Dissolved organic carbon production and transport in a constructed watershed in the Athabasca Oil Sands Region, Alberta

by

Sarah Irvine

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Within the Western Boreal Plains, a significant amount of surface cover has been removed through open-pit oil sands mining activities, which includes fen peatlands. Fen construction has been performed on the post-oil sands mined landscape, with the goal of returning ecohydrologic function such that the fen may become a carbon sink. Early results from studies within the Nikanotee Fen watershed indicate that groundwater is directed from the upland towards the fen, which has become a carbon sink. Work within the carbon budget includes dissolved organic carbon (DOC), and early post-succession concentrations and quality have been compared to natural analogues within the region. It was determined that initial conditions do not resemble that of reference sites; DOC concentrations were lower at the constructed site, and DOC appeared large and aromatic. However, DOC quantity and quality may shift as vegetation becomes established on the fen. However, no work has been done to determine the importance of other DOC sources in relation to both DOC dynamics within the fen, and how all DOC sources interact to affect DOC export quantity and quality. DOC export is typically highest in wetland-dominated watersheds, and can have important impacts on nutrient cycling, metal mobility, acidity, and availability of organics downstream. Therefore, it is important to ascertain if vegetation has become an important DOC source, and to consider hydrologic sources of DOC as well. This will be important when determining the best strategies for fen integration into a larger landscape.

For this research, DOC concentration, flux, and quality was assessed through all sources within the watershed, to determine the relative importance of each input for determining DOC export from the site. DOC concentration and quality within the fen was then compared to reference sites, to assess the evolution of DOC sources post-construction. Water sampling occurred from May-August, 2015 in and July-August in 2016. It was determined that hydrological fluxes

represented minimal inputs to the fen compared to the net production from vegetation, specifically as root exudates. However, when compared to reference sites, the constructed fen displayed less variability in its sources of DOC, whereas natural analogues displayed characteristics of both vegetation and microbially-sourced DOC. This is unlikely to change until mosses become dominant on site, or peat accumulation occurs. When considering all hydrological sources of DOC, groundwater represented the largest in 2015, while precipitation was the largest input in 2016. DOC concentration from each input did not significantly vary seasonally or by event size, therefore DOC fluxes were dependent on the volume of water mobilised. Yet, DOC quality varied substantially between sources. Both 2015 and early 2016 received less than average precipitation, this limited groundwater recharge and runoff in 2015. In wetter years, hydrologic inputs would increase, however will still be considerably less than the net production within the fen. This is evident when analyzing DOC quality at the outflow; DOC quality most resembled that in the fen. Total DOC export was limited, due to dry conditions. As DOC export only occurs through surface flow, dry conditions limited surface runoff within the fen, also promoting DOC accumulation. It is unlikely that hydrologic inputs will increase enough to represent a significant portion of the DOC budget in the fen even in wet years, therefore when the outflow is situated adjacent to the fen, monitoring should be most intensive within the fen. However, in constructed watersheds that do not contain wetlands, it will be important to monitor each contributing area to determine which areas within the watershed represent important DOC fluxes downstream, and how the DOC quality from each source may impact downstream biogeochemical dynamics.

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Chapter 1: Introduction

Wetlands are an important feature on the landscape, that provide many ecosystem services, including water retention (Bay, 1969), long-term carbon storage (Gorham, 1991), and ecological diversity (Vitt, 2006). Within northern regions of Alberta, they can represent up to 50% of the landscape, with 95% being classified as fen peatlands (Vitt et al., 1996). Peatlands develop when the rate of accumulation of organic matter exceeds that of decomposition, which is facilitated by saturated conditions that create an anoxic environment (Clymo, 1984). Exchanges within this carbon pool occur through gaseous (carbon dioxide, methane) and dissolved organic carbon (DOC) fluxes, and to a lesser extent dissolved inorganic carbon (DIC) and particulate organic carbon (POC) (Fraser et al., 2001). The Western Boreal Plains (WBP) exist within a sub-humid climate, where precipitation (P) is typically less than potential evapotranspiration (PET) (Petrone et al., 2007). Consequently, water storage is an important feature of this landscape. Within the WBP, 844 km^2 has been disturbed through surface mining activities as of 2013 (Alberta Government, 2014), removing a substantial cover of peatlands. Therefore, peatland construction has been proposed as a reclamation strategy to limit carbon losses and retain these ecosystem services (Price et al., 2010; Daly et al., 2012; Ketcheson et al., 2016). This study identifies controls on the production, transport, and quality of DOC within a constructed watershed that includes a fen peatland.

The Government of Alberta requires oil sands companies to return the land to a state of equivalent land capability for wildlife habitat (OSWWG, 2000). Most wetland creation projects have centered on the establishment of open water wetlands or marshes as they are hydrologically simpler (Raab and Bayley, 2013). However, fen creation is considered to be difficult due to the hydrological complexity and long-term development of these ecosystems (Price et al., 2010) and therefore had not been attempted until recently. It is important to test peatland construction success within this region to assess its potential outcomes and determine aspects that may be improved for future peatland reclamation. Therefore, a fen peatland was constructed near Fort McMurray, Alberta based on the models outlined by Price et al. (2010), the Nikanotee Fen. The goal of this project was to create a watershed that would provide sufficient water to support fen vegetation and create a self-sustaining, carbon accumulating ecosystem (Daly et al., 2012). The Sandhill Fen, another constructed fen watershed, has been created within this region on the Syncrude Canada Ltd. oil sands lease (Wytrykush et al., 2012). Both sites use donor peat from a nearby fen (Nwaishi et al., 2015); however, the Nikanotee Fen used both seedlings and seeds to establish vascular vegetation, and the moss-layer transfer technique to establish plant communities (Daly et al., 2012). Wood mulch was applied to the fen to limit ET losses (Price et al., 1998). The upland is constructed from litter, fibric, and humic (LFH) mineral mix soil layer on a tailings sand aquifer, while the constructed hillslopes were reclaimed using 50 cm of peat/mineral mix, overlying a secondary capping layer (low sodic soil) (Ketcheson and Price, 2016).

Currently, there is no successfully reclaimed peatland to use as a comparison for construction fens in the WBP. Though peatland reclamation is untested, restoration has been attempted on multiple peatlands in eastern Canada (Petrone et al., 2001; Rochefort et al., 2003; Waddington et al., 2008) and to a lesser extent in western Canada (Wind-Mulder et al., 1996; Strack et al., 2014). Therefore, restored sites may be used for evaluation when considering techniques to recreate peatland functions. A common approach to restore peatlands is the moss-layer transfer technique, which involves spreading donor vegetation such as *Sphagnum* diaspores, and covering the restored area in straw mulch to reduce evapotranspiration (ET) losses (Price et al., 1998). While this method is largely used on bogs, the moss–layer transfer technique has also been used on fen peatlands (Rochefort et al., 2016). For vascular species, planting of seedlings, along with straw cover have been used (Cooper and Macdonald, 2000; Graf and Rochefort, 2010). The use of mulch to cover seedlings and moss diaspores has been employed on restored fens (Daly et al., 2012). Techniques to promote natural recolonization include ditch blocking and re-wetting, peat disturbance, and mowing (Mälson et al., 2010). While good vegetation reestablishment has been observed with bog restoration, the results of fen restoration are still being evaluated (Rochefort et al., 2016), and it is still too early to predict the effects of using the above recolonization methods on a constructed fen.

