occurred at the WSP (0.94±0.04), margin (0.86±0.20), outlet (0.71±0.03) and lowland (0.69±0.10). Similar to 2014, β/α was greatest at the WSP (0.98±0.02), margin (0.89±0.21), lowland (0.70±0.08) and outlet (0.65±0.03) in 2015. The β/α within the lowlands and margin positions were considerably variable depending on the location of an individual sampling well in 2014 and 2015. Sampling wells in the southern lowlands approaching the margins (ie. B3W2) had the highest average β/α in both study years, whereas wells located in the central lowlands had the lowest β/α. Additionally, wells in the northern margin area located near the lowlands (ie. TRW5), had a β/α greater than the lowlands but less than wells in the south of the margin area located closer to the uplands.

The margins and WSP had significantly different β/α from the lowland and outlet in 2014 and 2015 (Figure 4.8c; Figure 4.8d; Table 4.5; Table 4.6). There was no change in the β/α at any position within SFW during the May to August field season in both study years; however, the β/α observed at the outlet was significantly different between 2014 and 2015 (Table 4.6).

4.4.1.1.3. Humification Index (HIX)

SFW had a similar spatial pattern for the HIX in 2014 and 2015 (Figure 4.8e; Figure 4.8f). In 2014, the highest average HIX was observed at the lowlands (0.84±0.08), followed by the margins (0.82±0.08), outlet (0.80±0.03) and WSP (0.59±0.01), whereas in 2015, the greatest average HIX occurred at outlet (0.86±0.01), followed by the lowlands (0.83±0.07), margins (0.79±0.10) and WSP (0.54±0.01) (Table 4.4). Although the average HIX was similar among the lowlands, outlet and margin positions, the margins and lowlands were considerably variable in both study years, whereas the outlet and WSP had little variation (Table 4.4). The margin area and lowlands had a similar HIX range; however, the majority of the lowlands had a higher HIX than the margin areas. The lowest HIX in the lowlands was observed at B1S1, located near the

WSP and the access road to SFW (Figure 3.2). Within the margin position, the HIX was greater at wells located near the lowlands and was lower in wells near the uplands.

In 2014, the HIX observed at the WSP was significantly different from the other positions within SFW (Figure 4.8e; Table 4.5; Table 4.6), whereas in 2015, the WSP and outlet had a significantly different HIX (Figure 4.8f; Table 4.5; Table 4.6). There was no change in the HIX at SFW from May to October in both years; however, between 2014 and 2015, there was significant difference in the HIX observed within the outlet (Table 4.6).

4.4.1.1.4. Specific Ultraviolet Absorbance at 254 nm (SUVA$_{254}$)

The SUVA$_{254}$ observed in SFW was similar in both 2014 and 2015 (Figure 4.8g; Figure 4.8h). The lowlands and margins had higher variability in SUVA$_{254}$, unlike the outlet and WSP, which had smaller variability (Table 4.4). Average SUVA$_{254}$ in 2014 and 2015 was greatest at the outlet (2.47±0.24, 3.11±1.21), followed by the lowlands (2.30±0.58, 2.45±0.58), margins (1.99±0.55, 1.99±1.01) and WSP (0.97±0.06, 0.94±0.14). Overall, the outlet and lowland had higher SUVA$_{254}$ compared to the margin area, which had a relatively lower SUVA$_{254}$ (Figure 4.8g; Figure 4.8h). In the central lowlands, sampling wells had higher SUVA$_{254}$ (ie. B2W7, B3S1 and B3W3) relative to wells located in the southern lowlands (ie. B3W2). The SUVA$_{254}$ observed in the northern margins (TRW5) had higher SUVA$_{254}$ than wells located in the south (TRW4). Additionally, the WSP had a considerably lower SUVA$_{254}$ in comparison to the other positions in SFW (Figure 4.8g; Figure 4.8h).

In both study years, the SUVA$_{254}$ at the WSP was significantly than the SUVA$_{254}$ at the lowlands, outlet and margins (Figure 4.8g; Figure 4.8h; Table 4.5; Table 4.6). Additionally, there was significant difference in SUVA$_{254}$ between the outlet and margin areas (Figure 4.8g;

Figure 4.8h; Table 4.5; Table 4.6). SUVA_{254} did not change at any position from May to October and there was no significant difference in SUVA_{254} between 2014 and 2015 (Table 4.6).

4.4.1.2. Reclaimed vs. Natural Lowland-Wetlands

4.4.1.2.1. Fluorescence Index (FI)

The FI was significantly different among the lowlands of all three wetlands during the 2015 field season (Figure 4.9a; Table 4.8; Table 4.9). The average FI was greatest at PP (1.56±0.02), followed by SFW (1.51±0.05) and PC (1.47 ±0.04). Although the average FI was greatest at PP, SFW had the greatest variability (Figure 4.9a; Table 4.10). The sampling locations in the central SFW lowland had FI values less than 1.6; however, B3W2, located in the southern lowlands, had FI values greater than 1.6 (Figure 3.2). In contrast, all sampling wells throughout the entire lowlands of PC and PP were less than 1.6. Additionally, there was no temporal change in the FI from May to August within the lowlands at the reclaimed and natural wetlands.

4.4.1.2.2. Freshness Index (β/α)

The β/α was significantly different among the three lowlands (Figure 4.9b; Table 4.8; Table 4.9). There was greater variation in the β/α at the reclaimed lowland compared to the two natural lowlands (Figure 4.9b; Table 4.10). During the 2015 field season, the highest average β/α was observed at SFW (0.70±0.08), followed by PP (0.59±0.02) and PC (0.45±0.01). Variability in the β/α within the SFW lowlands was observed between sampling wells in the central lowland and wells near the uplands. B3W2 had the highest β/α, whereas wells such as B3W3 and B2W7 had lower β/α. At the PC and PP lowlands, wells in the central lowland and near the uplands had relatively consistent β/α. Additionally; the freshness index did not change temporally at SFW, PC or PP lowlands during May to August.

4.4.1.2.3. Humification Index (HIX)

The reclaimed lowland had the greatest HIX variability relative to the two natural lowlands; however, between the two natural wetlands, PC was more variable than PP (Figure 4.9c; Table 4.10). Although SFW had the greatest variability, it had the lowest average HIX (0.83±0.07), whereas PP had the greatest average HIX (0.94±0.01) and PC had an average HIX of 0.89±0.03 (Table 4.10). The difference in HIX within the SFW lowland was mainly observed between B1W3, located near the WSP (Figure 3.2) and the remainder of the wells. Unlike the reclaimed lowland, the HIX did not vary between the wells located throughout the PC and PP lowlands. There was significant difference in the HIX among the three lowlands (Figure 4.9c; Table 4.8; Table 4.9). Additionally, from May to August, there was no temporal pattern change in the HIX at the SFW, PC and PP lowlands.

4.4.1.2.4. Specific Ultraviolet Absorbance at 254 nm (SUVA$_{254}$)

The reclaimed lowland had the greatest variability for SUVA$_{254}$, whereas the natural lowlands had smaller variation (Figure 4.9d; Table 4.10). Furthermore, the average SUVA$_{254}$ was greatest at PC (3.41±0.93), followed by PP (2.99±0.02) and SFW (2.45±0.58) (Table 4.10). The SUVA$_{254}$ at the majority of sampling wells in the PC and PP lowlands, were greater than the average SUVA$_{254}$ observed throughout the SFW lowlands. Within the SFW lowland, B3W2 had the lowest observed SUVA$_{254}$ among all sampling wells. For the natural lowlands, the SUVA$_{254}$ at PP was consistent among all sampling wells, whereas there was variation observed at PC. Wells located near the discharge outlet at the perimeter of PC had lower SUVA$_{254}$ relative to wells located further into the central lowland. The SUVA$_{254}$ at the reclaimed lowland was significantly different than the SUVA$_{254}$ observed at the natural lowlands; however, there was no significant difference observed in $SUVA_{254}$ between PC and PP (Figure 4.9d; Table 4.8; Table 4.9). Furthermore, there was no change $SUVA_{254}$ at SFW, PC or PP during May to August.

4.5. Parallel Factor Analysis (PARAFAC) Modeling

4.5.1. Model Validation

A three-component PARAFAC model was identified using 200 EEMs from the SFW in 2014 and 2015. The core consistency of the calibration and validation dataset was 97% and 96% respectively, which suggested that the model did not over fit the data and the correct number of components was selected. Additionally, the percent variance explained for the calibration and validation sets using the SOLO+MIA software was 96.4% and 97.8% respectively. Finally, a split-half validation test was performed to validate the model, in which the split-half validation percentage for the SOLO+MIA was 90.7%.

4.5.2. Identification of Model Components

The excitation and emission spectra for each of the three components were compared to the five most common PARAFAC components reported in the literature (Table 2.2). The first modeled component had excitation and emission peaks of <250nm and 446nm respectively and accounted for 60.94% of the dataset. According to the literature, a component with an excitation less than 260nm and an emission peak between 380nm and 480nm a defined as Peak A: UVC-Humic-like (Figure 4.10a). The excitation and emission peaks of the second component were 295nm and 374nm respectively and had a model fit of 35.65%. The excitation and emission peaks observed in component two were similar to those defined by Peak M: UVA Marine Humic-like from the literature (excitation of 290 to 325 nm and emission of 370 to 430 nm) (Figure 4.10b). The third and final component represented 3.41% of the dataset and had an excitation peak of 270nm and an emission peak of 309 nm. The third component is described as

Peak B: Protein-like Tyrosine, which has a reported excitation peak of 270nm to 280nm and an emission peak of 300 nm to 320 nm (Figure 4.10c).

Each component was present throughout the SFW; however, individual components had a higher Fmax at specific positions within the reclaimed wetland. The lowlands were dominated by components one and two depending on the location of the individual sampling well. Wells located near the centre of the lowlands had a higher Fmax for component one, whereas wells near located in closer proximity to the margin position, were dominated by component two. Therefore, sampling locations B2S1, B3S1 and B3W3 were described as UVC Humic-like (Peak A), whereas B1S1, B1W3, B2W7 and B3W2 of the lowlands were classified as UVA Marine Humic-like (Peak M). Additionally, the model described the carbon at the outlet as components one and two (Peak A and M). The margin area was dominated by component two (Peak M), with the exception of TRW9, which was dominated by component 1 (Peak A). Finally, the WSP was dominated by components two and three (Peak M and B). The WSP was the only location in the fen to have component three dominate. The complete maximum fluorescence of each component for an individual EEM (sample) is reported in Table A.1.

SECTION 5: DISCUSSION

The overall goal of reclamation is to return the landscape to equal or better functioning capability prior to mining activities (Alberta, 2014). SFW was constructed with the intent on creating a watershed that sustains biogeochemical and ecological processes and is carbon accumulating (Alberta Government, 2009). Peatlands account for approximately one third of the world's soil carbon pool (Gorham, 1991), in which peatlands comprise more than 65% of the WBP (Price et al., 2010; Vitt et al., 2000); therefore, it is important to investigate the relationship between key ecosystem processes and the carbon cycling to assess the status of reclamation. At SCL's reclaimed wetland, DOC concentration and composition were assessed in 2014 and 2015 to investigate the influence of reclamation on aqueous organic carbon and compared with two reference fens in the Fort McMurray area. DOC concentrations, fluorescence indices and PARAFAC models were used to identify carbon sources, structure and age throughout the SFW and among the wetlands.

5.1. Environmental controls on DOC concentration

DOC is a complex and heterogonous mixture of organic molecules that influence chemical, biological and physical ecosystem processes. DOC is a crucial component of the carbon balance for peatlands and for biogeochemical processes of the WBP (Moore and Dalva, 2001; Pastor et al., 2003). From a reclamation perspective, DOC concentrations and quality provide information on ecosystem function and aqueous carbon cycling throughout the system. A large number of ecosystem variables (i.e. water table depth, temperature, salinity, wetland size and vegetation) are reported to influence DOC concentrations in peatlands of the WBP (Khadka et al., 2016).

The average DOC concentrations observed throughout SFW in 2014 and 2015, as well as the two natural wetlands, are similar to concentrations observed in other peatlands (i.e. 10 mg/L to

72 mg/L) (Figure 4.4, Table 4.4) (Pastor et al., 2003; Ågren et al., 2008; Strack et al., 2008; Olefeldt et al., 2013; Khadka et al., 2016). Khadka et al. (2016) investigated DOC dynamics at PC and PP, as well as Suncor's Nikanotee Fen (CF) and a natural saline fen (SF) in 2014. The average DOC concentrations were greatest at SF (71.5 ± 7.6 mg/L), followed by PC (50.8 ± 9.2 mg/), PP (44.4 ± 7.2 mg/L) and CF (39.8 ± 3.8 mg/L). DOC concentrations observed at Suncor's CF, as well as other sites, were much lower and less variable than that observed at the lowlands of SFW in 2014 (56.6 ± 22.4 mg/L).

WT position is a strong control on DOC concentrations as different layers of the peat profile are exposed depending on the WT depth, which may increase or decrease DOC concentrations through oxidation and reduction reactions (Pastor et al., 2003). Moore and Dalva (2001) reported an increase in DOC production at locations with a high WT under anoxic conditions. When the WT is high, microbial decomposition is reduced, resulting in higher DOC concentrations, as production is greater than decomposition. The lowlands at SFW had the highest average DOC concentration and an average WT above the ground surface for the majority of the growing season (Figure 4.2, Figure 4.4). In contrast, the margins at SFW, and the lowlands at PC and PP, had lower DOC concentrations with a WT below the ground surface (Figure 4.2 – Figure 4.4, Figure 4.6). A similar pattern was observed by Khadka et al. (2016) in which the SF had the highest WT and DOC concentrations among the wetlands. Additionally, Blodau et al. (2004) and Boothroyd et al. (2015) observed an increase in DOC concentrations as WT levels declined throughout the summer. A decline in the WT allows for the oxidation of peat material, which subsequently concentrates rich DOC compounds in the water during these dry conditions (Blodau et al., 2004; Boothroyd et al., 2015). At all study sites, an increase in DOC concentrations was mirrored by a decrease in WT position from May to August (Figure 4.5,

Figure 4.7). The higher DOC concentrations at the reclaimed SFW lowland may also be attributed to the management strategies and overall design of the watershed. During the 2014 and 2015 field seasons, the pumps at SFW were off for the vast majority of the summer and there was no a "flushing" of DOC within the system, whereas the natural wetlands had a small discharge outlet that allowed for the removal of DOC (Khadka et al., 2016). Catchment outlets are common in natural wetlands in which DOC is exported out of the system; however, the design of SFW requires a constructed pump to be manually turned on to allow for the removal of water from the system. As landscape reclamation continues, SFW will be integrated into the closure landscape and a defined outlet will exist.

High levels of electrical conductivity (EC – reported as corrected for 25 ^{o}C) and sodium (Na^{+}) have potential negative implications for reclaimed wetlands in the oil sands region and may influence DOC concentrations (Trites and Bayley, 2009). A significant positive correlation between DOC and EC was observed at the lowlands, outlet and WSP ($p<0.05$); however, it was not significant at the margins ($p=0.09$) (Table 5.1). Khadka et al. (2016) observed a positive correlation between DOC and EC at all sites in 2014; however, in 2015, the correlation was not significant at PC ($p=0.13$) or PP ($p=0.53$) (Table 5.1). Khadka et al. (2016) suggested that sites with high EC provide nutrients to microbial communities, thereby enhancing microbial decomposition in these areas. Similarly, Marschner and Kalbitz (2003) suggested that areas with high EC and DOC may have increased biodegradation processes due to flocculation, in which the substrate aggregate breaks off into smaller groups. This increases the opportunity for microbes to attach to the substrate and increase decomposition of OM. Khadka et al. (2015) confirmed the relationship between EC and DOC through a lab incubation experiment, in which an increase in salinity resulted in greater DOC production. Khadka et al. (2015) concluded that

EC was a strong control on DOC concentrations at PC, PP, SF and CF. Additionally, there was a significant positive correlation between Na^+ and DOC concentrations at all locations within the SFW and at PC ($p<0.05$); however, it was not observed at PP ($p=0.23$) (Table 5.1). Biagi (2015) observed Na^+ "hotspots" at the base of the margin and upland interface at B1S1, B1W3, TRS1, TRS2, TRW2, B2S1 and WSP. These "hotspots" are areas that indicate the upward diffusion and seepage of OSPW into the lowlands of SFW. In humic organic molecules, cations such as Na^+ are able to bind with negatively charged functional groups during flocculation (Skyllberg and Magnusson, 1995). Skyllberg and Magnusson (1995) reported that the greatest amount of DOC extracted from solution occurred when Na^+ was bound to organic molecules. This suggests that the Na^+ "hotspots" in the reclaimed wetland correlate to higher DOC production. Furthermore, the EC and Na^+ at the reclaimed lowland was 1 to 2 orders of magnitude greater than the natural lowlands, which suggests that the seepage of OSPW strongly influences DOC production in the reclaimed SFW wetland.

Water temperature is a controlling factor for microbial communities, in which warmer temperatures generally increase microbial activity, thereby increasing the rate of DOC decomposition (Kalbitz et al., 2000; Stewart et al., 2010). Khadka et al. (2015) reported an increase in net DOC production at higher incubation temperatures (25°C) compared to lower temperatures (10°C) and concluded that water temperature was an important controlling variable for DOC decomposition. As temperatures increased during the summer and decreased in the fall, DOC concentrations followed a similar pattern; however, the pattern was found to not be significant and did not match the laboratory findings observed by Khadka et al. (2015). Eimers et al. (2008) determined for wetland catchments in Ontario that changes in the WT position was more influential than water temperature on DOC concentrations.