DOC is an important component of peatland biogeochemical processes, as it provides organic sources for microbial populations within the peat, can occupy sorption sites on the peat (Kalbitz et al., 2000), and contributes to carbon cycling within the site (Blodau, 2002). Additionally, it can have many implications for downstream ecosystems. It is an important source of organic substrate for microbial communities in large, open bodies of water, particularly in ocean, lacustrine, and fluvial environments (Aitkenhead and McDowell, 2000). This input of organic material also promotes the release of nutrients, which become available to other organisms (Steinberg, 2003). However, DOC can also create damaging conditions; DOC can bind with toxic metals, and transport them downstream, though their release is dependent on the recalcitrance of the DOC structure (Steinberg, 2003). DOC is commonly released as an organic acid, altering the pH of an ecosystem (Steinberg, 2003). The ecohydrology of a peatland affects its carbon cycling (Strack et al., 2008) and the transport of DOC (Moore, 2009). Groundwater has been shown to have a significant impact on the DOC balance of peatlands (Waddington and Roulet, 1997) and quality (Olefeldt et al., 2013; Rastelli, 2016). Additionally, surface runoff is typically limited within the WBP (Devito et al., 2012), but has recently been observed in WBP watersheds (Wells et al., 2017). Surface runoff is also a commonly observed phenomenon within the Nikanotee fen watershed (Ketcheson et al., 2016); it is important to derive the surface runoff DOC contribution to the constructed fen, as it is difficult to predict how this may impact the quantity and quality of DOC outflow. Water table fluctuations can affect the mobility of DOC, as lower water tables promote peat deformation and mobility within highly decomposed peat layers (Price, 2003), restricting DOC movement to smaller pores. The rise and fall of the water table can also enhance the oxidation of peat (Strack et al., 2008), which can reduce pore sizes within the peat and limit mobility (McCarter and Price, 2013). Long-term water table fluctuations may also modify vegetation communities, which alters DOC input quantity and quality (Strack et al., 2006). Vegetation community composition has been shown to impact DOC inputs through root exudates (Robroek et al., 2015) and litter inputs (Khadka et al., 2015). It is important to determine the effect of DOC production and transport on carbon losses from the watershed, because of their potential impacts on downstream ecosystems.

Within restored peatlands, DOC has been assessed pre- and post-restoration. Strack et al. (2011) found that vegetation is an important source of DOC in early years (1-3) post-restoration, and that it may take decades before DOC concentrations and quality resemble what is seen in nearby natural sites (Strack et al., 2015). DOC transport is an important factor for downstream ecosystem water quality (Wilson and Xenopoulas, 2008). Export of DOC generally decreases post-restoration (Waddington et al., 2008; Strack et al., 2015) due to reductions in DOC concentration and surface runoff, and its magnitude is largely controlled by snowmelt and large precipitation events (Waddington et al., 2008). Some work has been done on DOC dynamics in constructed wetlands (Pinney et al., 2000; Hammersley et al., 2002), however, this research is primarily to assess their success in sewage treatment, and not for reintegration within the landscape. Previous research has also been done on early post-construction DOC dynamics within constructed Nikanotee Fen (Khadka et al., 2016) and Sandhill Fen (Rastelli, 2016); however, the long timeframes needed for development of fen watersheds necessitates that DOC concentrations and quality be monitored for longer periods of time. Additionally, previous work has been limited to fens, and has not expanded to include other aspects of the watershed, that are likely to act as important external controls on DOC dynamics within constructed fens. Rastelli (2016) investigated DOC dynamics in transition zones between upland and a constructed fen, although gaps in knowledge still exist regarding hillslope and upland runoff contributions to the fen DOC pool.

1.1 Objectives

Khadka et al. (2016) reported on DOC concentration and quality 1-2 years post-construction; however, it is important to monitor long-term development of DOC dynamics within the fen to determine the carbon storage capacity of the system, and assess its biogeochemical function in reference to natural fens within the WBP. It is also necessary to determine the relative contribution of additional sources of DOC within the watershed other than the fen, as these may prove to be significant for the quantity or quality of DOC exported from the fen. Further understanding of the contribution from multiple sources to the DOC pool can be used to improve upon future projects and successfully integrate constructed fens into a larger reclaimed landscape. Therefore, the objectives of this study are to:

1. Characterize controls on DOC concentration and quality within a constructed fen watershed and nearby reference sites over a two-year period
2. Characterize and quantify hydrologically driven DOC fluxes within a constructed fen watershed

Chapter 2: Temporal shifts in dissolved organic carbon sources at a constructed fen in the Athabasca Oil Sands Region, Alberta

2.1 Introduction

Peatlands within the western boreal plains (WBP) can account for up to 50% of the landscape cover (Vitt, 1996). Within this region, peatlands play an important role for water storage across the landscape, and provide habitat for indigenous species. As this WBP area is sub-humid, and potential evapotranspiration (PET) commonly exceeds precipitation (P), water storage is an important feature to support adjacent ecosystems (Devito et al., 2012). Interconnected groundwater flow that exists between hydrologic response units, such as peatlands, helps to sustain water exchange and storage within the WBP. However, ~844 km^2 of this area has been disturbed within the Athabasca Oil Sands Region (AOSR) through surface mining activities as of December, 2013 (Government of Alberta, 2014). Wetland construction has been attempted (Raab and Bayley, 2013); however, attempts to construct peatlands are a recent development due to the hydrological complexity, and long time needed for development of peatlands (Price et al., 2010). Currently, there is a requirement for companies extracting bitumen to return the land to "equivalent capability" (OSWWG, 2000); therefore, a constructed fen and watershed has been created near Fort McMurray, Alberta to test the concept. It has been suggested that the development of this wetland will differ from that at natural sites within the region (Nwaishi et al., 2015), and may develop to become a novel ecosystem within the WBP. Early work on this fen indicates it is a small CO_2 sink (Nwaishi et al., 2016), emits very little methane (Murray et al., 2017), and has low DOC concentrations (Khadka et al., 2016). However, carbon exchanges are likely to change as vegetation communities, hydrology, water chemistry, and environmental conditions develop over time.

Dissolved organic carbon is produced through either the degradation of organic matter, or by living vegetation as root exudates (Flores et al., 1999). The structure of DOC is dependent on its source, as well as the degree of degradation it has undergone (Robroek et al., 2015). Differences in DOC structure are often referred to as DOC quality. Vegetation can produce a variety of DOC compounds with highly complex structures. The plant tissues are largely composed of cellulose and lignin. While cellulose is easily broken down, microbial communities typically have a difficult time breaking down the large number of aromatic structures in lignin (Robroek et al., 2015). Root exudates also encompass a range of organic compounds, and may vary according to the plant's environment (Walker et al., 2014). Commonly found root exudates include amino acids, sugars and polysaccharides, and organic acids (Jones, 2014). Microbes often preferentially target simple sugars or polysaccharides as an energy source, compared to more complex sources that have a humic appearance (Crow and Wieder, 2017). Once DOC is broken down, it will often be released as CO_2 (Glatzel et al., 2003); however, certain compounds such as acetate, can promote methanogenic archaea to produce CH_4 under anaerobic conditions (Ding et al., 2005). Simpler compounds are more likely to form organometallic complexes that increase mobility of metals (Steinberg, 2003). Therefore, DOC quality and quantity are important to monitor together, as this interaction can have variable effects on carbon losses and the fate of DOC in downstream ecosystems.

DOC production can be impacted by many environmental variables, including water level, ion availability, acidity, and temperature. A decrease in water level has been shown to increase DOC production by increasing the size of the oxic zone (Strack et al., 2008). Freeman et al. (2001) displayed a positive relationship between temperature and DOC export. Warming and water table changes can also have indirect impacts on DOC production; greater CO_2, which can occur as a release from increased peat oxidation, promotes root exudate production in vascular plants (Freeman et al., 2004; Fenner et al., 2011). Both anions and cations can impact the solubility and production of DOC. As DOC can interact with organic substrates, such as peat, it can compete for sorption sites with other ions (Kalbitz et al., 2000). Anions, such as nitrate or phosphate, may increase both plant productivity and decomposition as these are often limited in wetland ecosystems (Vitt and Chee, 1990). Khadka et al (2015) determined that peat and vegetation incubated in a saline solution resulted in higher DOC production compared to de-ionized (DI) water. Interactions between these variables can have compounding or neutral effects on DOC production. Decreases in water level can create a shift in vegetation community from *Sphagnum* spp. to vascular vegetation (Strack et al., 2006), that may increase DOC production. Following a decrease in water level, soil temperatures may increase as latent heat losses decrease, while the oxic zone will become larger, further increasing peat degradation (Waddington et al., 2015). However, increasing the aerobic zone may also favour CO_2 over DOC as the end product of microbial metabolism (Strack et al., 2006). As DOC production increases, the associated organic acids released may decrease pH, decreasing DOC solubility and limiting further increases in DOC concentration, particularly as it pertains to hydrophobic acids (Clark et al., 2005). It is important to monitor environmental variables in tangent with vegetation communities to assess the potential interactions that may affect DOC production.

DOC quality can be assessed using spectrophotometric and fluorescence spectroscopy methods, allowing inferences about DOC structure to be made. Spectrophotometric properties reported include specific absorbance of ultraviolet wavelengths normalized to DOC concentration ($SUVA_{254}$), which is positively correlated with aromaticity (Weishaar et al., 2003), and the ratio of absorbance at 250 nm to 365 nm (E2/E3), which is negatively correlated with molecular weight

(Helms et al., 2008). Absorption of light at shorter wavelengths (ultraviolet) is more common within carbohydrates, whereas conjugated systems, such as alkenes and aromatics, absorb light within the UV-vis spectrum (190-780 μm) (Aiken, 2014). Fluorescence is the emission of light that can be measured as electrons return to ground state from an excited state when exposed to a photon (Valeur, 2001). Common fluorescence indices include the fluorescence index (FI), humification index (HIX), and freshness index (β/α). The humification index (HIX) has been previously used in aquatic (Bourbonniere, 2010) and terrestrial (Kalbitz et al., 2003) landscapes to determine the degree of humification of organic carbon sources. The fluorescence index (FI) can be used to indicate the degree of microbial or terrestrial contribution to the DOC pool. Cory and McKnight (2005) found that DOC with an FI of 1.4 had greater microbial influences, whereas an FI closer to 1.9 indicated greater terrestrial inputs. The freshness index (β/α) has also been used to indicate the relative age of organic compounds; Wilson and Xenopolous (2009) modified the method determined by Parlanti (2000) such that β refers to the amount of recently produced or authochthonous organic matter, while α is associated with older, allochthonous organic matter. Rastelli (2016) found that areas within a constructed wetland and outflow had lower FI and β/α relative to the margin and upland, while the HIX was comparable between all locations. This indicates that though humification was similar across the site, DOC within the wetland was more processed, externally produced, and influenced by microbial activity. To contrast, the upland and margin were influenced by terrestrial inputs, with minimal influence from external sources.

Undisturbed peatlands have been studied extensively to assess DOC quality, and must be used as a reference when assessing the success of restoration or reclamation attempts (SER, 2004; Nwaishi et al., 2015). Restored peatlands can show variable DOC quality, resembling both undisturbed and disturbed sites, or can indicate a transition in DOC quality and sources. Olefeldt et al. (2013) found subarctic peatlands to have a highly aromatic signature as $SUVA_{254}$ values increase in areas dominated by peatlands. Restoration activities have been shown to produce a lower $SUVA_{254}$ compared to unrestored sites, indicating a greater vegetation influence on DOC production (Strack et al., 2015). This is due to the release of labile carbon through both root exudates and litter (Strack et al., 2015). Glatzel et al. (2003) found that DOC concentrations at restored sites more closely resembled natural sites compared to unrestored sites, although there was no difference in the humification of DOC across locations. Strack et al. (2015) reported an increase in E2/E3 values post-restoration. This indicates that smaller molecules are being released, which is likely due to limited decomposition and vascular plant inputs. However these values were still not significantly different from an unrestored site, indicating that a deep water table continued to have an impact on biogeochemical dynamics at the restored peatland. As the Nikanotee Fen may become a novel ecosystem, comparison to natural systems is important to ascertain which biogeochemical processes will dominate DOC production and influence DOC quality. Therefore, the objective of this study is to characterize vegetation and environmental controls on DOC quantity and quality within a constructed fen watershed and nearby reference sites over a two-year period.

2.2 Study Sites

The study sites, including the experimental fen and natural reference sites are located in northeastern Alberta, within a 40 km radius of Fort McMurray. This area receives on average (30-year climate normals) 419 mm of precipitation per year, and has an average temperature of 1.0 °C (1981-2010; Fort McMurray A station, Environment Canada, 2017). On May 1, 2016, the Horse River Fire began southwest of Fort McMurray and expanded through the Wood Buffalo region. It was declared to be under control on July 4, 2016, although the fire had already spread through two reference sites, the rich and saline fen (Figure 2-1). As a result, field work and all sampling was limited to July and August in the 2016 season.

Figure 2-1. Post-burn within the rich fen (left) and saline fen (right) at the beginning of July, 2016. Vegetation recovery is substantially greater at the vascular-dominated saline fen, relative to the forested rich fen, and depth of burn is much greater at the rich fen (13 cm) compared to the saline fen (<5 cm).

Constructed Fen

The constructed fen (CF) is a 2.9 ha fen, located within a 32.1 ha constructed watershed. This includes a 7.7 ha tailings sand aquifer that promotes water recharge, which is then directed towards the fen (Ketcheson et al., 2016). Surrounding the fen and upland are three reclaimed slopes comprising 50 cm of peat/mineral mix, on 100 cm of a secondary capping layer (low sodic soil) (Ketcheson and Price, 2016). Water infiltration through tailings sand produces groundwater enriched in dissolved solutes derived from residual amounts of oil sands process-affected water (OSPW) (Simhayov et al., 2017), with *EC* ranging between 1000 and 2800 μs/cm (Kessel, 2016) that discharges to the fen. Above the tailings sand layer, underneath the fen and transition zone is a high permeability petroleum coke underdrain which distributes the hydraulic head equally below the fen. This allows water to be conducted upwards through the fen profile (Figure 2-2).

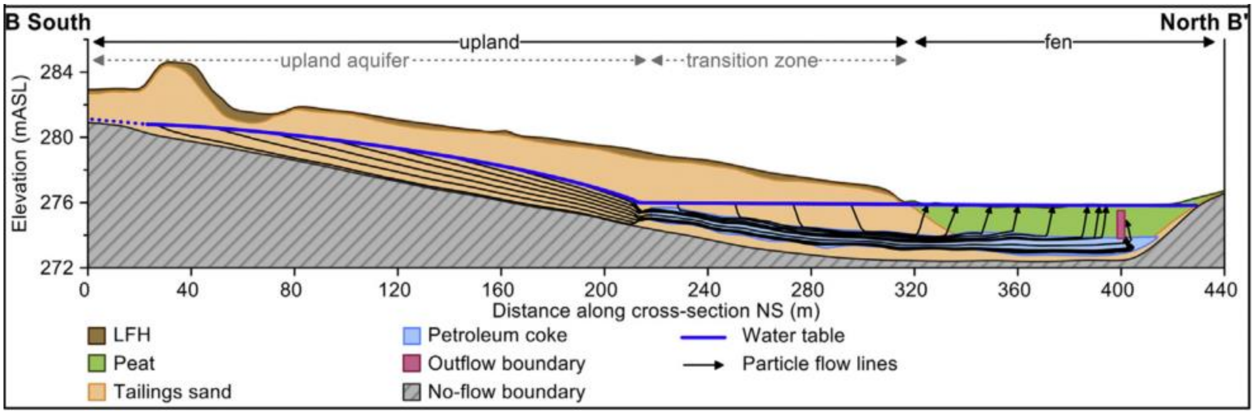

Figure 2-2. Soil material placement and depths across the constructed watershed (from Ketcheson et al., 2017). Black arrows indicate particle flow paths from upland (left) to fen (right).