Several studies have shown that DOC concentrations increase as the relative proportion of wetland in a watershed increases (Koprivnjak and Moore, 1992; Eimers et al., 2008; Laudon et al., 2011). Khadka et al. (2016) suggested that greater wetland area contributed to higher DOC concentrations observed at PC; however, in this study, the SFW lowlands were much smaller (an area of approximately 17 hectares) than the natural lowlands yet had the greatest DOC concentrations. This suggests that at the reclaimed lowland, there are additional variables that influenced the observed DOC concentrations. Khadka et al. (2016) also investigated the influence of peat depth on DOC concentrations and observed that more peat volume resulted in greater DOC production at the natural wetlands. This was also observed at PC and PP, in which the average peat depth at PC is approximately 4 m, whereas it is approximately 1.5 m at PP. However, the reclaimed SFW lowland had the highest average DOC concentration, yet only 0.5 m of the soil profile was peat. DOC has quick adsorption and desorption reactions with the surface of non-decomposed peat (Pastor et al., 2003) resulting in higher DOC concentrations, whereas mineral soils have a strong adsorption affinity for DOC (Macrae et al., 2005), suggesting lower concentrations. As peat is only located within the lowlands of SFW, and a mineral-peat mixture was used throughout the fen (with the exception of the top of the hummocks), the higher DOC concentrations at the lowlands relative to the margins may be attributed to the presence of strictly peat material.

The presence of terrestrial vegetation influences DOC concentrations as increases in primary productivity result in greater DOC production (Freeman et al., 2004). At the SFW lowlands, the vegetation is dominated by sedges and is more dense and rich in vegetation than the surrounding margins and WSP (Vitt et al., 2016). At the natural lowlands, PC was dominated by *Sphagnum* moss species, whereas brown mosses and sedges dominated PP. Moore (2009) reported that the poor nutrient status of *Sphagnum* decreased the rate of organic matter decomposition by microbes and resulted in peat accumulation. Additionally, Khadka et al. (2016) suggested that moss species were more structurally complex than sedges and therefore were more difficult to decompose resulting in higher DOC production. This pattern was observed when comparing the two natural wetlands as higher DOC concentrations were observed at the nutrient-poor, *Sphagnum* dominated wetland and lower DOC concentrations were observed at the nutrient-rich, sedge dominated wetland.

5.2. Characterization of DOC composition

In Chapter 4, the lowlands, outlet and WSP at SFW, as well as the lowlands at PC and PP, had an average FI < 1.6, whereas the margins had a FI > 1.6 (Figure 4.8, Figure 4.9). McKnight et al. (2001) applied the FI on known terrestrially- and microbially-derived end members and reported that water bodies dominated by terrestrial vegetation and SOM had an average FI of approximately 1.4, indicating the carbon source was terrestrially-derived. In contrast, those dominated by microbial and algal communities with sparse terrestrial vegetation had an average FI of approximately 1.9 and suggested a microbially-derived carbon source. The FI observed in this study was similar to those observed by McKnight et al. (2001), in which the carbon in the reclaimed and natural lowlands, WSP and outlet were derived from living, higher plant material, whereas the carbon at the margins was derived from microbial decomposition organic matter.

The freshness index (β/α) at the reclaimed SFW lowland was higher than at the natural lowlands (Figure 4.9); however, within the reclaimed wetland, the lowland had low β/α in comparison to the margin and WSP locations (Figure 4.8) suggesting that the DOC at lowlands was older compared with more recently produced DOC at the margins. Wilson and Xenopoulos (2009) observed high β/α in areas with higher autochthonous carbon production, as well as in areas with increasing cropland coverage. Among the reclaimed and natural lowlands, the higher β/α at the reclaimed lowland suggests that the carbon was newer than the natural lowlands; however, this may be attributed to the age of the actual wetlands themselves. The construction of SFW was complete in 2012 and the peat used in the construction process was obtained from a nearby previously drained peatland. The peat was stockpiled and along with prior drainage, would have undergone oxidation, reducing the organic carbon content. Additionally, the vegetation at SFW is young; therefore DOC is newly produced, whereas the vegetation at the natural wetlands is well established suggesting that the DOC is older (Khadka et al., 2016).

The average humification index (HIX) was relatively high at the lowlands, outlet and margins at SFW, which indicated a higher degree of humification; however, the WSP and some wells within the marginal area had a much lower HIX indicating the carbon had a low degree of humification (Figure 4.8). The natural lowlands had very high HIX and therefore high humic content, whereas the reclaimed lowland a relatively lower HIX (Figure 4.9). Huguet et al. (2009) observed high humification in areas with low autotrophic productivity and highly decomposed organic matter and low humification in areas marine waters with high autotrophic productivity. Additionally, Wickland et al. (2007) found that high HIX observed in Alaskan Boreal Forests correlated to highly humified organic matter. Fresh lake water is supplied from Mildred Lake to the WSP and has a low HIX as it does not interact with the groundwater system at SFW due to the heavy compact clay liner; therefore, any traces of humified content may be attributed to interactions between water and organic matter externally. Among the reclaimed and natural lowlands, the high variability observed at the reclaimed lowland is due to the influence of the margin and upland areas, whereas the low variability at PP and PC were likely attributed to the rich and poor fen-like characteristics of the wetlands.

The average $SUVA_{254}$ at the lowland and outlet were greater than the margins, and significantly greater than the WSP (Figure 4.8). This suggests that the lowlands and outlet have higher aromaticity and molecular weight, whereas the WSP had low aromatic content and molecular weight. Among the reclaimed and natural lowlands, $SUVA_{254}$ was greater at PC and PP indicating that the carbon had higher aromaticity and molecular weight in comparison to SFW (Figure 4.9). Ågren et al. (2008) observed high $SUVA_{254}$ in wetland-dominated streams and low $SUVA_{254}$ in forested [upland] streams, indicating that the high aromaticity and molecular weight at wetland streams was more difficult for microbial decomposition than the lower aromatic and small molecular weight carbon compounds found in upland streams.

PARAFAC modeling was used in this study to supplement and further characterize DOC composition within the SFW (Stedmon and Bro, 2008). Component 1 was within the maximum excitation and emission range reported in the literature (Table 5.2) and was characterized as Peak A: UVC Humic-like (Table 2.2). Stedmon and Markager (2005) observed that this component was greatest in wetlands and was the dominant component in DOC exported from natural catchments. Additionally, Cory and McKnight (2005) reported that the fluorophore associated with this carbon component was likely oxidized. At SFW, peat used in the construction of the lowlands was extracted from a previously drained peatland and stockpiled. The peat may have been oxidized suggesting why the carbon at the lowlands was dominated by component 1. Component 2 had a similar excitation and emission maxima to Peak M: UVA Marine Humic-like (Table 5.2, Table 2.2). Although this component is most commonly found in marine systems, Stedmon and Markager (2005) observed this component in wastewaters and attributed the terrestrial humic component to anthropogenic origins. Component 2 was mostly dominant in the marginal transition areas of SFW, particularly around the boundary between the margin and upland hummocks. This location of SFW is characterized by the fluorescence indices as being associated with microbial activity, which may suggest why component 2 was dominant at this location. Component 3 had excitation and emission maxima similar to that observed in Peak B: Protein-like Tyrosine-like (Table 5.2, Table 2.2). Stedmon and Markager (2005) indicate that carbon characterized by peak B was correlated to terrestrial fluorescent material found in forested [upland] catchments and was derived from microbial processes. Component 3 was only found to be dominant at the WSP, suggesting the origin of the carbon is biological; however, the low FI observed at the WSP suggests the carbon is terrestrially-derived. Tyrosine-like compounds are not present in their pure form; therefore, the fluorescence properties only resemble the pure reference standard of the amino acid (Reynolds, 2003; Stedmon et al., 2003; Yamashita and Tanoue, 2003; Baker and Inverarity, 2004; Cory and McKnight, 2005). The fluorescing group of tyrosine is a simple phenol group, which is associated with higher plant material and although tyrosine is an amino acid, it may be considered a phenol from a fluorescence perspective (Aiken, 2014) and explain the discrepancy in suggested carbon source.

5.3. Influence of reclamation on DOC dynamics

The use of DOC concentration, fluorescence spectroscopy and PARAFAC modeling at SFW provides insight into DOC characteristics within the watershed such as where the carbon is coming from, where it may end up and its structural complexity, as well as it allows for an understanding if the wetland is functioning similarly to natural systems in the WBP from an aqueous carbon perspective. Also, it is important to note that each PARAFAC component is present at each individual sampling location; however, the maximum fluorescence of a component (i.e. which component is more dominant) is different.

The lowlands (more specifically B3W3, B3W4, B3S1 and B2S1), the outlet and TRW9 were dominated by component 1 (Figure 5.1). At these locations, the PARAFAC model and fluorescence indices describe the carbon composition similarly (Table 5.3). Furthermore, the DOC concentrations observed at these locations are relatively greater than other locations in SFW. The lowlands had a persistently high WT for the majority of the field season, lower water temperatures, rich vegetative species and 0.5 m of peat. Peat and dense vegetation are known to have high humic content and complex molecular structures; therefore, the presumed decomposition of rich vegetative species and peat material reflect the high aromaticity and humification observed at the lowlands. The contribution of the high water table and lower water temperatures promotes terrestrial DOC production rather than microbial decomposition and indicates a terrestrially-derived carbon source as described by the indices and PARAFAC model. B1S1, B1W3, B2W7 and B3W2 of the lowlands, the margin, outlet and WSP are all dominated by component 2 (Figure 5.1). At the marginal areas, the results from the fluorescence indices were similar to what was observed by the PARAFAC model (Table 5.3) and the DOC concentration was slightly lower than the lowlands; however the difference was not significant. The margins had a combination of a lower WT, warmer water temperatures, less dense vegetation (dominated by sedges), a mineral-peat soil mixture and high EC and Na^+ concentrations (section 5.1) which are optimal conditions for microbial DOC decomposition and explain the biological origin of DOC suggested by the fluorescence indices and PARAFAC model. Additionally, the low humification, aromaticity and molecular weight can be explained by the low humic content in the mineral-peat soil mix and the easier decomposition of sedge species. At these areas, it appears that microbial DOC decomposition is greater than net DOC production.

The WSP was the only location dominated by component 3 (Protein-like Tyrosine-like). The tyrosine-like component and FI suggest different carbon sources at the WSP in which the model indicates biological activity, whereas the FI suggests a terrestrial source (Table 5.3). The observed concentration, humification and aromaticity of DOC at the WSP are likely due to the lack of interaction with the fen, suggesting that any influence from vegetation and peat sources observed at the WSP are likely due to biogeochemical processes that occurred at Mildred Lake, not SFW.

Of the seven potential Na^+ "hotspots" identified at SFW in 2014 by Biagi (2015), B2S1 was dominated by component 1, whereas the other sites were dominated by component 2 (and component 3 at the WSP only). There was a significant positive correlation between DOC and Na^+ concentrations at B1S1, TRS1, B2S1 and WSP. Biagi (2015) suggested that B1S1 and TRS1 were influenced by the seepage and advection of OSPW from hummocks 2 and 7, whereas, the WSP was isolated from the groundwater flow system and the Na^+ concentrated as evaporation occurred and B2S1 was a Na^+ "hotspots" because it was hydrologically connected to other Na^+ "hotspots". The high Na^+ concentrations allows for an increase in DOC solubility at these Na^+ "hotspots", which may increase DOC production. At B2S1, the influence of Na^+ combined with the indices and PARAFAC results suggest that the DOC production is due to terrestrial vegetation, whereas at B1S1, TRS1 and B3W2, DOC was influenced by microbial activity.

When the results from DOC concentration, fluorescence indices and PARAFAC analysis are mapped, a "transition zone" emerges between the lowlands and margins on the southern portion of the fen (Figure 5.2). This transition zone refers to a change in carbon characteristics between the two locations, in which carbon in the lowlands changes from old, terrestrially-derived with high aromatic carbon, molecular weight and humic compounds to newly produced, microbially-derived with lower aromatic carbon, molecular weight and humic compounds. A transition zone was not observed at sampling locations near the margins at the natural wetlands and suggests that previous mining activities and reclamation techniques have produced complex biogeochemical processes at SFW.

Overall, the carbon dynamics at the reclaimed wetland are generally different than what was observed in the two natural wetlands investigated in this study. SFW is a constructed wetland, in which the reclamation design and construction process has strongly influenced the observed DOC concentration and composition. The controlling factors on DOC (i.e. water table depth, water temperature, salinity, peat depth and vegetation) reported in the literature apply well to the DOC patterns observed at the natural wetlands; however, Na^+ concentrations and EC are orders of magnitude greater an the WT is very high at SFW. This suggests that reclamation efforts at SFW have influenced DOC dynamics at present time; however, since SFW is relatively young, the observations made for the 2014-2015 field season do not necessarily indicate what the DOC patterns will be in the future, as well as its future impact on carbon cycling at SFW.

5.4. Potential implications and future research

There are several challenges associated with wetland reclamation in the WBP including the potential for salinization (Trites and Bayley, 2009), the sub-humid climate (Devito et al., 2012b) and peatlands can take upwards of thousands of years to develop. DOC concentrations and composition may be negatively affected if salinity and Na^+ concentrations continue to increase because the upward diffusion of OSPW may stress vegetation and decrease primary production, thereby changing DOC production. An increase in temperature due to a warming climate enhances microbial activity and may result in enhanced decomposition and reduced primary production. Additionally DOC decomposition will increase as EC continues to increase considerably in the upcoming years and will result considerable amounts of aqueous carbon exported from the system. Therefore, it is important to investigate DOC export within the SFW to quantify how much carbon is lost as DOC and how DOC export would impact the systems overall carbon balance. Additional DOC samples are needed from SFW, PC and PP to continue to build a library of EEMs for future PARAFAC modeling of each wetland. More EEM's will enhance the quality of the model and will detect any changes in carbon composition within the wetlands in the future. Finally, it is crucial to investigate the influence of the 2016 Fort McMurray wildfire on DOC dynamics in the reclaimed and natural systems and determine if there are any changes in DOC concentration and quality and how it will affect decomposition and production rates.

SECTION 6: SUMMARY AND CONCLUSIONS

Mining in the oil sands region has destroyed a significant area of the WBP affecting the natural ecosystem functions of forests and wetlands. The recent focus on wetland reclamation aims to construct wetlands that mimic ecological and environmental processes similar to the previously existing system. This study identified DOC concentration and quality of a reclaimed watershed and two natural wetlands in the Fort McMurray, Alberta area over the 2014 and 2015 study period. DOC is an important component of natural peatland carbon balances; therefore, it is crucial to understand where the carbon is derived, what are the specific properties of the organic molecules, what environmental controls influence the rate of DOC production and decomposition, where will the carbon go and how much will be lost from the system. To assess the current status of reclamation efforts from a carbon perspective, it is valuable to investigate and understand DOC dynamics observed in natural wetlands and compare it to those observed in previously disturbed systems.

The objective of this study was to characterize DOC concentration and composition of a reclaimed wetland and compare observations to natural peatlands in the oil sands region. Based on the results from this study, key findings and conclusions can be made for DOC concentration and composition at SFW, PC and PP:

1) Results suggested by the 3-component PARAFAC model and fluorescence indices (i.e. FI, β/α, HIX and $SUVA_{254}$) suggest the presence of a "transition zone" at SFW between the lowlands and margins, in which carbon composition changes from terrestrially-derived source, high aromaticity and high humification to microbially-derived, low aromaticity and low humification respectively.

2) At SFW, DOC concentrations were greatest at the lowlands and decreased upslope. The reclaimed wetland had considerable variability and the highest average DOC concentration in comparison to the two natural wetlands.
3) The observed DOC concentrations at SFW is strongly controlled by WT position, Na^+ concentration and EC, in which the WT was very high and Na^+ and EC were orders of magnitude greater than the natural wetlands. In contrast, DOC at the natural wetlands was influenced by controls such as vegetation species, peat depth and relative proportional wetland size in a catchment.
4) DOC concentration and composition at SFW had great spatial variability, whereas the DOC patterns at PC and PP had a more uniform distribution.

Results from this study suggest that although the dissolved organic carbon at the natural wetlands was characterized similarly to that observed at the reclaimed wetland, DOC was more variable at the reclaimed wetland and the primary environmental controls were different. Therefore, the DOC at the reclaimed SFW wetland is strongly influenced by previous mining practices and reclamation efforts and currently is not similar to natural wetlands in the oil sands region.

To date, there are no certified reclaimed wetlands in the oil sands region. The current preliminary findings indicate that DOC patterns at the reclaimed wetland are not identical to natural wetlands; however, it is possible that DOC dynamics at SFW may function similarly to natural wetlands in the Fort McMurray area in the future. Understanding carbon source, how much is produced and decomposed and how much DOC is exported from the system will help assess the future success of SFW, as well as for wetland reclamation projects in the upcoming years by providing contextual comparison with natural sites and allow an improved understanding how biogeochemical and carbon cycling processes re proceeding. Although there is a considerable amount of information required to successfully design and construct a wetland system in the oil sands region, results from this study provide necessary baseline data for future wetland reclamation projects.

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TABLES

Table 2.1. Common groups of organic fluorophores reported in the literature.

Fluorophore "type"	**Fluorophore Functional Group**	**Fluorophore Compound**	**Description**
Protein-like	Phenol	Tyrosine-like**	• Amino acid • Bound to a protein or free • Excitation: 270-275 nm • Emission: 305-315 nm • Associated with higher degraded peptide bonds and biological activity • Resembles pure tyrosine
Protein-like	Indole	Tryptophan-like	• Amino Acid • Bound to a protein or free • Excitation: 270-280 nm (<240 nm) • Emission: 330-368 nm • Associated with poorly degraded peptide bonds and biological activity • Resembles pure tryptophan
Humic-like	Phenol	Tannin	• Produced by higher plant material • Terrestrially-derived source of carbon
Humic-like		Lignin	• Highly observed in terrestrially-derived DOM environments • Most abundant source of aromatic compounds

Note: The fluorophore group of tyrosine if a phenol functional group, and although is classified as an amino acid, can be considered a phenol from a fluorescence perspective (Aiken, 2014)

Table 2.2. Summary of the five most common components observed in the literature for PARAFAC analysis.