The fen is composed of two metres of peat, collected from a nearby fen dewatered for two years prior to extraction, placed on 50 cm of highly conductive petroleum coke that overlies 50 cm of tailings sands similar to that which forms the upland aquifer. Fen pore-water also has elevated *EC*, ranging from 1500 µs/cm to 2500 µs/cm due to groundwater inputs from the tailings sand aquifer. Construction was completed in January 2013, while vegetation planting was not completed until July 2013. The experimental design of the fen revegetation scheme is a randomized split-block, split-split plot design with 12 replicates (Figure 2-3). However, due to wet conditions only six blocks were fully planted, with three blocks partially planted. The remaining three blocks were revegetated in 2014 following further peat placement. Vegetation planted on site includes *Carex aquatilis*, *Juncus balticus*, mosses via the moss layer transfer technique (Quinty and Rochefort, 2003), and bare control cover types. Seedlings used for vascular plant establishment were propagated in a commercial nursery (Borkenhagen, unpublished). The direct sowing of fen plant (vascular) seeds also occurred, assuming moss species would naturally colonize (Daly et al, 2012).

Donor material for the moss layer transfer technique, collected from a nearby rich fen, was applied in July 2013, at a 1:10 area ratio of donor to reclamation site (Quinty and Rochefort, 2003). Though equal area was allotted for the establishment of each treatment, *C. aquatilus* has become the dominant vegetation type within the fen, followed by *J. balticus,* and in 2016 virtually no bare areas existed except those included in this study. *Typha* spp. has also colonized large areas where standing water occurs, and was included in the analysis in July, 2015 (Figure 2-3).

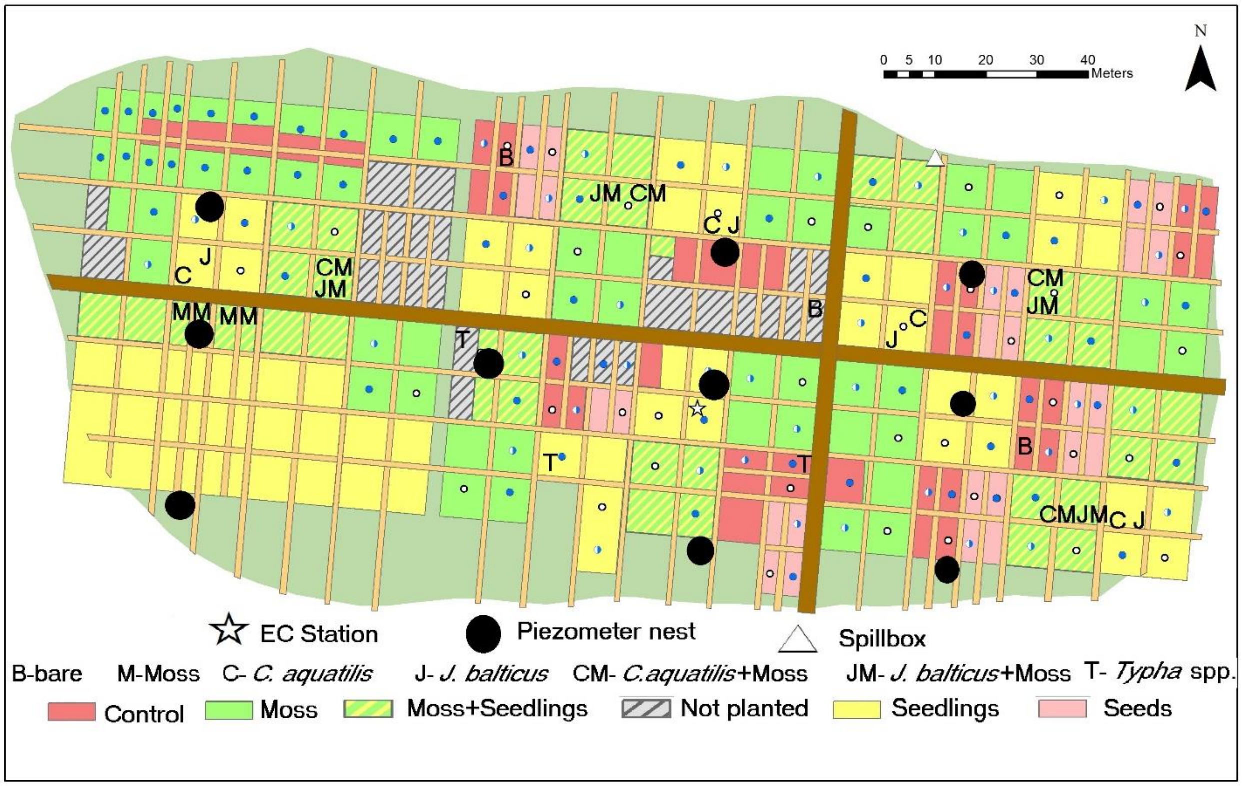

Figure 2-3. Random split-block design for vegetation, mulch, and weeding treatments at the CF (adapted from Borkenhagen (Fen Experimental Design), 2015). Blank circles (no outline): mulch-no weeding, blank circles (outline): no muclh-no weeding, blue/white circles: mulch-weeding, and blue circles: no mulch-weeding treatments. All treatments placed on no mulch-no weeding treatments

Saline Fen (SF)

The saline fen (SF) is located ~10 km south of Fort McMurray (56°34.398 N, 111°16.518 W), is dominated by *Juncus balticus, Calamagrostis stricta*, and *Triglochin maritima*. The site is extremely saline due to the presence of halite deposits, which produces a saline groundwater source. *EC* values have been recorded above 30 ms/cm at southern areas (Wells and Price, 2015), however values in the north end range 11-17 ms/cm (Murray, 2017). Peat depth ranges 0.75-1.5 m.

Rich Fen (RF)

The rich fen (RF), or Poplar Fen, is located ~20 km north of Fort McMurray (56°56.330 N, 111° 32.934 W), is a treed moderate-rich fen, dominated by *Larix laricina, Betula pumila, Equisetum fluviatile*, *Smilcina trifolia, Carex* spp., and brown mosses, primarily *Tomenthypnum nitens*. Peat depth is about 1-1.5 m thick.

Poor Fen (PF)

The poor fen (PF), or Pauciflora fen, is located ~40 km south of Fort McMurray (56°22.610 N, 111° 14.164 W), is a ~8 ha fen, with a forested upland. Characteristic plant species include *Sphagnum* spp., *Carex* spp., *Picea mariana*, *Betula pumila*, and *Chamaedaphne calyculata*. The northern and southern areas are dominated by *Sphagnum angustifolium* and *Sphagnum fuscum*, with almost no presence of trees. *Picea mariana* density is largest in the central portion of the fen. Average peat depth is ~4 m, ranging from 1-10 m across the site.

2.3 Methods

Instrumentation

To assess vegetation effects on DOC production, pore water samplers were installed adjacent to gas flux collars targeting the treatments/vegetation covers at CF, PF, and SF. This includes seedlings of *C. aquatilus, J. balticus*, moss, moss+seedlings, *Typha* spp. and bare (control) plots at CF, *J. balticus* and bare at SF, *C. aquatilus*+moss and moss at PF. Four sets of samplers were placed at 20 cm (rooting zone) and 70 cm (below rooting zone; A. Borkenhagen, unpublished) within each treatment (Murray et al., 2017). Pore water (PW) samplers were made using 20 cm long, 2.54 cm inner diameter PVC pipe slotted in the middle 10 cm, with stoppers inserted at both ends. Nitex screening (250 µm mesh size) covers were sewn and placed around the slotted intake to prevent clogging, and Tygon® tubing was attached to the top stopper and extended above the surface (Strack et al., 2004). A three-way valve was attached to the end of the tubing at the surface.

Ten piezometer nests were installed across the constructed fen, with depths targeting each soil material layer; 30, 50, 90, 150 cm (peat), 225 cm (petroleum coke), 275 cm (tailings sand) (Figure 2-3).

Previous research has shown no significance difference in DOC concentration and quality between 50, 75, and 100 cm depths at the reference sites (Khadka et al., 2016). Therefore, all reference sites used water samples extracted from piezometers at 50 cm in transects that were installed parallel to the flow direction at each site. Piezometers were paired in three groups of two, with one piezometer in each group placed in each of a hummock and hollow. All piezometers were constructed from PVC pipe (2.54 cm inner diameter), with a 20 cm slotted intake, and wrapped with filter sock. Only 50 cm piezometers were used for comparisons across sites.

Water Sampling

Water samples for DOC concentration and spectrophotometric analysis were extracted once each month during the growing season from piezometers in June-August (2015) and July-August (2016). In July of 2015, all piezometers were additionally sampled for fluorescence spectroscopy samples. The piezometers were purged (minimum three well volumes) within 24 hours of extraction. All samples were extracted using a 12V peristaltic pump with vinyl tubing, and each soil type had designated tubing to minimize contamination. The tubing was flushed with de-ionized water prior to sampling. To collect samples from 200 mL PW samplers, one pore volume was flushed prior to sample extraction the same day. Porewater samples were extracted once each month from June-August (2015) for DOC concentration, spectrophotometric, and fluorescence spectroscopy analysis. Due to sampling limitations, *Typha* plots were only sampled in July 2015. A volume of water (~50 mL) was collected into a clean reservoir for in-field measurements of environmental variables (electrical conductivity, pH, temperature). An electrical conductivity (*EC*) and temperature (*T*) probe (Thermo Scientific™ Orion™ Conductivity and Temperature probe) and a pH probe (Thermo Scientific™ Orion™ Economy Series pH Combination Electrode) were inserted into this extracted volume. *EC* probes were calibrated to 1413 μS/cm monthly, and pH probes were three-point calibrated to a pH of 4, 7, and 10 daily before use. Water table was measured in tandem with sampling at each location. After the above procedures, another water sample was taken in a clean 60 mL high density polyethylene vial for concentration and spectrophotometric analysis, or 40 mL amber borosilicate vial for fluorescence spectroscopy samples, and stored in a cooler until they were returned that day to the laboratory, where they were stored at 4°C. Samples were filtered within 24 hours through 0.45 μm nitrocellulose filters, then decanted into 60 ml vials for DOC concentration, spectrophotometric, and fluorescence spectroscopy analysis.

DOC Concentration and Chemistry Analysis

All samples were analyzed using a PerkinElmer UV/VIS Spectrophotometer Lambda 35 to measure absorbance at 250 nm, 254 nm, and 365 nm wavelengths. The concentration of DOC was determined using a Shimadzu TOC analyzer (Environmental Sciences Program, University of Calgary) by the Non-Purgeable Organic Carbon (NPOC) method. This includes sparging samples with gas, converting inorganic carbon (IC) to CO_2, which is subsequently released. As TOC was determined on filtered samples, this represents DOC. In 2015, a 20% subset of samples were selected to measure DOC, with values regressed against absorbance at 250 nm (a250) to estimate DOC for all samples. Correlations were determined for each site, and sediment type (peat, mineral) (Appendix 1). In 2016, all water samples were analyzed for DOC concentration. In cases where DOC concentration or absorbance were high enough to saturate the instrument, samples were diluted. DOC concentration and $SUVA_{254}$ were converted to actual values using the dilution ratio for each sample as necessary. Fluorescence Dissolved Organic Matter (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. Fluorescence index tests were performed in R (Core

Team, 2016) using codes provided by Dr. Claire Oswald at Ryerson University, and edited by Nadine Shatilla at McMaster University.

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 as:

At an excitation of 370 nm: $$\frac{Emission\ at\ 470\ nm}{Emission\ at\ 520\ nm} \tag{2-1}$$

The freshness index (Wilson and Xenopoulos, 2008) was used to indicate the relative proportion of recently produced dissolved organic matter. The β/α for an individual sample can be calculated as:

At an excitation of 310 nm: $$\frac{Emission\ at\ 380\ nm}{\begin{array}{c}Maximum\ emission\ between\\ 420\ nm\ and\ 435\ nm\end{array}} \tag{2-2}$$

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

$$\frac{Sum\ of\ emission\ from\ 435\ nm\ to\ 480\ nm}{(Sum\ of\ emission\ from\ 300\ nm\ to\ 345\ nm) + (Sum\ of\ emission\ from\ 435\ nm\ to\ 480\ nm)} \tag{2-3}$$

$SUVA_{254}$ (Weishaar et al., 2003) was used to indicate the relative amount of aromatic carbon present, in which a high $SUVA_{254}$ correlated to higher aromatic carbon. $SUVA_{254}$ was calculated as:

$$\frac{UVA\ (cm^{-1})}{DOC\ concentration\ (mg/L)} * (\frac{100cm}{m}) \tag{2-4}$$

E2/E3 (Helms et al., 2008) was used to assess the relative molecular weight of the organic matter present, in which a high E2/E3 value indicates a low molecular weight. E2/E3 was calculated according to:

$$\frac{a250}{a365} \qquad (2\text{-}5)$$

Data Analysis

R (R Core Team, 2016), was used for all statistical analyses. All variables were tested for normality using the Shapiro-Wilks test prior to analysis. Log-transformation was performed when data did not meet the requirement for normality. Linear mixed effect model (function “lme”, package “nlme”; Pinheiro et al., 2015) was used to test the effect of vegetation treatment, depth, and site on DOC concentration and quality, where the sampling cycle was treated a random factor to account for repeated measures. When there was a significant effect, a post-hoc analysis using Tukey pairwise comparisons (function “glht”, package “multcomp”; Hothorn et al., 2008) was used to assess differences between locations. A pairwise t-test was used to determine if DOC concentration or quality was significantly different between sampling years at each site. Linear regressions were used to assess correlations between environmental variables and DOC concentration and quality. A value of $p \leq 0.05$ was used to determine significant effects for all analyses.

2.4 Results

Environmental Conditions

There was no significant relationship between vegetation treatment and water table at the CF or PF, although at the SF the water table was significantly ($p<0.001$) shallower at bare plots (16 ± 11.5 cm) than at *J. balticus* plots (27 ± 7.5 cm). No significant relationship between all other environmental variables (pH, *EC, T*) and vegetation type was observed.

Although environmental near-surface variables (*WT, EC, T, pH*) did not vary at CF between treatments; they did exhibit depth dependency. Depth did not have a significant impact on *EC* within the CF in 2015, while in 2016 depth did have an influence ($F_{6,63}=3.12$, $p=0.01$). Specifically, in 2016 samples from 30 cm exhibited significantly higher *EC* values than all other peat depths. In 2015 ($F_{5,50}=12.32$, $p<0.001$) and 2016 ($F_{6,63}=20.42$, $p<0.001$), mineral layers had a significantly higher pH than peat layers. In 2015, there was a significant influence of depth on pore water *T*, as *T* decreased with depth ($F_{5,53}=18.01$, $p<0.001$). All peat depths had higher *T* than in mineral layers, except for 150 cm, which had a comparable *T* to both petroleum coke and tailings sand. Near-surface (30 cm) peat was significantly warmer than all other depths except for 50 cm. There was no effect of depth on *T* in 2016.

Environmental conditions also varied among sites, particularly *WT*, *EC*, and pH. Site had a significant effect on water table in 2015 ($F_{3,24}=13.09$, $p<0.001$). Seasonal average water table at the CF was significantly shallower than at reference sites (Table 2-1). In 2016, there were differences between all sites ($F_{3,27}=8.59$, $p<0.001$), except SF that was comparable to CF and PF. *EC* varied among sites in both 2015 ($F_{3,24}=261.08$, $p<0.001$) and 2016 ($F_{3,27}= 99.89$, $p<0.001$). SF had the highest seasonal *EC*, and CF had a seasonal average an order of magnitude lower, while PF and RF had an *EC* more characteristic of many fens within the region (Table 2-1). The pH was significantly different across all sites except when comparing CF to SF and RF ($F_{3,22}$= 35.933, p<0.001) in 2015. This was the same in 2016, although CF and SF were significantly different as well (Table 2-1). Sample water *T* exhibited no site dependency in 2015. However, in 2016 CF had a significantly lower *T* than RF and SF ($F_{3,27}$=4.6, p=0.01) (Table 2-1).