Component Label	Name	Description	Excitation Maxima (nm)	Emission Maxima (nm)
A	Humic-like	• UVC humic-like • High molecular weight • High aromaticity • High humification • Associated with higher plant material • Dominant in wetlands and forests (widely distributed)	<260	380-480
C	Humic-like	• UVC (visible) humic-like • High molecular weight • High humification • Not aromatic • Dominant in wetlands and forests (widely distributed)	320-360	420-480
M	Marine humic-like	• Ultraviolet A (UVA) Humic-like • Low molecular weight • Low humification • Found in marine waters (although has been observed in non-marine waters such as wetlands and wastewaters) • Associated with biological activity	290-325	370-430
B	Tyrosine-like	• Protein-like • Amino acid (can be free or bound in proteins) • May suggest a mode degraded peptide molecules	270-280	300-320
T	Tryptophan-like	• Protein-like • Amino acid (can be free or bound in proteins) • May suggest intact or less degraded peptide molecules	270-280	320-360

Table 4.1. Precipitation and Air Temperature data for the 2014 and 2015 field seasons and the climate normal for Fort McMurray.

Month	**Precipitation (mm)**			**Air Temperature (^oC)**		
	2014	**2015**	**CN**	**2014**	**2015**	**CN**
April	19.2	4.9	21.4	0.9	4.5	3.4 ± 2.6
May	82.9	17.7	36.5	7.9	9.9	9.9 ± 1.8
June	68.7	20.5	73.3	15.3	16.0	14.6 ± 1.0
July	55.7	99.7	80.7	18.8	17.8	17.1 ± 1.0
August	36.3	31.3	57.1	17.0	16.6	15.4 ± 1.8
September	62.8	36.1	39.7	9.4	8.5	9.4 ± 1.8
October	30.3	11.7	26.2	5.2	5.6	2.8 ± 1.8
Total	353.3	221.9	334.9	N/A	N/A	N/A
Average	51.0	31.7	47.8	10.6	11.4	10.4

Table 4.2. Average water table position throughout SFW from May to October in 2014 and 2015.

2014						
Position	**Month**	**Min.**	**Median**	**Max.**	**Mean**	**St. Dev.**
Lowland	May	0.07	0.09	0.11	0.09	0.03
	June	0.03	0.14	0.21	0.13	0.09
	July	-0.09	-0.01	0.07	-0.01	0.08
	August	-0.22	-0.14	-0.07	-0.14	0.07
	September	-0.26	-0.04	-0.01	-0.11	0.14
	October	-0.22	0.04	0.04	-0.04	0.15
	Overall	**-0.26**	**-0.01**	**0.21**	**-0.02**	**0.13**
Margin	May	-0.83	-0.33	-0.05	-0.37	0.34
	June	-0.87	-0.26	0.05	-0.35	0.29
	July	-1.07	-0.52	-0.12	-0.54	0.29
	August	-1.10	-0.58	-0.29	-0.62	0.26
	September	-1.09	-0.52	-0.21	-0.56	0.28
	October	-1.08	-0.40	-0.15	-0.51	0.30
	Overall	**-1.10**	**-0.51**	**0.05**	**-0.50**	**0.29**
Upland	May	N/A	N/A	N/A	N/A	N/A
	June	-0.65	-0.62	-0.59	-0.62	0.05
	July	-0.74	-0.67	-0.60	-0.6	0.10
	August	-0.77	-0.69	-0.60	-0.69	0.12
	September	-0.77	-0.68	-0.59	-0.68	0.13
	October	-0.77	-0.68	-0.60	-0.68	0.12
	Overall	**-0.77**	**-0.63**	**-0.59**	**-0.67**	**0.08**
WSP	May	N/A	N/A	N/A	N/A	N/A
	June	N/A	N/A	N/A	N/A	N/A
	July	N/A	N/A	N/A	N/A	N/A
	August	N/A	N/A	N/A	N/A	N/A
	September	N/A	N/A	N/A	N/A	N/A
	October	N/A	N/A	N/A	N/A	N/A
	Overall	**-0.57**	**-0.50**	**-0.24**	**-0.44**	**0.15**
2015						
Position	**Month**	**Min.**	**Median**	**Max.**	**Mean**	**St. Dev.**
Lowland	May	0.22	0.25	0.30	0.26	0.04
	June	0.05	0.10	0.15	0.10	0.05
	July	-0.08	0.04	0.05	0.00	0.07
	August	-0.12	-0.11	-0.08	-0.10	0.02
	September	-0.15	-0.02	-0.01	-0.06	0.08
	October	-0.20	-0.08	-0.05	-0.11	0.08
	Overall	**-0.20**	**-0.02**	**0.30**	**0.01**	**0.14**
Margin	May	-0.92	-0.30	0.19	-0.29	0.34
	June	-0.78	-0.56	-0.24	-0.544	0.20
	July	-1.10	-0.53	-0.07	-0.54	0.34
	August	-0.78	-0.56	-0.24	-0.54	0.20

	September	-0.73	-0.46	-0.17	-0.46	0.23
	October	-1.10	-0.57	-0.23	-0.59	0.28
	Overall	**-1.10**	**-0.48**	**0.19**	**-0.48**	**0.30**
Upland	May	-0.73	-0.66	-0.59	-0.66	0.10
	June	-0.75	-0.68	-0.61	-0.68	0.10
	July	N/A	N/A	N/A	N/A	N/A
	August	N/A	N/A	N/A	N/A	N/A
	September	N/A	N/A	N/A	N/A	N/A
	October	-0.74	-0.65	-0.57	-0.65	0.12
	Overall	**-0.77**	**-0.73**	**-0.57**	**-0.68**	**0.08**
WSP	May	N/A	N/A	N/A	N/A	N/A
	June	N/A	N/A	N/A	N/A	N/A
	July	N/A	N/A	N/A	N/A	N/A
	August	N/A	N/A	N/A	N/A	N/A
	September	N/A	N/A	N/A	N/A	N/A
	October	N/A	N/A	N/A	N/A	N/A
	Overall	**-0.71**	**-0.64**	**-0.37**	**-0.59**	**0.13**

Table 4.3. Average water table position for SFW, PC and PP during the 2015 field season.

Wetland	**Month**	**Min.**	**Median**	**Max.**	**Mean**	**St. Dev.**
Sandhill Fen	May	0.23	0.26	0.32	0.27	0.04
	June	0.01	0.10	0.15	0.09	0.07
	July	-0.07	0.05	0.08	0.02	0.08
	August	-0.16	-0.10	-0.04	-0.10	0.06
	Overall	**-0.17**	**0.06**	**0.32**	**0.07**	**0.15**
Pauciflora Fen	May	-0.28	-0.14	-0.10	-0.15	0.07
	June	-0.30	-0.19	-0.10	-0.20	0.08
	July	-0.33	-0.26	-0.20	-0.26	0.06
	August	-0.38	-0.26	-0.18	-0.27	0.08
	Overall	**-0.38**	**-0.22**	**-0.10**	**-0.22**	**0.08**
Poplar Fen	May	N/A	N/A	N/A	N/A	N/A
	June	-0.37	-0.09	-0.01	-0.15	0.16
	July	-0.37	-0.11	0.02	-0.17	0.16
	August	-0.55	-0.28	-0.07	-0.31	0.20
	Overall	**-0.55**	**-0.14**	**0.02**	**-0.21**	**0.18**

Table 4.4. Descriptive statistics for DOC concentration and fluorescence indices for SFW in 2014 and 2015.

Year	**Test**	**Position**	**Min.**	**Median**	**Max.**	**Mean**	**St. Dev.**	**25%**	**75%**
2014	*DOC*	Lowland	30.2	52.3	124.6	56.6	22.4	41.7	61.8
		Outlet	39.7	46.0	51.5	46.0	3.8	45.8	46.8
		Margin	21.6	41.3	86.9	46.2	15.5	35.5	55.1
		WSP	26.8	31.5	38.6	33.0	5.1		
	FI	Lowland	1.51	1.51	1.66	1.52	0.06	1.48	1.54
		Outlet	1.48	1.50	1.55	1.51	0.03	1.49	1.52
		Margin	1.50	1.66	1.82	1.64	0.07	1.60	1.67
		WSP	1.43	1.45	1.51	1.47	0.04	1.44	1.50
	β/α	Lowland	0.58	0.64	0.97	0.69	0.10	0.63	0.76
		Outlet	0.67	0.70	0.76	0.71	0.03	0.69	0.73
		Margin	0.54	0.81	1.40	0.86	0.20	0.72	0.98
		WSP	0.90	0.92	0.99	0.94	0.04	0.91	0.97
	HIX	Lowland	0.57	0.87	0.93	0.84	0.08	0.83	0.88
		Outlet	0.74	0.82	0.82	0.80	0.03	0.80	0.82
		Margin	0.61	0.85	0.92	0.92	0.08	0.76	0.87
		WSP	0.57	0.59	0.61	0.59	0.01	0.57	0.59
	SUVA	Lowland	0.60	2.39	3.46	2.30	0.58	1.98	2.62
		Outlet	2.16	2.48	2.76	2.47	0.24	2.29	2.63
		Margin	1.17	1.88	3.67	1.99	0.55	1.60	2.14
		WSP	0.91	0.98	1.05	0.97	0.06	0.92	1.00
2015	*DOC*	Lowland	23.7	41.4	93.2	44.8	14.6	34.5	50.7
		Outlet	17.5	30.8	34.8	29.6	4.5	29.9	31.5
		Margin	7.3	42.5	96.0	43.9	19.6	36.6	50.8
		WSP	20.9	28.4	62.0	34.9	19.4	21.0	42.3
	FI	Lowland	1.45	1.50	1.70	1.51	0.05	1.48	1.52
		Outlet	1.44	1.48	1.55	1.49	0.03	1.47	1.49

		Margin	1.48	1.64	1.74	1.63	0.06	1.60	1.68
		WSP	1.40	1.44	1.45	1.44	0.02	1.44	1.45
	β/α	Lowland	0.57	0.65	0.90	0.70	0.08	0.63	0.75
		Outlet	0.62	0.64	0.73	0.65	0.03	0.63	0.67
		Margin	0.56	0.84	1.29	0.89	0.21	0.75	1.04
		WSP	0.94	0.99	1.00	0.98	0.02	0.98	0.99
	HIX	Lowland	0.68	0.86	0.92	0.93	0.07	0.79	0.87
		Outlet	0.84	0.87	0.88	0.86	0.01	0.85	0.87
		Margin	0.55	0.81	0.92	0.79	0.10	0.72	0.86
		WSP	0.52	0.53	0.55	0.54	0.01	0.53	0.55
	SUVA	Lowland	0.79	2.60	3.60	2.45	0.58	1.98	2.84
		Outlet	2.11	2.83	7.05	3.10	1.21	2.77	2.90
		Margin	0.27	1.99	4.84	2.01	1.01	1.53	2.20
		WSP	0.73	1.01	1.01	0.94	0.14	0.93	1.01

Table 4.5. Significance statistics for DOC concentration and fluorescence indices for SFW in 2014 and 2015. Cells highlighted in yellow indicate statistical significance ($p < 0.05$).

Year	Test	Position	Shapiro	Skewness	Kurtosis	Levene	Barlett	One-Way ANOVA	Welch ANOVA
2014	*DOC*	Lowland	**3.81E-4**	1.40	4.58	**0.04**	N/A	N/A	**1.06E-4**
		Outlet	0.33	-0.34	2.96				
		Margin	**0.01**	0.87	3.12				
		WSP	0.47	0.06	1.44				
	FI	Lowland	**4.76E-4**	1.07	3.25	0.41	N/A	N/A	**4.77E-7**
		Outlet	0.40	0.85	2.50				
		Margin	0.08	-0.12	3.34				
		WSP	0.16	0.32	1.25				
	β/α	Lowland	**4.24E-5**	1.10	3.19	**3.32E-3**	N/A	N/A	**5.46E-9**
		Outlet	0.86	0.46	2.08				
		Margin	**0.03**	0.82	3.39				
		WSP	0.28	0.47	1.49				
	HIX	Lowland	**2.52E-6**	-1.78	5.72	0.20	N/A	N/A	**4.78E-15**
		Outlet	**9.98E-3**	-1.47	3.54				
		Margin	**1.70E-3**	-0.95	2.90				
		WSP	0.38	0.10	1.60				
	SUVA	Lowland	0.30	-0.70	3.88	0.12	N/A	N/A	**3.86E-14**
		Outlet	0.68	-0.06	1.49				
		Margin	**3.40E-3**	1.17	4.06				
		WSP	0.59	0.21	1.66				
2015	*DOC*	Lowland	**1.74E-4**	1.27	4.46	0.07	N/A	N/A	**9.06E-4**
		Outlet	**3.25E-3**	-1.70	5.16				
		Margin	0.19	0.51	3.45				
		WSP	0.19	0.77	1.95				
	FI	Lowland	**4.10E-8**	2.02	6.97	0.08	N/A	N/A	**9.01E-11**
		Outlet	0.18	0.71	2.89				
		Margin	0.15	-0.67	3.10				
		WSP	0.10	-1.20	2.88				

	β/α	Lowland	**1.91E-6**	0.83	2.25	**1.57E-4**	N/A	N/A	**2.20E-16**
		Outlet	**8.58E-3**	1.66	5.57				
		Margin	0.09	0.50	2.25				
		WSP	0.28	-1.02	2.68				
	HIX	Lowland	**5.34E-7**	-0.98	2.45	0.08	N/A	N/A	**3.16E-7**
		Outlet	**0.04**	-0.85	2.43				
		Margin	**0.04**	-0.72	2.59				
		WSP	0.45	0.22	1.39				
	SUVA	Lowland	0.04	-0.62	3.06	0.19	N/A	N/A	**9.06E-4**
		Outlet	**4.95E-6**	2.98	10.42				
		Margin	**0.02**	1.08	4.47				
		WSP	**3.27E-3**	-1.15	2.33				

Table 4.6. The Games-Howell *post-hoc* statistical significance for SFW in 2014 and 2015. Cells highlighted in yellow represent statistical significance ($p < 0.05$).

Year	**Position**	**DOC**	**FI**	**β/α**	**HIX**	**SUVA**
2014	*Lowland-Outlet*	5.87E-2	7.714E-1	7.015E-1	2.01E-1	6.32E-1
	Lowland-Margin	1.56E-1	**0.00E+0**	**2.77E-4**	7.83E-1	1.46E-1
	Lowland-WSP	**4.49E-5**	1.14E-1	**1.40E-6**	**0.00E+0**	**0.00E+0**
	Outlet-Margin	9.91E-1	**1.79E-6**	**2.17E-3**	7.00E-1	**1.69E-2**
	Outlet-WSP	**7.80E-3**	3.04E-1	**3.39E-5**	**5.94E-6**	**3.40E-5**
	Margin-WSP	**4.08E-3**	**2.81E-4**	**3.57E-2**	**0.00E+0**	**5.39E-5**
2015	*Lowland-Outlet*	**9.76E-8**	8.67E-2	**4.61E-3**	**6.66E-3**	2.77E-1
	Lowland-Margin	9.44E-1	**2.57E-11**	**1.32E-3**	7.10E-1	1.22E-1
	Lowland-WSP	7.60E-1	**3.35E-4**	**3.07E-12**	**0.00E+0**	**3.50E-9**
	Outlet-Margin	5.44E-2	**7.04E-12**	**6.75E-5**	**3.57E-2**	**3.34E-2**
	Outlet-WSP	9.42E-1	**1.07E-2**	**2.13E-9**	**0.00E+0**	**1.36E-4**
	Margin-WSP	9.02E-1	**3.66E-10**	1.13E-1	**4.41E-12**	**1.32E-3**

Table 4.7. Statistical significance at SFW between the two study years (2014 and 2015). Cells highlighted in yellow represent statistical significance ($p < 0.05$).

Test	**Position**	**Year**	**Shapiro**	**Levene**	**Bartlett**	**One-way ANOVA**	**Welch ANOVA**
Lowland	*DOC*	2014	**3.81E-4**	N/A	**4.19E-3**	N/A	**7.40E-3**
		2015	**4.10E-8**				
	FI	2014	**4.24E-5**	N/A	0.42	N/A	0.59
		2015	**1.91E-6**				
	β/α	2014	**2.52E-6**	N/A	0.50	N/A	0.68
		2015	**5.34E-7**				
	HIX	2014	0.2952	N/A	0.99	N/A	0.39
		2015	**3.94E-2**				
	SUVA	2014	**9.81E-4**	N/A		N/A	0.23
		2015	**1.74E-4**				
Outlet	*DOC*	2014	3.26E-1	N/A	0.65	N/A	**3.15E-6**
		2015	**3.25E-3**				
	FI	2014	4.01E-1	0.91	N/A	0.20	N/A
		2015	1.76E-1				
	β/α	2014	8.59E-1	N/A	0.78	N/A	**3.13E-3**
		2015	**8.58E-3**				
	HIX	2014	**9.98E-3**	N/A	**0.02**	N/A	**6.00E-3**
		2015	**3.90E-2**				
	SUVA	2014	0.68	N/A	**1.66E-3**	N/A	0.09
		2015	**4.95E-6**				
Margin	*DOC*	2014	**1.14E-2**	N/A	0.16	N/A	0.45
		2015	7.59E-2				
	FI	2014	7.99E-2	0.75	N/A	0.67	N/A
		2015	1.45E-1				
	β/α	2014	**2.89E-2**	N/A	0.95	N/A	0.38
		2015	9.27E-2				
	HIX	2014	**1.70E-3**	N/A	0.23	N/A	0.16
		2015	**4.40E-2**				

	SUVA	2014	**3.40E-3**	N/A	**1.57E-3**	N/A	0.77
		2015	**2.39E-2**				
WSP	*DOC*	2014	4.67E-1	0.14	N/A	0.84	N/A
		2015	1.89E-1				
	FI	2014	1.62E-1	0.27	N/A	0.15	N/A
		2015	1.02E-1				
	β/α	2014	2.80E-1	0.39	N/A	0.09	N/A
		2015	2.78E-1				
	HIX	2014	3.78E-1	0.85	N/A	**4.70E-4**	N/A
		2015	4.55E-1				
	SUVA	2014	0.59	N/A	0.14	N/A	0.71
		2015	**3.27E-3**				

Table 4.8. Significance statistics for DOC concentration and fluorescence indices for SFW, PC and PP in 2015. Cells highlighted in yellow indicate statistical significance ($p < 0.05$).

Wetland	**Test**	**Shapiro**	**Skewness**	**Kurtosis**	**Levene**	**Barlett**	**One-Way ANOVA**	**Welch ANOVA**
Sandhill	*DOC*	**1.74E-4**	1.27	4.46	**0.01**	N/A	N/A	**9.69E-13**
Pauciflora		0.98	-0.07	2.60				
Poplar		0.17	0.82	2.92				
Sandhill	*FI*	**4.10E-8**	2.11	6.97	0.17	N/A	N/A	**1.16E-12**
Pauciflora		0.30	-0.57	2.64				
Poplar		0.07	1.02	3.39				
Sandhill	β/α	**1.91E-6**	0.83	2.25	**3.73E-5**	N/A	N/A	**2.20E-16**
Pauciflora		0.25	-0.32	2.24				
Poplar		0.45	-0.39	2.61				
Sandhill	*HIX*	**5.34E-7**	-0.98	2.45	**4.65E-4**	N/A	N/A	**2.20E-16**
Pauciflora		0.05	-0.21	1.74				
Poplar		0.67	-0.33	3.45				
Sandhill	*SUVA*	**3.94E-2**	-0.62	3.06	**0.03**	N/A	N/A	**6.38E-6**
Pauciflora		0.47	0.24	3.76				
Poplar		0.48	-010	3.90				

Table 4.9. The Games-Howell *post-hoc* statistical significance for SFW, PC and PP in 2015. Cells highlighted in yellow represent statistical significance ($p < 0.05$).

Wetland	**DOC**	**FI**	β/α	**HIX**	**SUVA**
Pauciflora-Poplar	**6.03E-11**	**6.00E-11**	**4.60E-14**	**1.10E-10**	1.20E-1
Pauciflora-Sandhill	**1.28E-3**	**1.30E-3**	**2.00E-11**	**2.80E-6**	**6.20E-5**
Poplar-Sandhill	**3.17E-6**	**3.20E-6**	**0.00E+0**	**1.40E-11**	**7.30E-4**

Table 4.10. Descriptive statistics for DOC concentration and fluorescence indices for SFW, PC and PP in 2015.

Wetland	Test	Min.	Median	Max.	Mean	St. Dev.	25%	75%
Sandhill	*DOC*	23.7	41.4	93.2	44.8	14.6	34.5	50.7
Pauciflora		18.5	39.7	58.3	39.6	9.7	32.8	45.9
Poplar		17.6	22.7	36.2	24.4	5.22	20.3	27.3
Sandhill	*FI*	1.45	1.50	1.70	1.51	0.05	1.48	1.52
Pauciflora		1.38	1.47	1.54	1.47	0.04	1.45	1.51
Poplar		1.53	1.55	1.60	1.56	0.02	1.55	1.56
Sandhill	β/α	0.57	0.65	0.90	0.70	0.08	0.64	0.75
Pauciflora		0.42	0.45	0.48	0.45	0.01	0.44	0.46
Poplar		0.55	0.59	0.62	0.59	0.02	0.58	0.59
Sandhill	*HIX*	0.68	0.86	0.92	0.93	0.07	0.79	0.87
Pauciflora		0.84	0.89	0.93	0.89	0.03	0.85	0.91
Poplar		0.93	0.94	0.95	0.94	0.01	0.94	0.94
Sandhill	*SUVA*	0.79	2.60	3.60	2.45	0.58	1.98	2.84
Pauciflora		1.56	3.42	5.88	3.41	0.93	2.98	3.85
Poplar		1.99	2.99	3.96	2.99	2.99	2.91	3.21

Table 5.1. Spearman correlation for environmental factors that influence DOC concentrations. Note: Cells highlighted in yellow represent statistical significance at a 95% confidence interval and the Rho value ranges from -1 to +1.

Variable	**Location**	**p-Value**	**Rho**
EC	Lowland	2.21E-5	0.39
	Margin	0.10	0.18
	Outlet	2.03E-4	0.85
	WSP	1.91E-3	0.82
	PC	0.13	-0.30
	PP	0.53	0.15
Na^+ Concentration	Lowland	5.05E-7	0.44
	Margin	6.85E-6	0.47
	Outlet	4.63E-10	0.94
	WSP	2.38E-5	0.89
	PC	0.02	0.46
	PP	0.23	0.28
pH	Lowland	3.10E-3	-0.30
	Margin	0.70	-0.05
	Outlet	0.08	-0.52
	WSP	0.01	-0.76
	PC	0.35	0.19
	PP	0.06	0.42
Water Temperature	Lowland	0.70	-0.04
	Margin	0.23	0.13
	Outlet	0.11	0.47
	WSP	0.08	-0.56
	PC	0.28	0.22
	PP	1.22E-6	0.86

Table 5.2. The identified components as reported in previous studies.

Description	**Reported Component Identification**					
	Rastelli (2016)	*Coble (1996)*	*Coble et al. (1998)*	*Cory and McKnight (2005)*	*Stedmon and Markager (2005)*	*Yamashita and Jaffé (2008)*
UVC Humic-like	1 (Peak A)	A	A	Q2	1	1
UVA Marine Humic-like	2 (Peak M)	M	M	C3	6	6
Protein-like Tyrosine-like	3 (Peak B)	B	B	C13	8	7

Table 5.3. Comparison of the descriptions provided by the PARAFAC model and fluorescence indices at SFW.

Location	PARAFAC	Fluorescence Indices	DOC Concentration
Lowland	-Higher plant material -High humification -High aromaticity -High molecular weight	-Terrestrially-derived -Old -Higher humification -Higher aromaticity -Higher molecular weight	-Higher concentrations
Margin	-Biological origin -Low humification -Low aromaticity -Low molecular weight	-Microbially-derived -Newly produced -Lower humification -Lower aromaticity -Lower molecular weight	-Relatively lower concentrations
Outlet	-Mixture of higher plant and biological origin -Low to high humification -Low to high aromaticity -Low to high molecular weight	-Terrestrially- and microbially-derived -Moderate humification -Moderate aromaticity -Moderate molecular weight	-Moderate concentrations
WSP	-Biological origin (amino acids) -Low humification -Low aromaticity and degraded peptide bonds -Low molecular weight	-Terrestrially-derived -Low humification -Low aromaticity -Low molecular weight	-Low concentrations

FIGURES

Figure 3.1. Google Earth map of Sandhill Fen, Poplar Fen, Pauciflora Fen and the city of Fort McMurray in relation to each other.

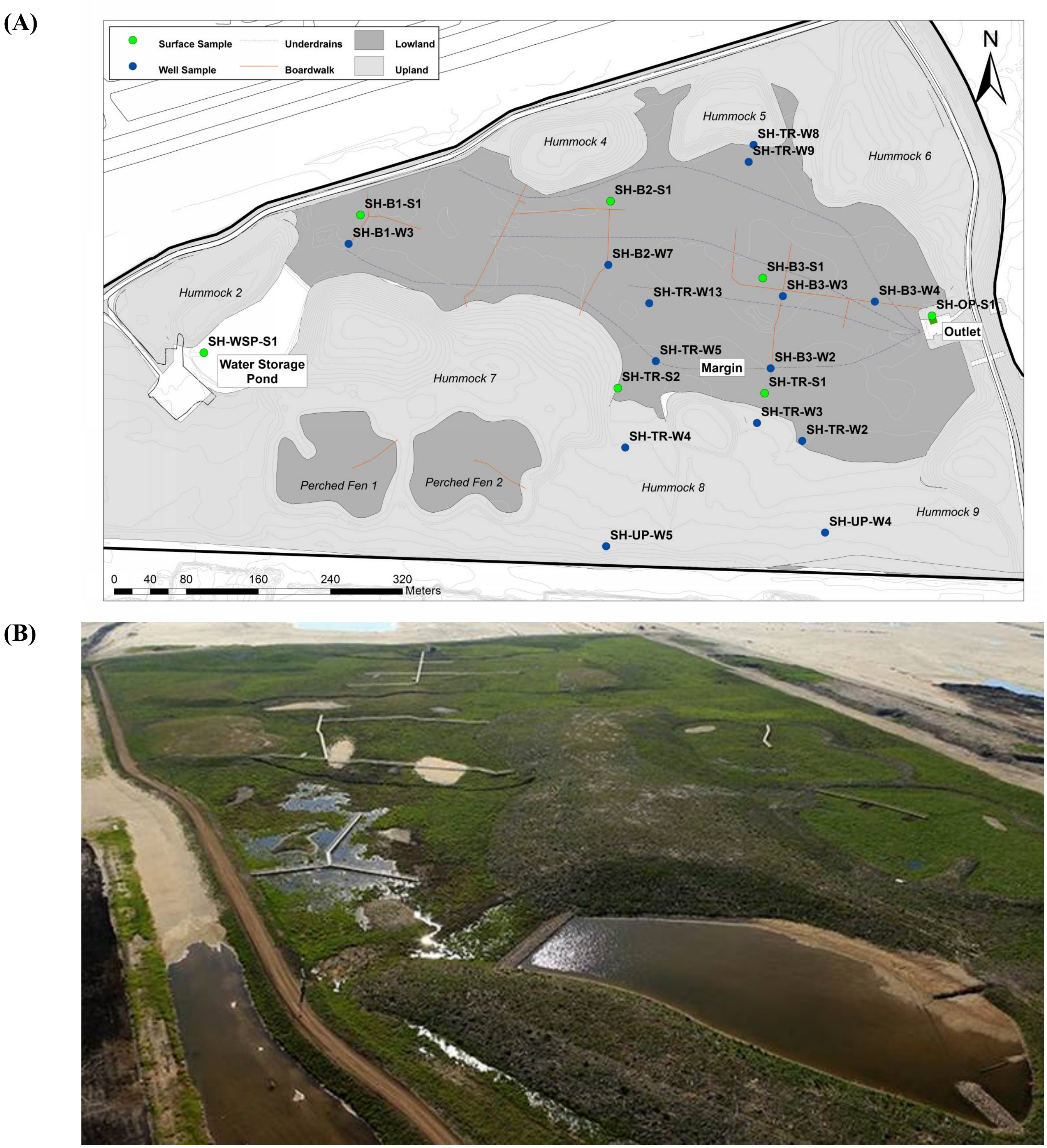

Figure 3.2. (A) Positions and well location of the SFW. The dark gray area represents the wetland area, whereas the light gray area indicates the uplands. The dashed lines represent the location of the underdrains and the solid orange lines represent the constructed boardwalks throughout the SFW. **(B)** An east-facing aerial photograph of the SFW, in which the WSP is located in the bottom-right hand corner.

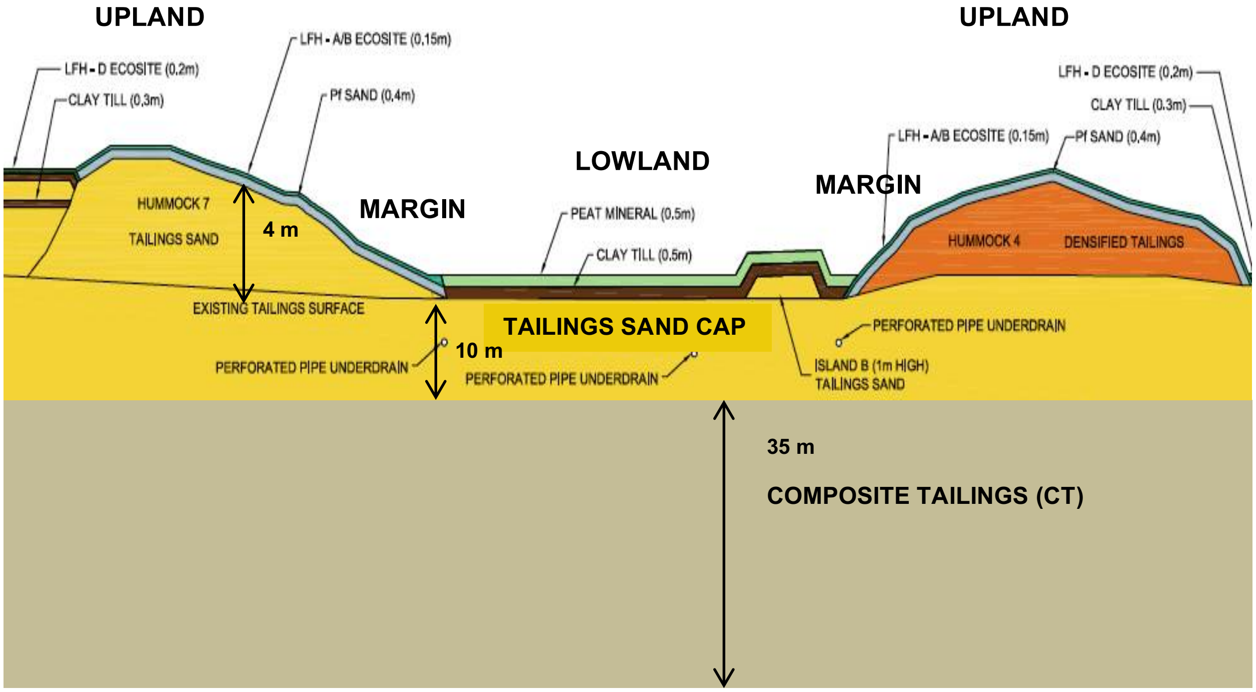

Figure 3.3. A cross-sectional diagram of the construction material of SFW facing north west. This cross section includes hummocks 7 and 4, as well as the wetland located between the two hummocks. Note: This diagram is not to scale. Figure modified from BCG Engineering (2008).

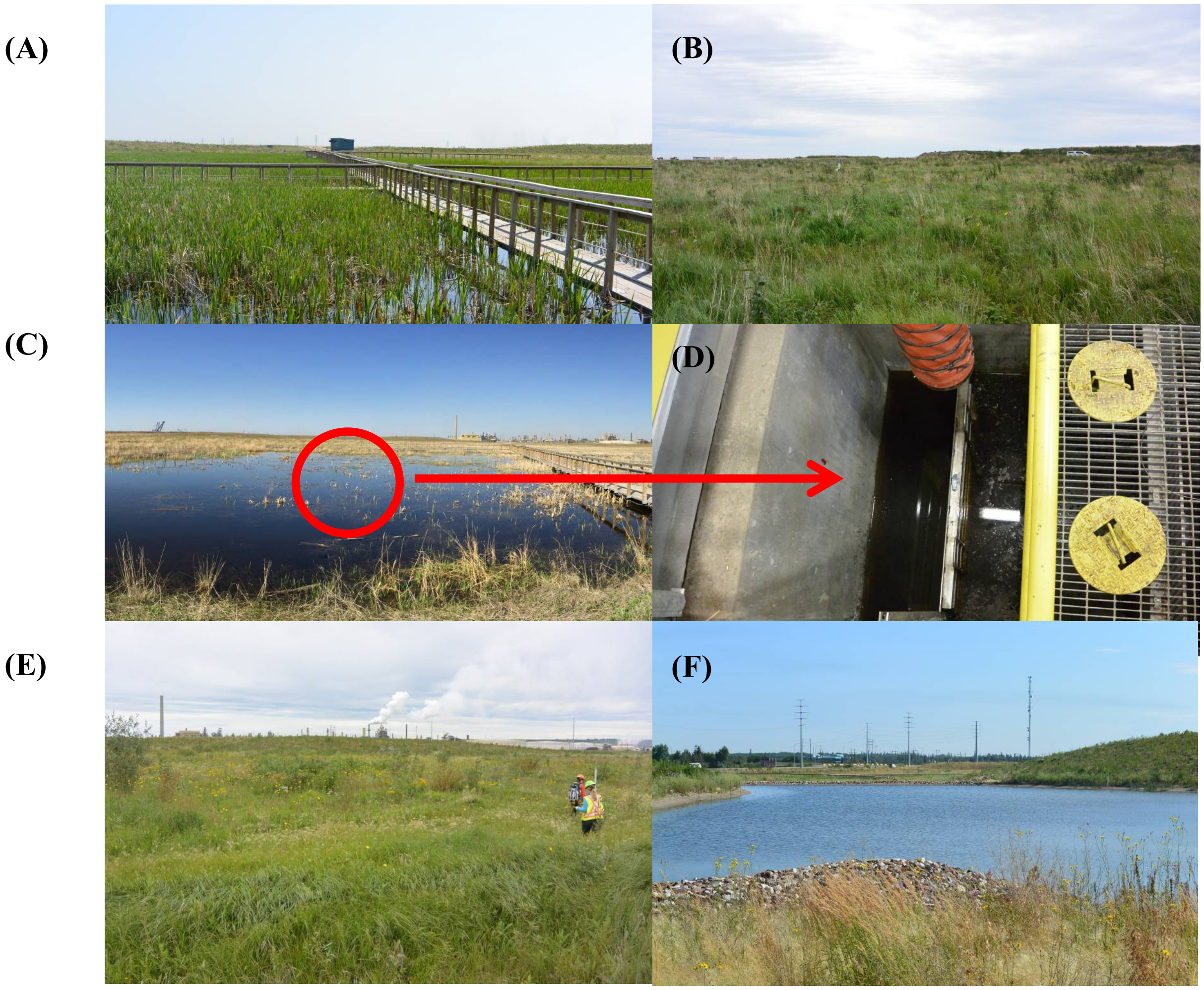

Figure 3.4. **(A)** The lowlands, **(B)** Margin, **(C)** Outlet Pond, **(D)** Weir **(E)** Upland and **(F)** WSP.