Table 2-1. Average (+/-SD) values for environmental variables measured at all sites in 2015 and 2016 growing seasons. All data were collected from piezometers at a depth of 50 cm. Letters that are different indicate a significant difference in values. Water table was measured in wells adjacent to piezometers. Temperature used for analysis was measured in collected water samples.

	Water Table (cm)		*EC* (µs/cm)		pH		*T* (°C)	
	2015	2016	2015	2016	2015	2016	2015	2016
CF	4.0 (8.7)[a]	10.7 (7.3)[b]	2784.1 (898.5)[a]	3403.4 (1637)[a]	7.2 (0.4)[ab]	7.0 (0.3)[a]	16.9 (3.7)[ab]	14.1 (8)[a]
PF	22.6 (8.0)[d]	19.0 (9.5)[c]	59.2 (51)[b]	54.4 (14.7)[b]	5.4 (0.7)[d]	5.1 (0.3)[d]	15.8 (3.3)[ab]	17.8 (1.3)[abc]
RF	20.8 (17.8)[cd]	1.8 (4.2)[a]	341.6 (91.2)[c]	481.3 (119.8)[c]	7.3 (0.7)[a]	7.0 (0.2)[a]	14.8 (5.5)[ab]	19.9 (1.2)[c]
SF	15.5 (10.8)[bcd]	12.2 (11.8)[bc]	15221.2 (2733.1)[d]	17175 (5473)[d]	6.6 (0.7)[bc]	6.2 (0.1)[c]	16.5 (3.7)[ab]	19.4 (1.9)[c]

DOC Concentration

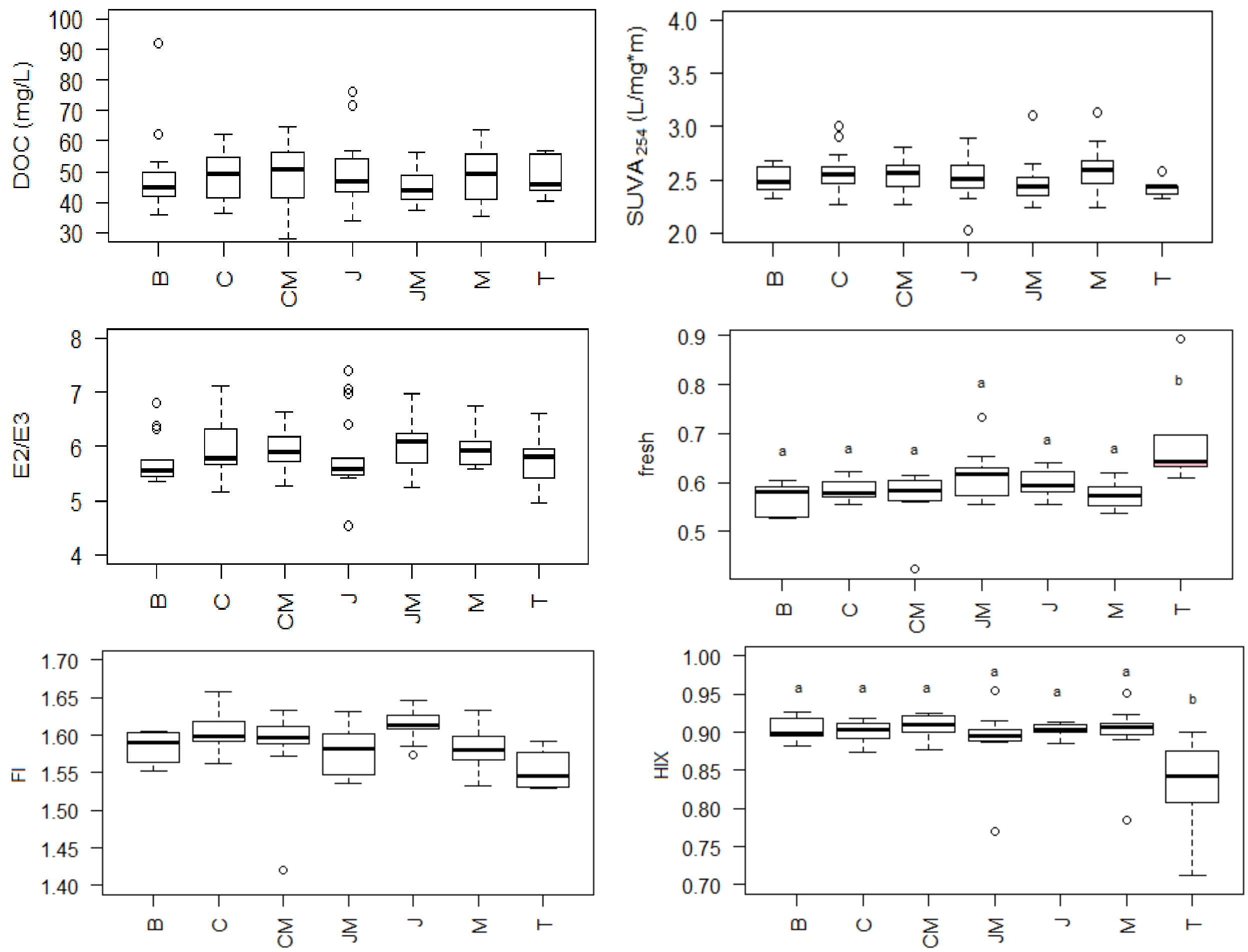

Figure 2-4. DOC concentration (mg/L), $SUVA_{254}$ (L/mg*m), E2/E3, β/α (fresh), FI, HIX across vegetation treatments at the constructed fen at both 20 and 70 cm in 2015. B=bare, C=*C. aquatilus*, CM=*C. aquatilus.* + moss, JM=*J. balticus* + moss, J=*J. balticus*, M=Moss, *T*=*Typha* spp. Different letters indicate a significant difference in values between plots; figures with no letters indicate all plots have similar values.

There was no effect of vegetation treatment on DOC concentration at the CF, PF, or SF at both 20 and 70 cm (Figure 2-4). At CF, depth within the peat profile had a significant impact on DOC concentration ($F_{7,51}$=14.24, $p<0.001$). Considering piezometer samples, in 2015 all depths in the peat profile had significantly higher DOC concentrations than in petroleum coke or tailings sand. Within the peat profile, near surface (30, 50 cm) had significantly higher ($p<0.01$) DOC concentrations than at 150 cm (Figure 2-5). DOC concentrations increased significantly ($p<0.001$)

from June to July, but did not change from July to August. In 2016, depth again had a significant impact on DOC concentration ($F_{6,63}$=5.98, p<0.001). However, DOC concentration was significantly higher only at 30 cm, than all depths within the fen profile. There was no change in DOC concentration between sampling months (July and August only in 2016).

Near surface processes and sediment layer types seemed to impact DOC concentrations within the CF; however, DOC concentration remained stable at this site throughout the sampling period. In contrast, reference sites display more annual variability. In 2015, site had a significant impact on DOC concentration ($F_{3,24}$=21.11, p<0.001). All sites had significantly different DOC concentrations, except CF and PF (Table 2-2). In 2016, DOC concentrations were again, significantly different between sites ($F_{3,27}$=10.85, p<0.001), as SF was significantly higher than all sites. Inter-annual differences in DOC concentration were limited to PF and RF, which decreased and increased, respectively.