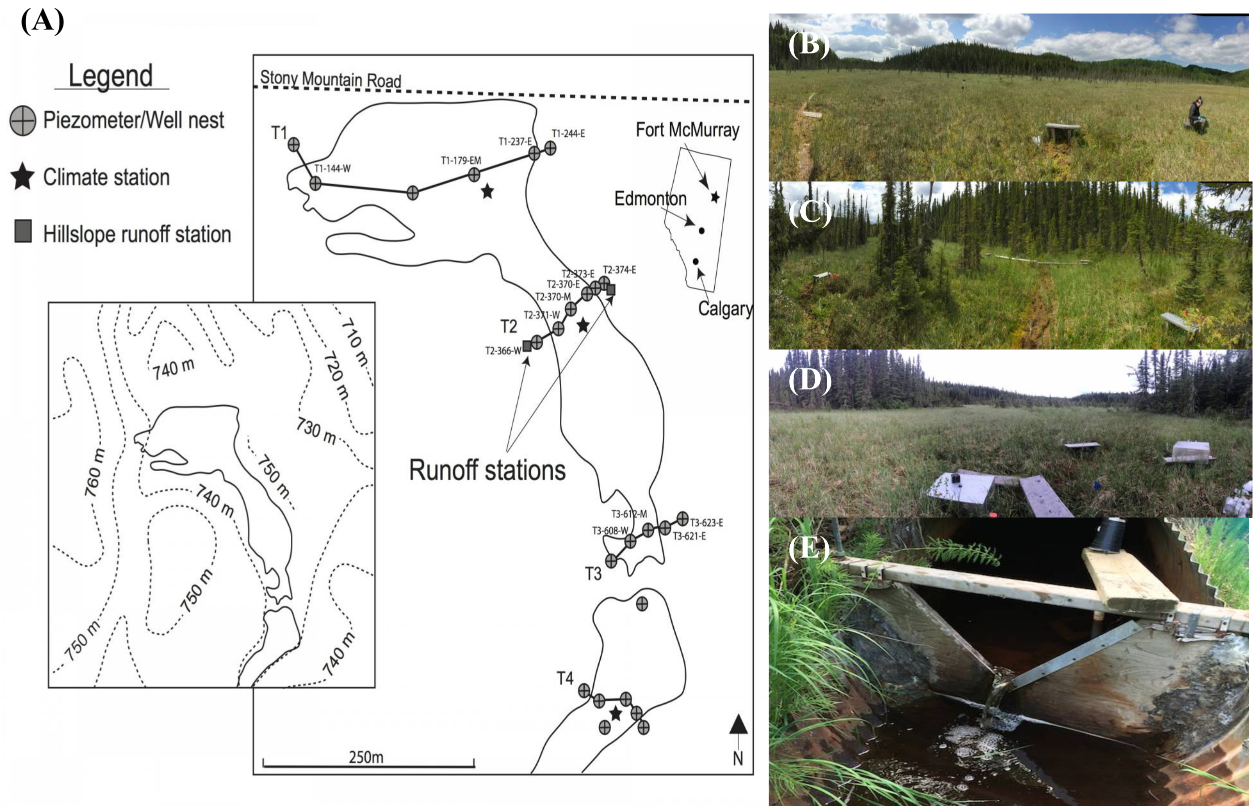

Figure 3.5. (A) Map of Pauciflora Fen. **(B)** Transect 1 (wells 1 and 2), **(C)** Transect 2 (wells 3 and 4), **(D)** Transect 3 (wells 5 and 6) and **(E)** Discharge outlet.

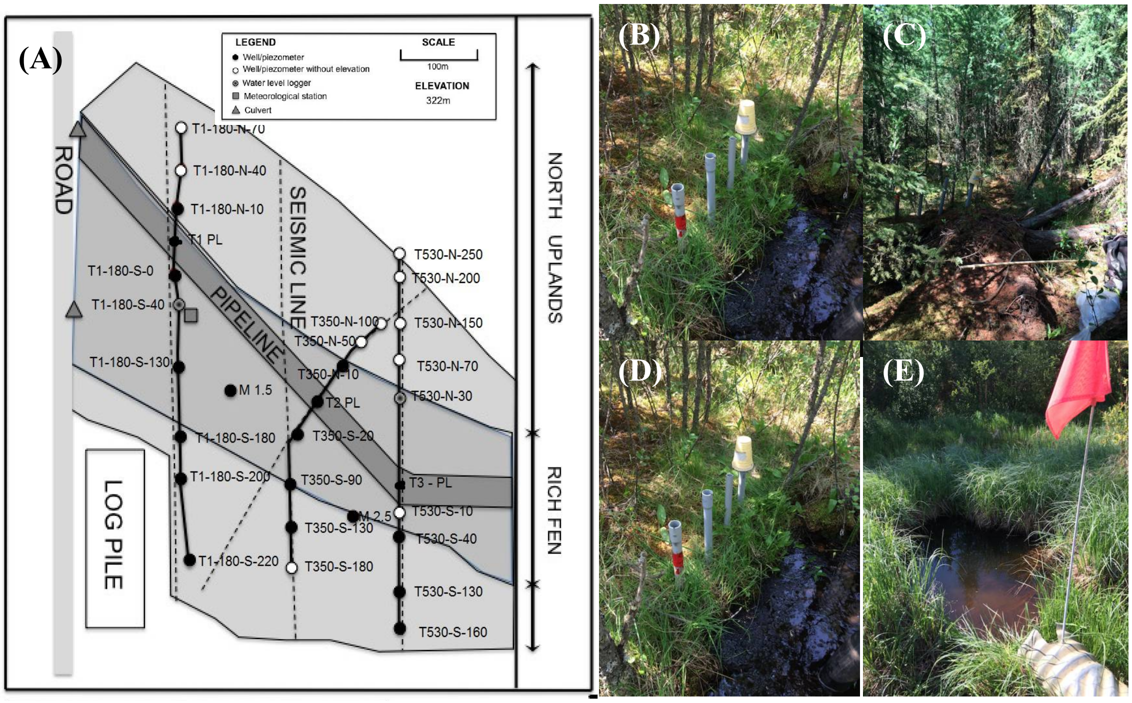

Figure 3.6. (A) Map of Poplar Fen. **(B)** Transect 1 (wells 1 and 2), **(C)** Transect 2 (wells 3 and 4), **(D)** Transect 3 (wells 5 and 6) and **(E)** Discharge outlet.

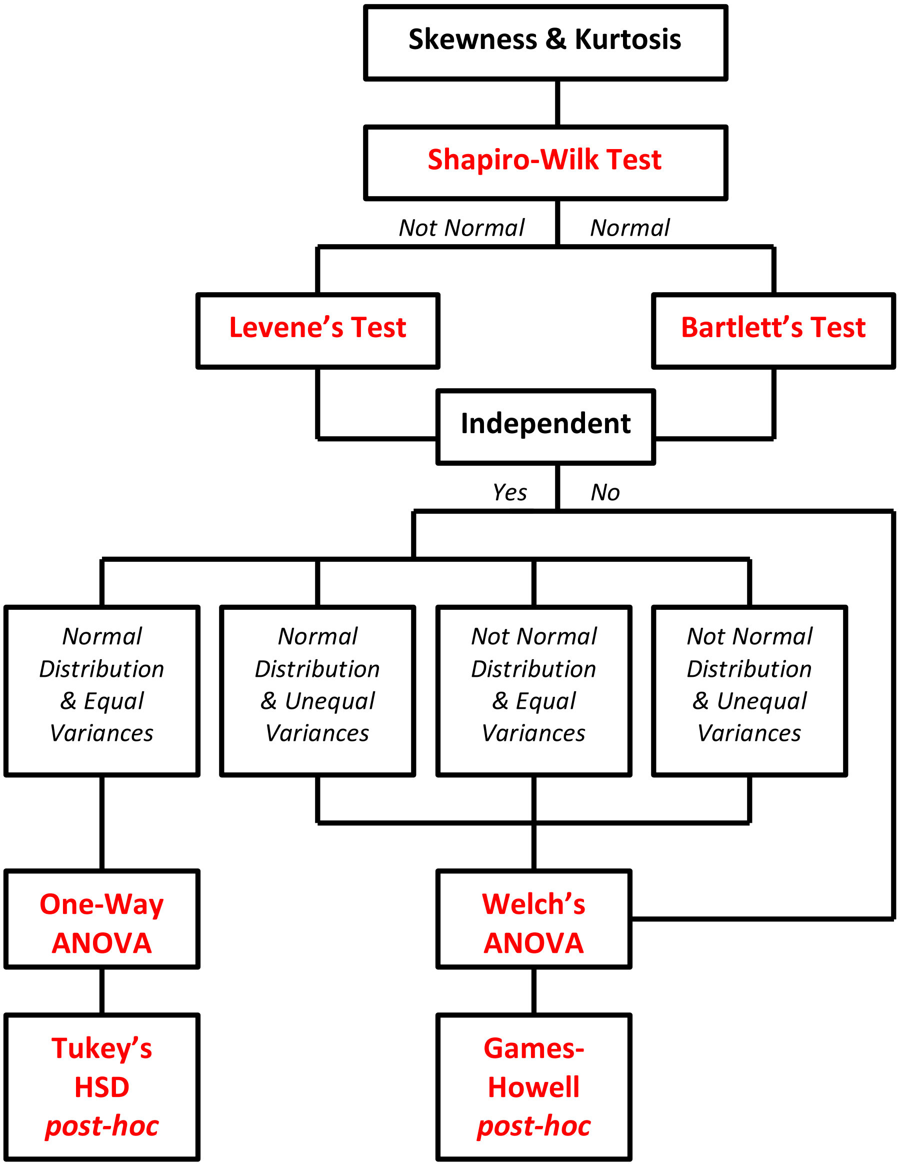

Figure 3.7. A conceptual flow chart of the steps taken to conduct statistical significance on the fluorescence data. The one-way ANOVA and Tukey's HSD *post hoc* were only used if the data was normally distributed and had homogenous variances. If both of these assumptions were not met, the Welch ANOVA and Games-Howell *post hoc* were used.

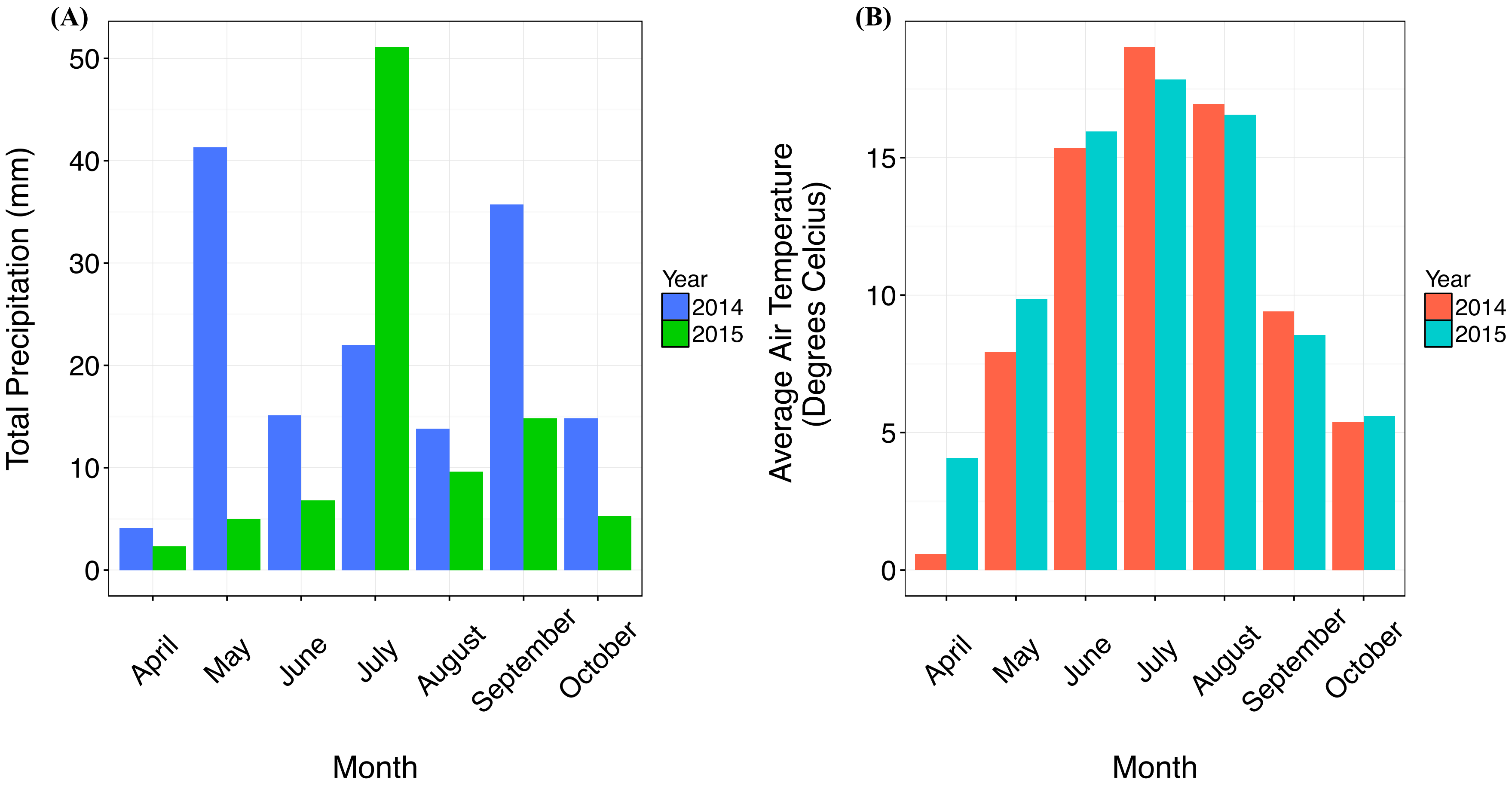

Figure 4.1. (A) Total precipitation and **(B)** Average air temperature for Fort McMurray during the 2014 and 2015 field seasons.

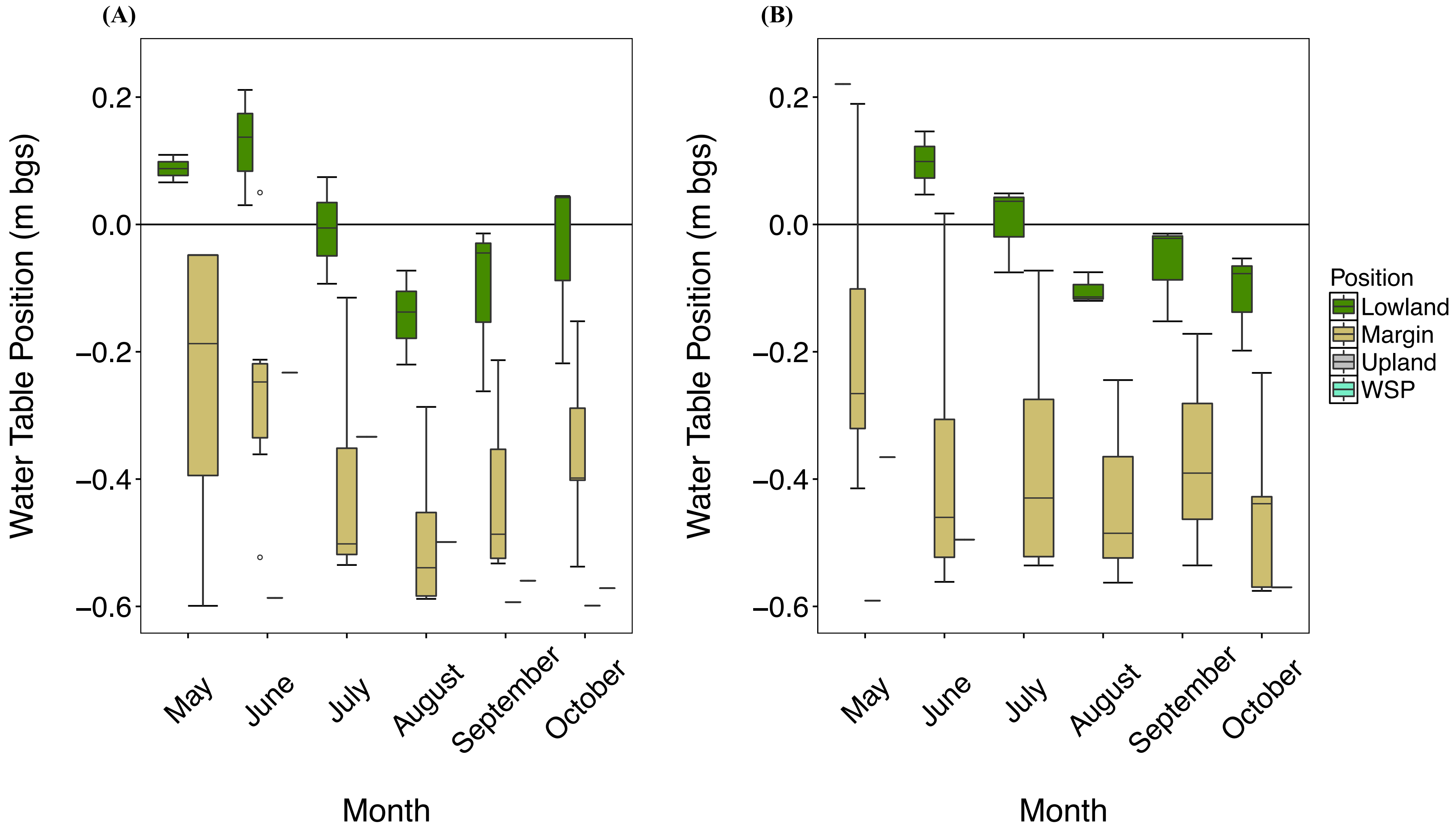

Figure 4.2. Average water table position at SFW in **(A)** 2014 and **(B)** 2015.

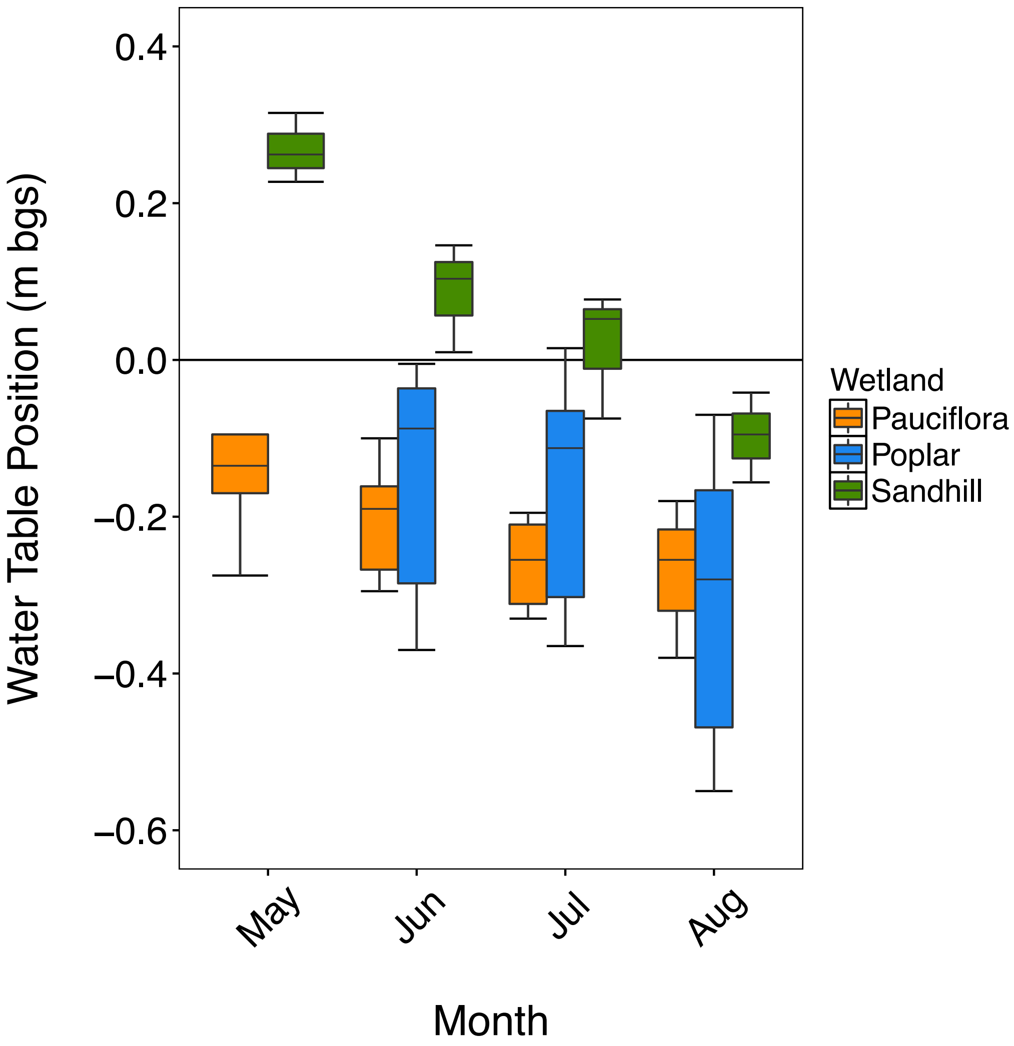

Figure 4.3. Average water table position at SFW, PC and PP during the 2015 field season.

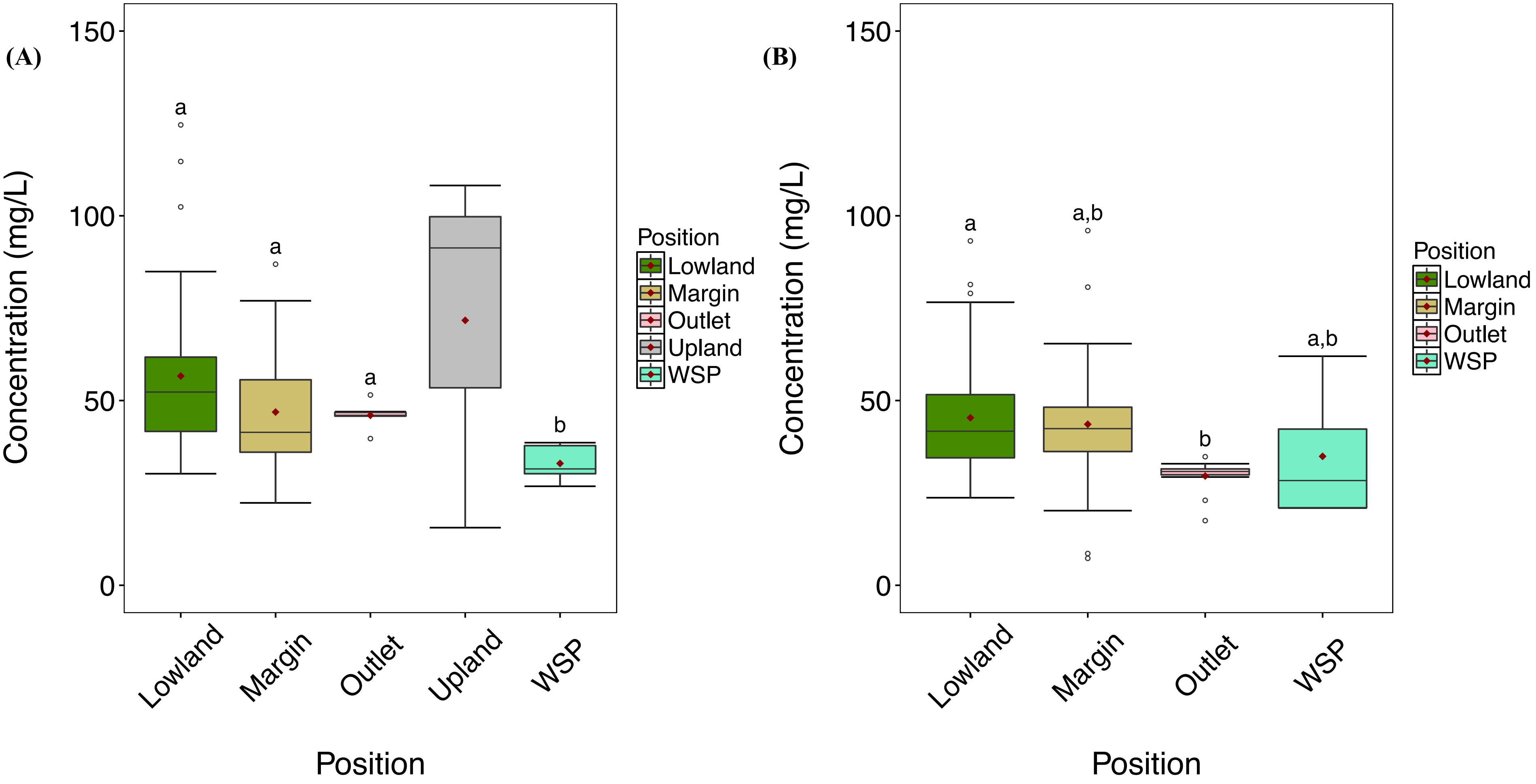

Figure 4.4. DOC concentrations observed at SFW in **(A)** 2014 and **(B)** 2015. The letters above the boxplot represent statistical significance among positions and the red diamond represents the average DOC concentration. Additionally, the uplands are shaded in grey in 2014 because there were a total of 3 samples collected during the field season and therefore, it was not enough data to conduct statistical analysis on.

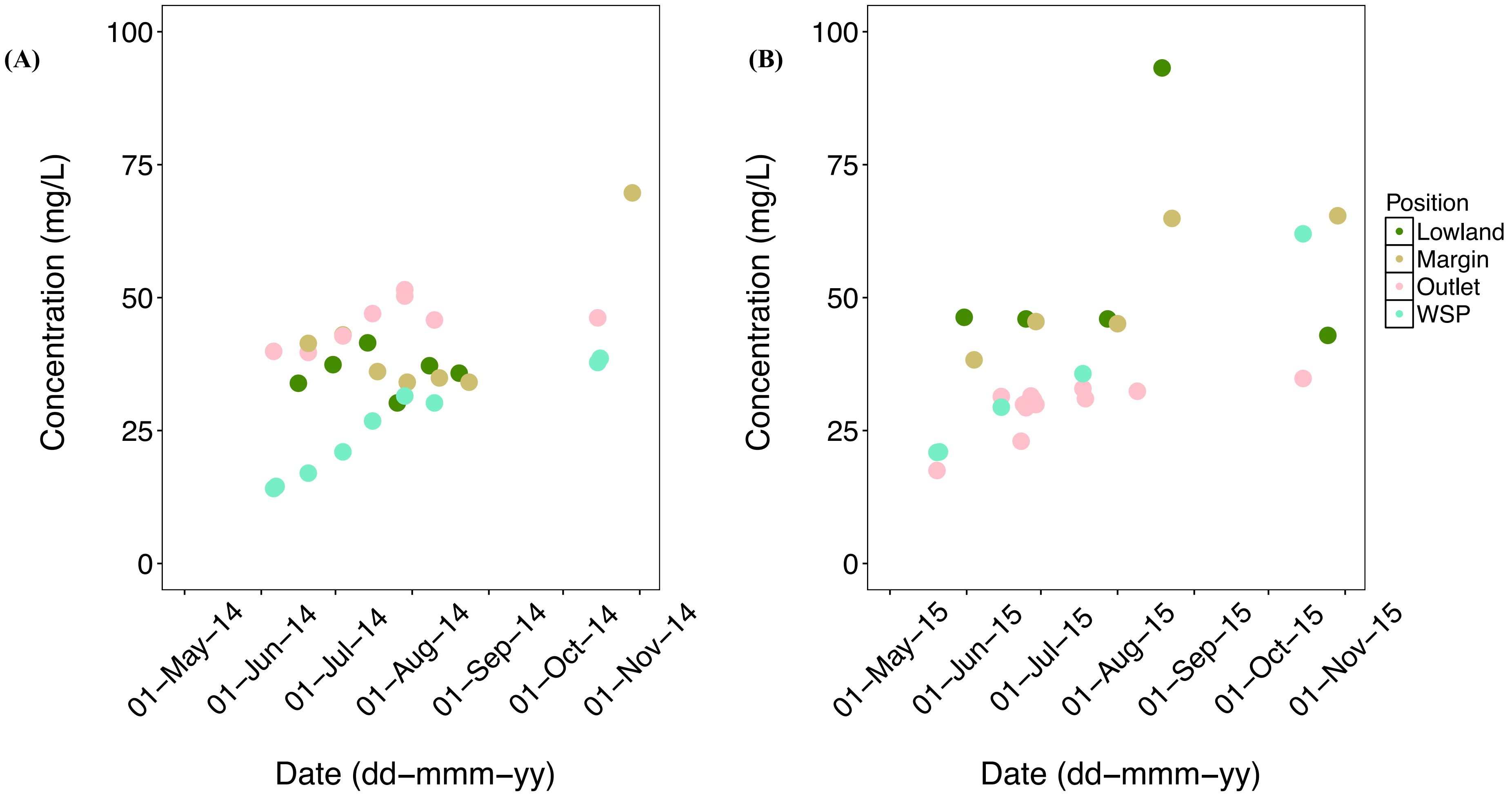

Figure 4.5. Temporal pattern of DOC concentration observed from May to October at SFW in **(A)** 2014 and **(B)** 2015. In both (A) and (B), sampling wells B3_W2 and TR_W8 represent the lowlands and margin positions respectively.

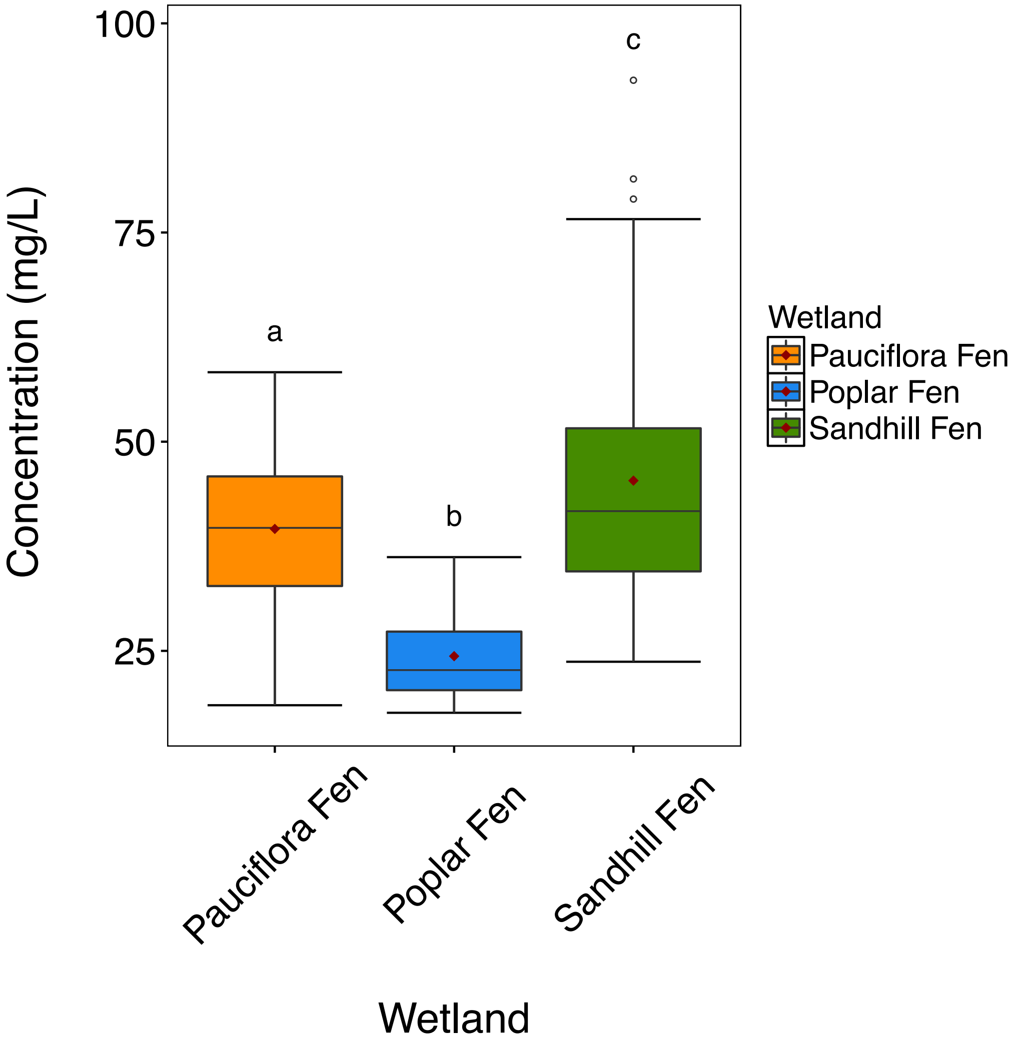

Figure 4.6. DOC concentrations observed at SFW, PC and PP. The letters above the boxplot represent statistical significance among positions and the red diamond represents the average DOC concentration.

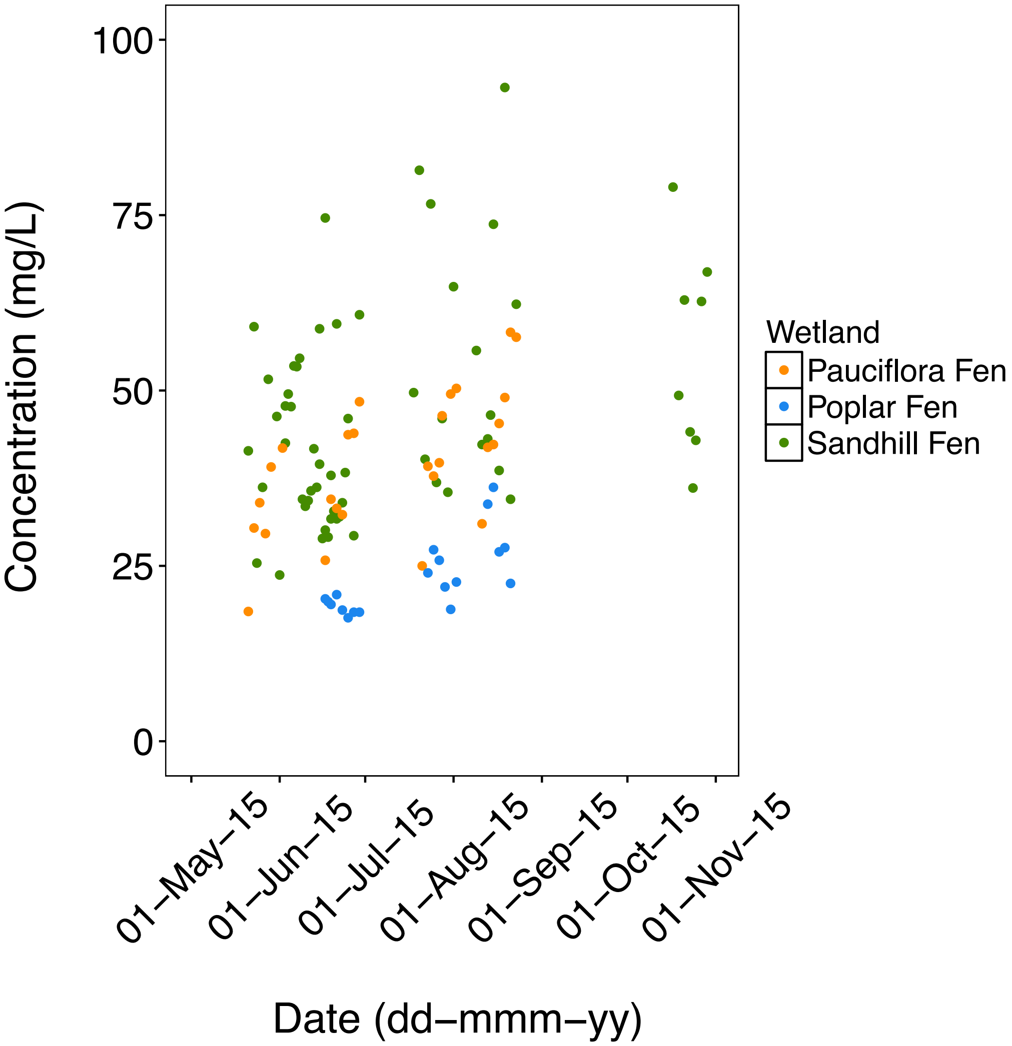

Figure 4.7. Temporal pattern of DOC concentration observed from May to August at SFW, PC and PP. Note: Samples were collected in October at SFW and are shown on this figure.