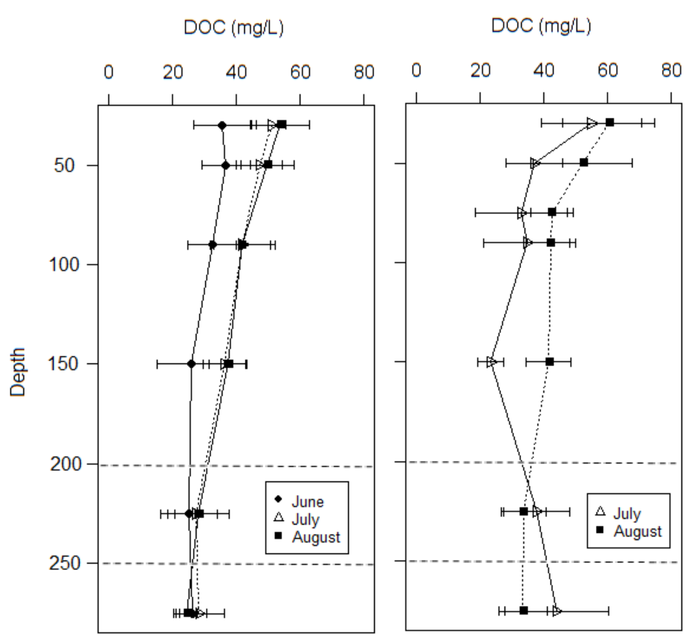

Figure 2-5. DOC concentrations at the constructed fen in a) 2015 and b) 2016 through the fen profile at depths of 30, 50, 75 (2016), 90, 150, 225, 275 cm bgs.

Table 2-2. DOC concentration , $SUVA_{254}$, E2/E3 values across all sites at 50 cm piezometers in 2015 and 2016. Letters which are different indicate a significant difference in values.

	PF		RF		SF		CF	
	2015	2016	2015	2016	2015	2016	2015	2016
DOC(mg/L)	48.7(2.9)^{a}	40.8(2.9)^{b}	23.3(2.0)^{c}	30.7(2.3)^{d}	69.0(4.9)^{e}	66.1(4.5)^{e}	44.5(1.8)^{a}	44.6(2.9)^{a}
$SUVA_{254}$(L/mg*m)	3.6(0.10)^{ab}	3.7(0.17)^{a}	3.9(0.11)^{a}	3.6(0.32)^{ab}	3.5(0.08)^{ab}	3.3(0.23)^{bc}	2.6(0.05)^{c}	2.8(0.10)^{b}
E2/E3	5.7(0.38)^{a}	4.9(0.07)^{bc}	4.9(0.13)^{b}	4.2(0.18)^{c}	5.6(0.26)^{a}	4.9(0.10)^{b}	5.9(0.11)^{ab}	6.1(0.17)^{a}

Environmental Controls on DOC Concentration

DOC concentration at plots with vascular vegetation were more greatly influenced by environmental conditions than bare locations. Reference sites had stronger relationships between *EC* and DOC concentration in *C. aquatilus* and *J. balticus* plots, at PF and SF, respectively (Appendix 2). At CF, DOC concentration across vegetation treatments had a moderate positive correlation with *T* and weak positive correlation with *EC*. Temperature exhibited significant positive correlations with DOC concentration at all treatments that had vascular vegetation, while bare plots did not have any correlation between *T* and DOC (Appendix 2). At the CF, *EC* varied in importance across vegetation treatments, but was most significant at moss, *C. aquatilus,* and *J. balticus* plots, and displayed no relationship at *C.aquatilus*+moss and bare plots.

In 2015, the changes in DOC concentration through the CF profile negatively correlated with pH ($F_{1,54}$=18.64, r^2=0.24, p<0.001), and positively correlated with *T* ($F_{1,168}$=93.25, r^2=0.35, p<0.001). In 2016, *EC* showed a significant positive relationship with DOC concentration ($F_{1,136}$=86.87, r^2=0.39, p<0.001).

In 2015, *EC* had a positive correlation with DOC concentration across all sites (Figure 2-6). However, in 2016 these correlations were less apparent, and became more site dependent. At

CF, the same variables displayed relationships with DOC concentration, in addition to *WT*. However, the DOC concentration became negatively correlated with pH at PF. Additionally, SF and RF no longer exhibited any control of environmental variables on DOC concentration (Appendix 3).

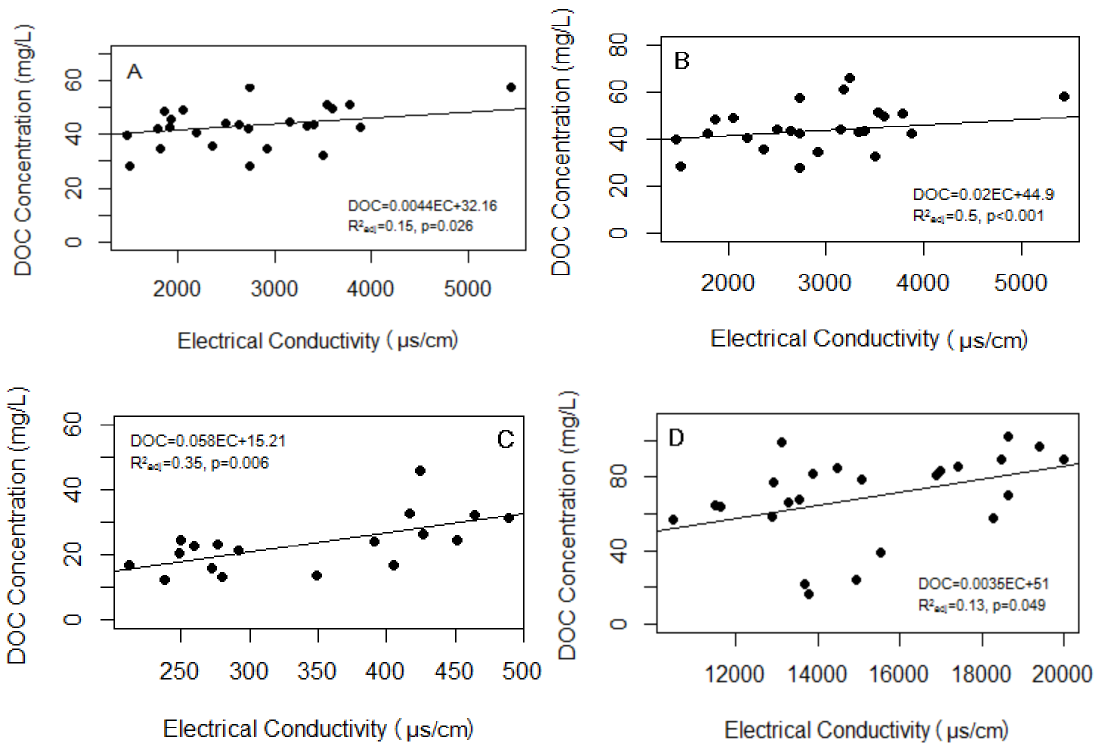

Figure 2-6. Regressions of *EC* and DOC concentration at the a) constructed fen b) poor fen c) rich fen and d) saline fen (bottom right) in 2015.

DOC Quality

At CF, vegetation treatment did not significantly affect FI, $SUVA_{254}$ or E2/E3; however, vegetation type did bring about differences in the β/α ($F_{6,19}$=3.45, p=0.018) and HIX ($F_{6,19}$=4.4, p=0.006), with the *Typha* having a significantly lower HIX and higher β/α than all other treatments (Figure 2-4). There was no difference in spectrophotometric and fluorescence indices between vegetation treatments at reference sites.

DOC quality also varied through the fen profile, appearing less aromatic (lower $SUVA_{254}$), smaller (higher E2/E3), and more microbial-sourced (higher FI) in mineral layers, relative to peat layers. In 2015, the fen profile at the CF showed no seasonal change in $SUVA_{254}$ and E2/E3. In 2016, there was a significant increase from July to August ($F_{1,133}=6.44$, $p=0.012$). This was due to an increase at 75 and 90 cm depths (Figure 2-7). However, E2/E3 did not show a corresponding change in values. β/α ($F_{5,57}=11.56$, $p<0.001$), FI ($F_{5,57}=13.6$, $p<0.001$), and HIX ($F_{5,57}=11.3$, $p<0.001$) varied significantly with depth; β/α and FI were significantly higher ($p<0.001$) in mineral layers relative to peat samples, while HIX was significantly lower in mineral layers ($p<0.001$). However, all fluorescence indices were similar within peat layers.