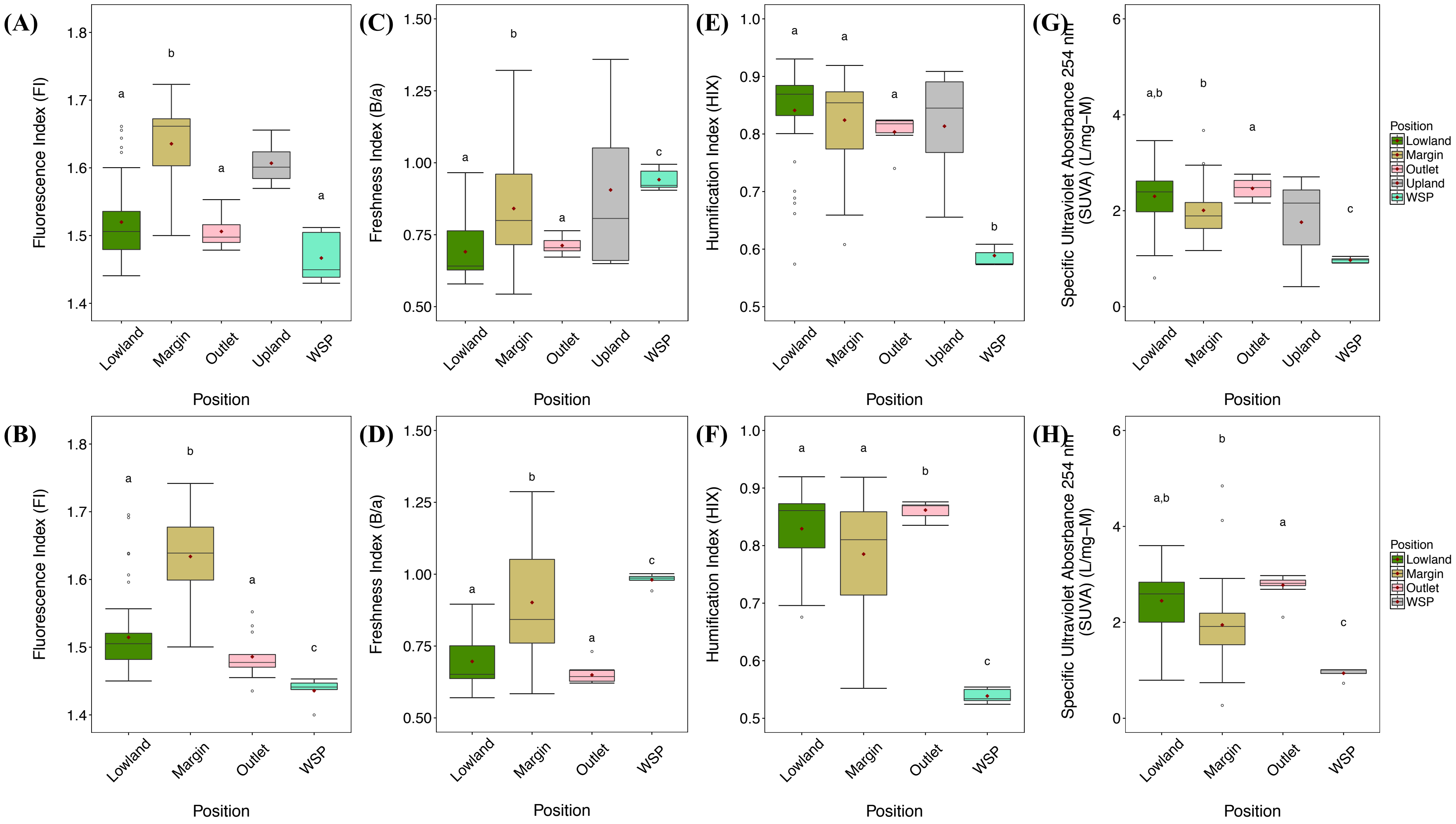

Figure 4.8. The fluorescence indices observed at SFW in 2014 and 2015. **(A)** FI 2014, **(B)** FI 2015, **(C)** β/α 2014, **(D)** β/α 2015, **(E)** HIX 2014, **(F)** HIX 2015, **(G)** SUVA$_{254}$ 2014 and **(H)** SUVA$_{254}$ 2015. The letters above the boxplot represent statistical significance among positions and the red diamond represents the average for the respective index. Additionally, the uplands are shaded in grey in 2014 because there were a total of 3 samples collected during the field season and therefore, it was not enough data to conduct statistical analysis on.

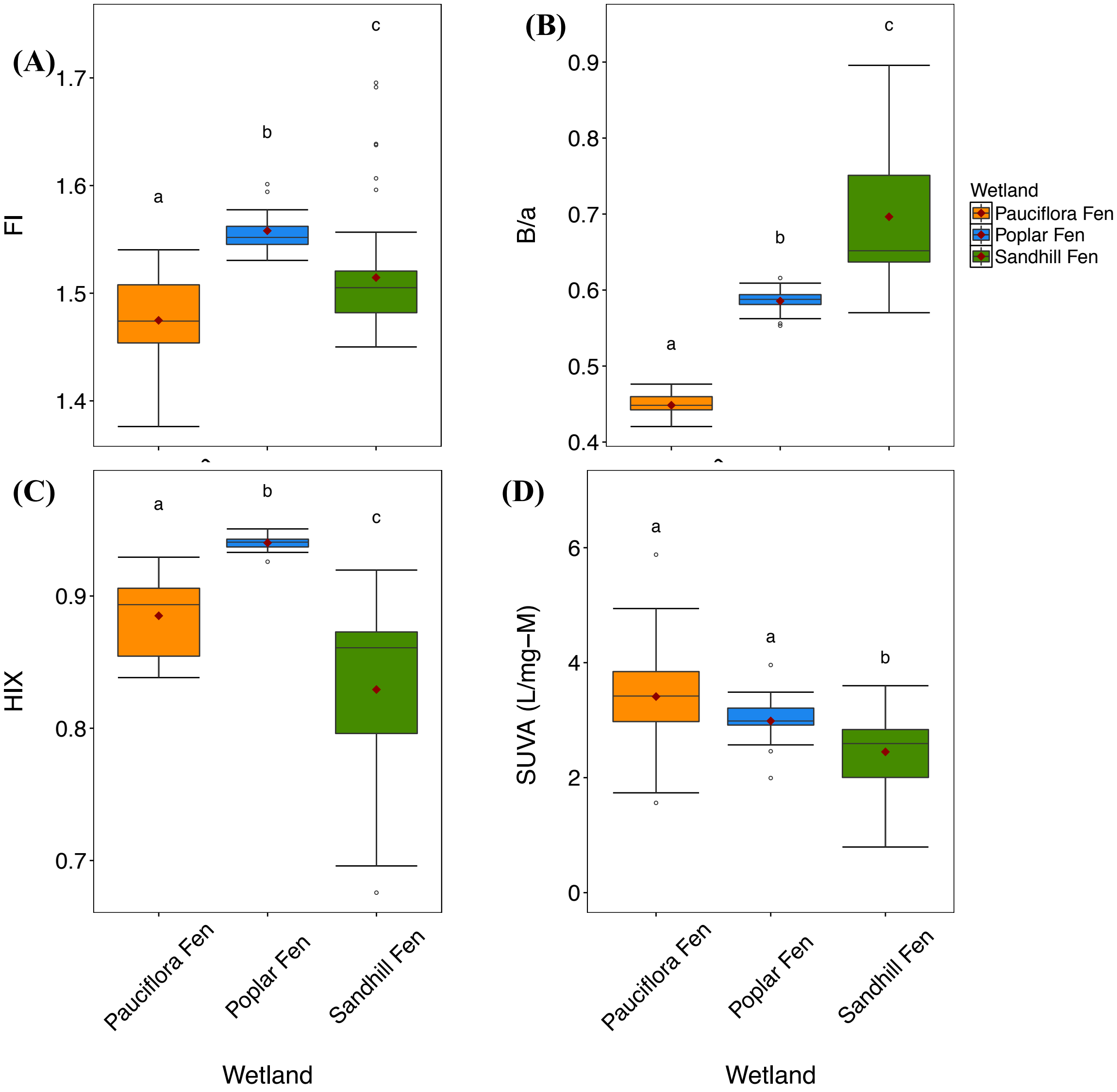

Figure 4.9. The fluorescence indices observed at SFW, PC and PP in 2015. **(A)** FI **(B)** β/α, **(C)** HIX and **(D)** SUVA$_{254}$. The letters above the boxplot represent statistical significance among positions and the red diamond represents the average for the respective index. Additionally, the uplands are shaded in grey in 2014 because there were a total of 3 samples collected during the field season and therefore, it was not enough data to conduct statistical analysis on.

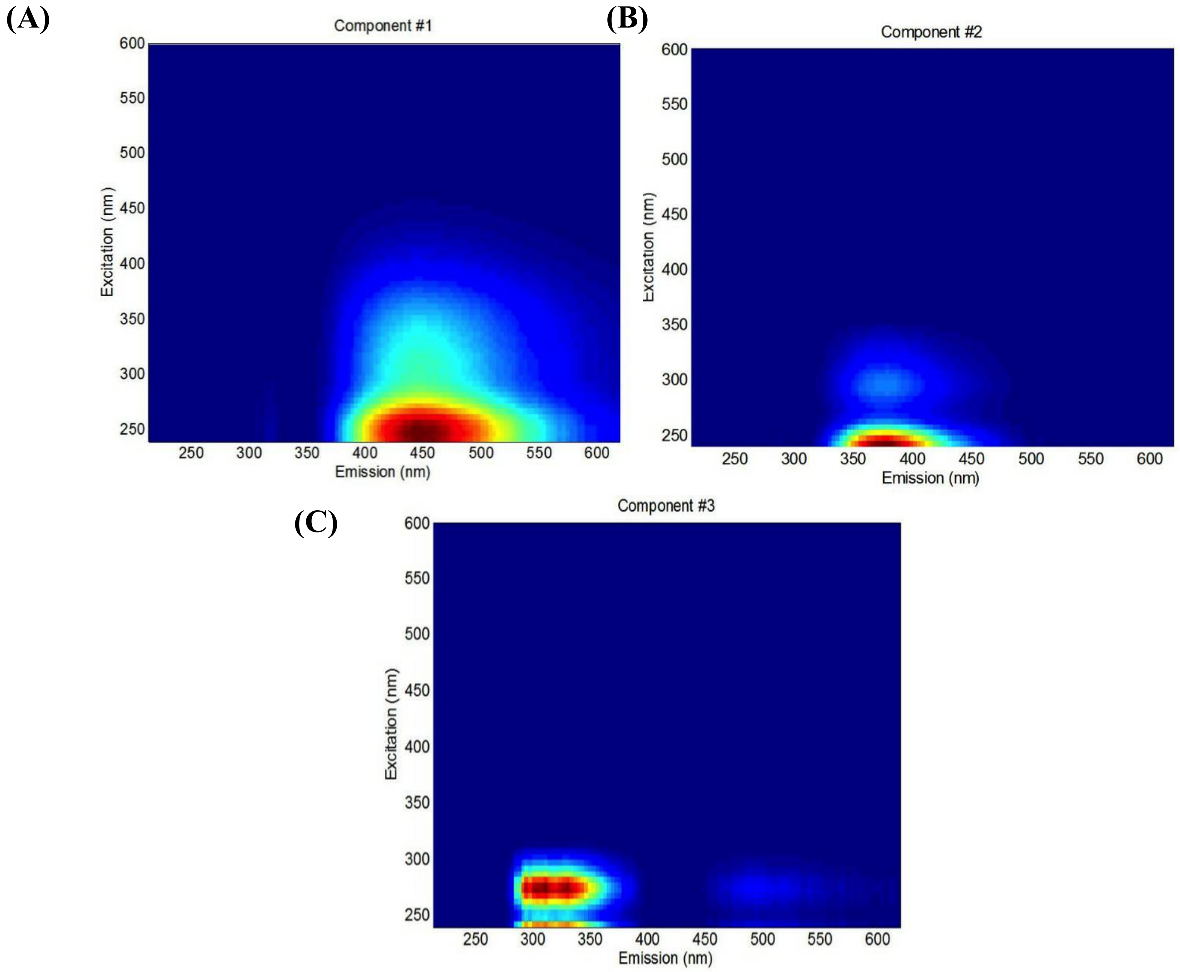

Figure 4.10. The excitation and emission maximum peak of each component obtained using a three component PARAFAC model. **(A)** Component 1: Peak A – UVC Humic-like , **(B)** Component 2: Peak M – UVA Marine Humic-like and **(C)** Component 3: Peak B – Protein-like Tyrosine.

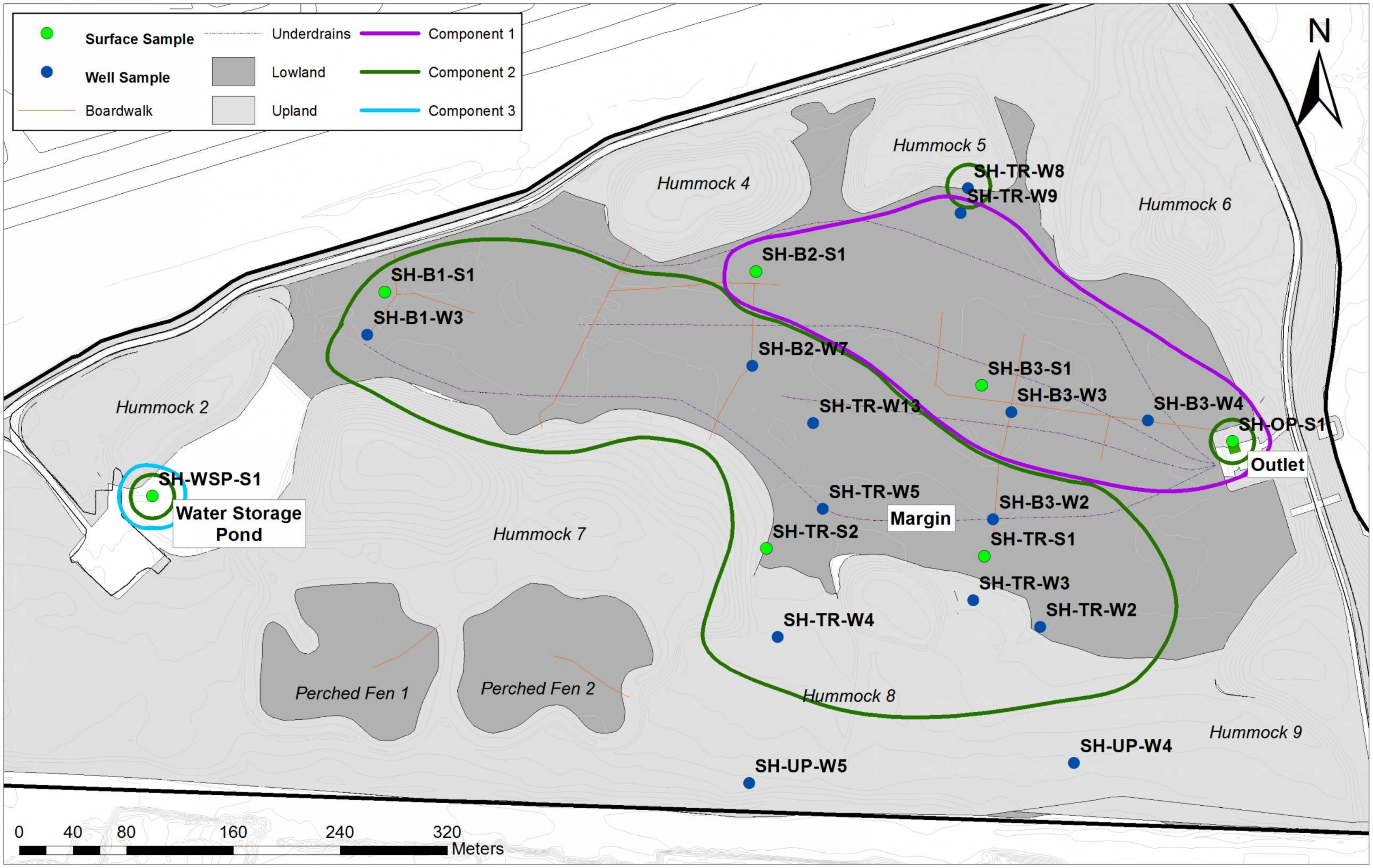

Figure 5.1. The location of the dominant component from the PARAFAC model, as well as the description of the fluorescence indices at SFW. Areas dominated by Component 1 are outlined in purple, Component 2 in green and Component 3 in blue. Furthermore, the description suggested by the fluorescence indices is outline in the white boxes.

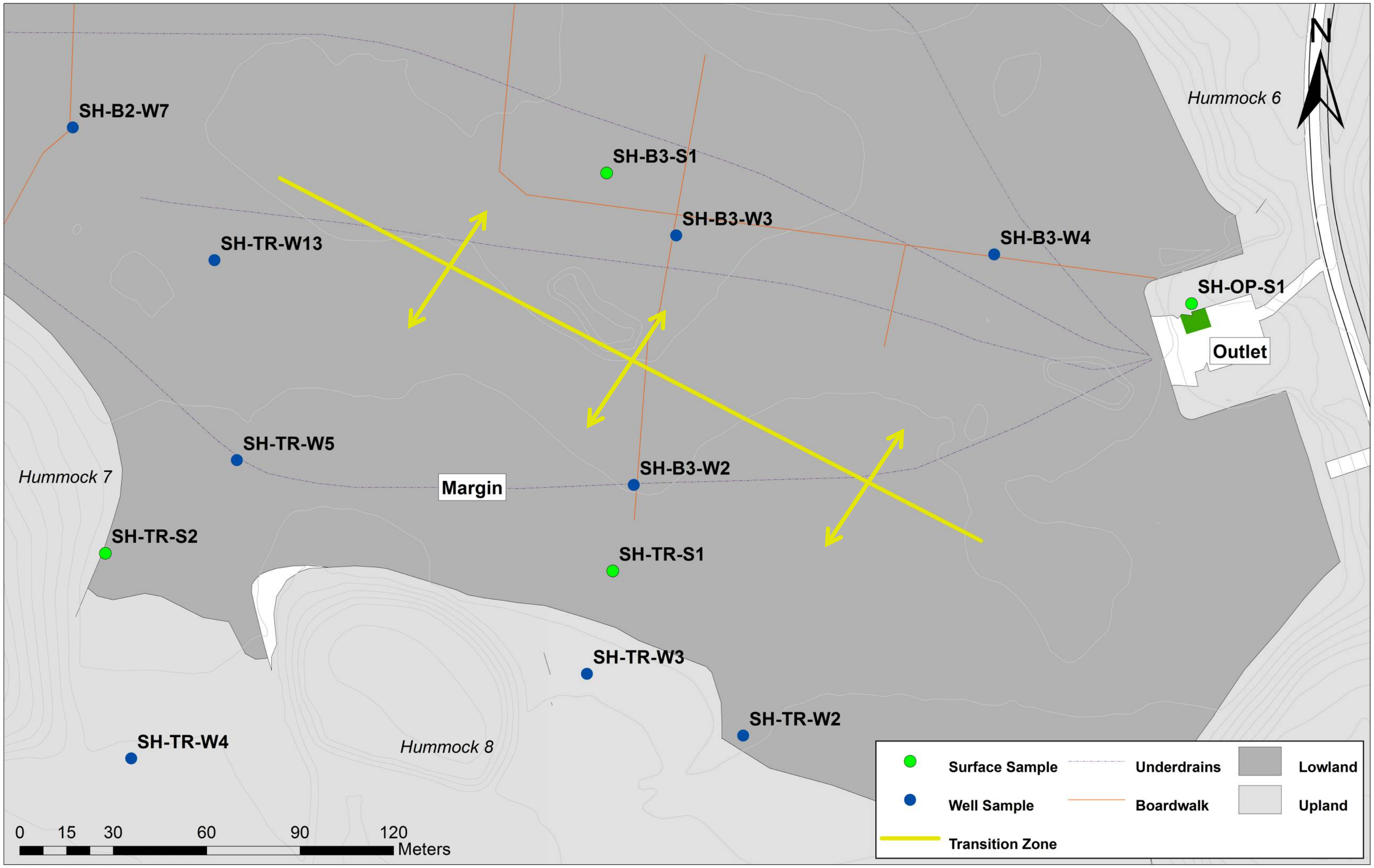

Figure 5.2. The suggested "transition zone" in the southern portion of SFW between the lowland and margin.

APPENDIX- Supplement Data

Table A.1. Fmax of each component using the PARAFAC model for each individual sample.

File Name	**Component1**	**Componen2**	**Component3**
B1S120140704.dat	12.54815855	23.99073344	9.757797273
B1S120140716.dat	15.60810945	27.18467076	10.68455177
B1S120140729.dat	16.43906079	25.77873063	9.697323686
B1S120140810.dat	16.64825667	26.73191693	9.872329809
B1S120141015.dat	8.651649676	23.89437211	11.30306199
B1S120150521.dat	6.194289729	11.52072473	4.532452039
B1S120150615.dat	10.20230788	17.20134075	5.579851765
B1S120150718.dat	13.09278863	17.91557147	5.889377279
B1S120150809.dat	9.120669256	10.32446892	3.527108988
B1S1FD220140716.dat	16.1387262	27.38702492	10.60313591
B1S1PT120150603.dat	8.930541075	15.90377252	5.457339911
B1S1PT220150603.dat	8.43955124	15.41285915	5.342637226
B1S1PT320150604.dat	8.568687215	15.23476773	5.22352413
B1S1PT420150604.dat	8.824641013	16.32087305	5.52066198
B1S1PT520150605.dat	9.745630089	17.14467472	5.828282978
B1S1PT620150605.dat	10.22534201	19.00394841	6.315071534
B1S1PT720150606.dat	9.520043903	17.04103795	5.832592028
B1W320140620.dat	20.66792863	22.4872964	6.465001265
B1W320140716.dat	6.793822897	4.335717513	1.362922982
B1W320140729.dat	9.960221615	4.922075406	1.313342073
B1W320140810.dat	8.533475468	4.126897415	1.106508734
B1W320141015.dat	9.72142289	5.478580938	1.500569259
B1W320150521.dat	10.26738705	18.77855443	5.894661647
B1W320150615.dat	5.538022647	6.86343683	2.011269138
B1W320150718.dat	4.305298038	3.641715699	0.961650655
B1W320150809.dat	4.329949195	2.295442915	0.637331055
B1W320151015.dat	3.645241415	2.133646104	0.689160511
B2S120140606.dat	6.086096549	7.160046487	2.585840921
B2S120140620.dat	7.379577506	6.101045526	1.615092765
B2S120140716.dat	13.61701884	9.742084415	1.905576464
B2S120140729.dat	16.73394578	12.06589661	1.936153667
B2S120140810.dat	15.27250272	9.866003229	1.73754603
B2S120141015.dat	10.04240324	5.056489822	0.853958276
B2S120150520.dat	5.585124113	4.426360469	0.925970963
B2S120150615.dat	10.250509	7.160722305	1.21291974

B2S120150718.dat	13.1971901	8.321522718	1.141151247
B2S120150809.dat	5.697886179	3.876542919	0.621997396
B2S120151015.dat	6.922188583	3.436527338	0.582021189
B2S1FD120150809.dat	5.577126217	3.700773639	0.591502497
B2S1PT120150603.dat	7.9902067	6.130027069	1.203685993
B2S1PT220150603.dat	7.805797977	5.885746292	1.160343229
B2S1PT320150604.dat	8.371651999	6.548915734	1.122698115
B2S1PT420150604.dat	9.014550839	6.479061302	1.247674605
B2S1PT520150605.dat	9.107943828	6.739482265	1.259879812
B2S1PT620150605.dat	8.883111311	6.766648559	1.210393839
B2S1PT720150606.dat	9.651387225	7.094547233	1.235586323
B2W420140620.dat	10.71053075	7.744553566	2.504072929
B2W720140704.dat	4.399333482	2.167540615	0.932411944
B2W720140716.dat	2.984999521	1.545964578	0.311189146
B2W720140729.dat	7.345393118	3.209415265	0.569102792
B2W720140810.dat	6.330301408	2.572444213	0.397044845
B2W720141015.dat	15.29922142	7.70800893	1.131369943
B2W720150520 (1).dat	8.216721844	7.608141481	2.460441808
B2W720150520.dat	8.373100645	7.555838472	2.472875291
B2W720150615.dat	1.845745831	1.259972255	0.418485059
B2W720150718.dat	4.651557901	3.594733293	1.51356759
B2W720150809.dat	4.764236692	5.617436062	2.885018968
B2W7FD120140620.dat	10.75815783	6.309052028	1.422974736
B3S120140606.dat	6.440167389	5.272172526	1.484743834
B3S120140620.dat	7.415455209	5.60697601	1.385482837
B3S120140704.dat	9.053473537	6.716219498	1.704718582
B3S120140716.dat	11.51430271	8.407810576	1.571853137
B3S120140729.dat	13.62083265	9.345301296	1.735495037
B3S120140810.dat	15.32040907	10.73791894	1.846025816
B3S120141015.dat	12.22558917	7.416335939	0.85573379
B3S120150520.dat	5.421051295	4.15436371	0.856330331
B3S120150615.dat	8.972667647	6.360339468	1.0759743
B3S120150718.dat	10.75103542	7.973935742	1.175791223
B3S120150809.dat	12.02717857	7.965809027	1.10370738
B3S120151015.dat	10.8002049	7.189227781	0.852874452
B3S1FD120150615.dat	9.513265863	6.791134475	1.132246061
B3S1FD120151015.dat	11.12672379	7.353643941	0.931635381
B3S1PT120150603.dat	8.485700343	6.224746836	1.109902174
B3S1PT220150603.dat	8.79570422	6.806081241	1.290158636

B3S1PT320150604.dat	8.403826576	6.377875895	1.224947887
B3S1PT420150604.dat	8.258009337	6.5795211	1.295304548
B3S1PT520150605.dat	8.611288197	6.490977096	1.159089479
B3S1PT620150605.dat	8.875651663	6.763373462	1.255132497
B3S1PT720150606.dat	8.665982835	6.48798408	1.22399223
B3W220140606.dat	8.416387105	6.696747068	1.172588036
B3W220140704.dat	9.648789062	8.99808301	1.563015811
B3W220140716.dat	7.913309062	11.70480149	1.769518346
B3W220140729.dat	8.400163388	11.64338562	1.77597081
B3W220140810.dat	9.319181966	11.56414813	1.638499647
B3W220141015.dat	8.399129466	7.617673722	1.279296822
B3W220150521.dat	11.83892004	9.834600887	1.538685471
B3W220150615.dat	12.86854737	10.95572229	1.758150817
B3W220150718.dat	14.48745265	12.54599916	1.957292218
B3W220150809.dat	11.45036222	13.71594326	2.363312416
B3W220151015.dat	7.992969777	10.98049762	2.175761399
B3W320140704.dat	8.854467306	6.500383708	1.647598017
B3W320140716.dat	12.22238124	8.780106323	1.435406018
B3W320140729.dat	14.24943112	9.009923167	1.594931892
B3W320140810.dat	14.16044201	9.016335944	1.385662757
B3W320141015.dat	11.95471929	6.422500166	0.804001842
B3W320150520.dat	6.371664449	4.154052116	0.856547844
B3W320150615.dat	10.11946387	6.216554906	0.947177873
B3W320150718.dat	9.978326557	6.800712568	0.954334778
B3W320150809.dat	11.28827787	7.282499657	1.00033809
B3W320151015.dat	3.297680287	1.24214465	0.205729241
B3W3FD220140810.dat	13.13046577	8.822028909	1.222900629
OP20140606.dat	7.902552796	9.288570358	3.514377504
OPFD120140729.dat	12.5706969	12.24983922	3.072840247
OPS120140716.dat	13.37997859	12.13425107	2.971531227
OPS120140810.dat	13.39796254	13.46168899	2.980129692
OPS120141015.dat	10.47812082	9.767132581	2.35075157
OPS120150520.dat	3.977272279	3.071180288	0.717099375
OPS120150615.dat	8.1378328	6.149836859	1.132997396
OPS120150718.dat	9.155935484	7.703392778	1.489412957
OPS120150809.dat	11.54348347	8.537086475	1.503802006
OPS120151015.dat	6.779700313	6.000758802	1.160064841
OPS1FD120150718.dat	8.855819677	7.208049884	1.210039273
OPS1FD220140729.dat	12.40155897	11.92761876	2.96505857

RPS120150521.dat	6.347691365	16.75499093	8.268691078
RPS120150718.dat	4.052852089	10.73790789	4.314405338
RPS120150809.dat	10.57299302	17.28915813	2.60700916
RPS120151015.dat	2.042616092	5.496988422	2.649330211
TRS120140606.dat	14.55060837	11.11798286	2.207331235
TRS120141015.dat	10.83929042	16.31162902	3.644292794
TRS120150520.dat	7.56452236	6.959986269	2.463240439
TRS120150718.dat	6.840680109	45.52119259	12.84182612
TRS1FD120140620.dat	17.38852729	12.8877313	3.120483312
TRS1FD220140620.dat	16.23156578	12.64225064	3.093934666
TRS220140620.dat	16.73505927	56.47630245	12.00536247
TRS220140729.dat	24.17828477	74.26687346	15.04255509
TRS220140810.dat	15.62637125	41.85507941	7.246798215
TRS220141015.dat	10.68898096	39.85198442	9.188406361
TRS220150520.dat	13.12610258	55.05652238	12.13256339
TRS220150718.dat	16.87036392	59.43962155	10.42526436
TRS2FD120140716.dat	21.32978336	31.21845824	4.193032744
TRS2FD220140716.dat	21.61730093	31.18669682	4.603957728
TRW1320140620.dat	11.95510464	6.681296521	1.030105736
TRW1320140716.dat	11.02606726	11.46106814	1.611376924
TRW1320140729.dat	10.13602175	12.65664636	1.671802703
TRW1320140810.dat	10.13668413	12.63362556	1.668444425
TRW1320141015.dat	10.07408914	10.78343433	1.576813098
TRW1320150615.dat	10.72175316	13.25135702	2.095118869
TRW1320150809.dat	10.58404937	17.31261936	2.744643192
TRW1320151015.dat	10.08382524	15.08147712	2.54797469
TRW13FD220141015.dat	9.701369774	10.49796915	1.435931353
TRW220140620.dat	13.18902106	6.532537672	1.439308989
TRW220141015.dat	8.32473908	6.647005827	1.205681188
TRW220150520.dat	12.66865237	6.410602418	1.266055357
TRW220150615.dat	11.30747581	8.850023119	2.135084146
TRW220150718.dat	13.04873082	10.118724	2.157979534
TRW220150809.dat	12.52703347	10.25001745	2.373631679
TRW220151015.dat	9.85564933	9.375683465	1.733634598
TRW320140620.dat	4.463591813	35.55500208	4.32416287
TRW320150520.dat	3.616618876	14.62408879	1.837619703
TRW320150615.dat	4.538932977	24.15488659	2.675209353
TRW320150718.dat	8.274918383	16.19362764	2.168900534
TRW320151015.dat	4.630731098	2.452737486	0.408711836

TRW420140606.dat	4.290033783	11.09694773	1.25997919
TRW420150521.dat	9.223943333	3.830416181	0.610695438
TRW420150615.dat	2.711630014	1.108606621	0.206009298
TRW520140606.dat	13.29719487	5.155050509	0.917280732
TRW520140620.dat	13.10487169	6.197682509	1.428449877
TRW520140716.dat	9.882358123	8.517281726	1.335495455
TRW520140729.dat	9.383132	8.466750627	1.548660336
TRW520140810.dat	9.00112318	8.730435137	1.487916344
TRW520141015.dat	8.302455166	8.230364602	1.56296851
TRW520150615.dat	9.28220325	9.653983519	2.493497346
TRW520150718.dat	11.46526331	8.196144609	1.899238753
TRW520150809.dat	10.28759092	11.70489745	3.127759327
TRW520151015.dat	9.092765945	11.80827082	3.683412262
TRW820140704.dat	10.0851677	18.72797642	2.091025183
TRW820140716.dat	8.79882358	30.0765878	3.516019009
TRW820140729.dat	8.66348181	30.36698094	3.490819469
TRW820140810.dat	8.523254764	33.90418523	4.332807878
TRW820141015.dat	7.743923249	60.35348117	10.47119835
TRW820150521.dat	10.43482816	8.885467045	1.183209637
TRW820150615.dat	9.124302237	27.3798151	4.635779942
TRW820150718.dat	8.850111962	39.10907086	5.501825867
TRW920140620.dat	15.58233276	5.612070295	1.52686896
TRW920140704.dat	7.676113247	2.229488016	0.902109416
TRW920150521.dat	7.491575694	2.930779582	0.503078771
TRW9FD120140606.dat	10.0096749	3.743691105	0.943095056
TRW9FD220140606.dat	10.23682349	3.266547482	0.837073322
UPW420140606.dat	7.684475407	3.317572178	0.673041307
UPW420140810.dat	3.94949399	9.702836323	3.345888187
UPW420141015.dat	7.94389509	10.8749522	2.292037162
UPW520140606.dat	4.196731386	1.794501013	0.595478841
WEIR20140704.dat	10.19528781	10.67284835	3.46694112
WEIRPT120150603.dat	5.961762318	4.491799314	0.953563567
WEIRPT220150603.dat	8.139559013	5.509496985	1.020418561
WEIRPT320150604.dat	7.997321677	5.296366803	1.003083079
WEIRPT420150604.dat	8.49087367	5.617924846	0.985009658
WEIRPT620150605.dat	8.321703544	5.704097849	1.024708764
WEIRPT720150607.dat	8.608991154	6.155575897	1.063835084
WEIRTPT520150605.dat	8.29421329	5.65038755	0.986723803
WSP20140716.dat	2.223031041	3.799749333	2.218131135

WSP20140729.dat	2.189795732	3.697258263	2.308303091
WSP20140810.dat	2.328879929	4.094980874	2.450269077
WSP20141015.dat	2.292172709	4.640628524	2.723465043
WSP20150520.dat	1.68049939	3.545384935	2.687182157
WSP20150718.dat	2.710272955	5.796764656	3.367117318
WSP20150809.dat	2.914052476	5.348523609	3.638839591
WSP20151015.dat	3.034777513	5.952637917	4.020162368
WSPFD120150520.dat	1.642722793	3.394209805	2.637222649
WSPFD220141015.dat	2.422585401	4.877756967	2.876029891