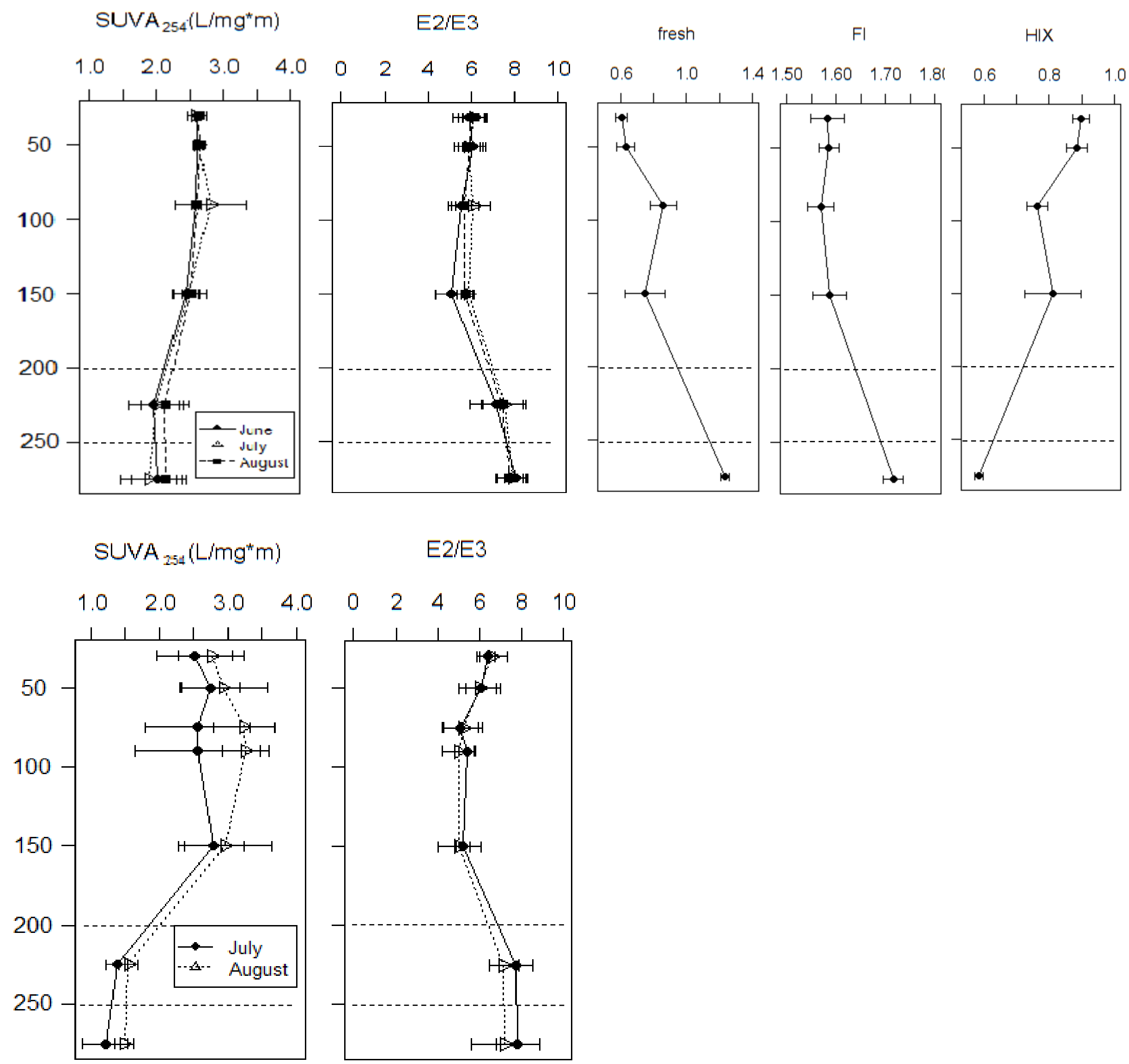

Figure 2-7. $SUVA_{254}$, E2/E3, β/α, FI, HIX values in 2015 (top) and 2016 (bottom) through the fen profile at the constructed fen at depths of 30, 50, 75 (2016), 90, 150, 225, 275 cm bgs. Dashed lines indicate boundary between peat/petroleum coke/tailings sand from top to bottom of the depth profile.

Across sites, $SUVA_{254}$ at CF was significantly lower when compared to reference sites ($F_{3,24}$=2225.2, p<0.001) (Table 2-2). However, in 2016 these effects diminished as CF was comparable to SF, but remained significantly lower than PF and RF. E2/E3 was similar among sites, except between RF and CF in 2015. However, in 2016 all reference sites had significantly lower E2/E3 values than CF ($F_{3,27}$=18.56, p<0.001). HIX was dependent on site ($F_{3,17}$=12.43, p<0.001), as CF and PF were significantly lower than RF and SF (Figure 2-8). FI ($F_{3,17}$=15.08, p<0.001) also displayed strong differences, as all sites had significantly higher values than PF. β/α ($F_{3,17}$=27.6, p<0.001) was also significantly higher at CF compared to RF and PF, and notably higher than SF (p=0.07). This indicates that DOC at the reference sites appears more aromatic, humic, microbial-sourced, and older than within the CF.

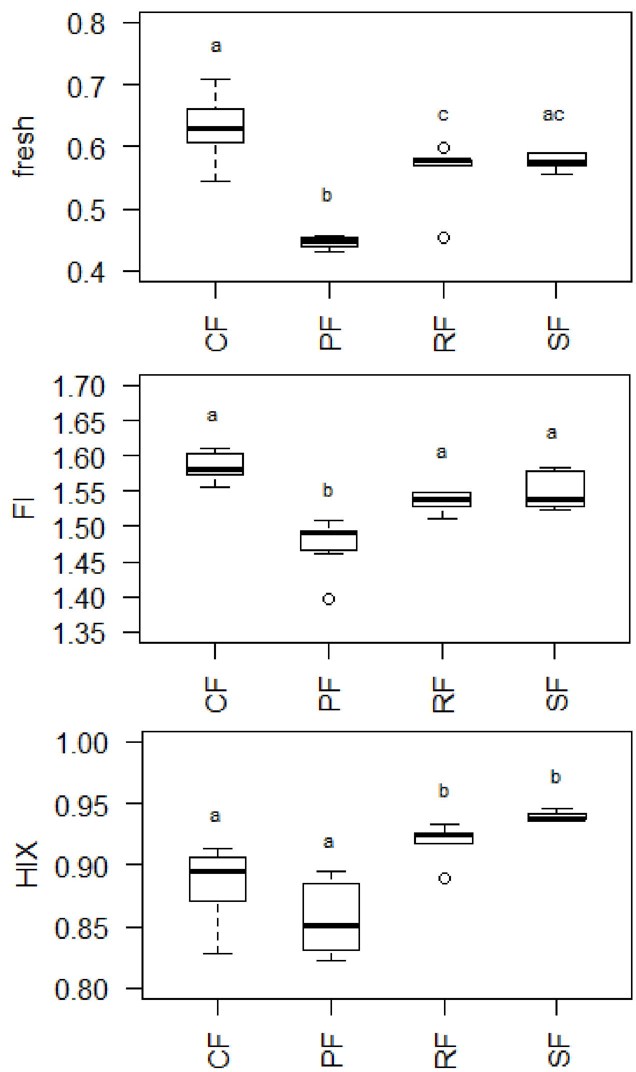

Figure 2-8. β/α (top), FI (middle), HIX (bottom) across all sites in 2015. Different letters indicate a significant difference in values between sites.

Environmental Controls on DOC Quality

DOC quality indices at vegetation plots are solely correlated with *EC* across all sites, with no significant correlations with *WT, T, or pH*. At CF, *EC* had a significant positive correlation with E2/E3 across all vegetation treatments (Appendix 2). All other environmental variables differed in the strength and significance of the correlation with E2/E3 across treatments. Within the reference sites, only a weak positive correlation existed between E2/E3 and β/α with *EC* at SF. This was largely controlled by the relationship that existed at *J. balticus* plots (Appendix 2). There was no significant association between monitored environmental variables, $SUVA_{254}$, HIX, and FI across vegetation treatments at all sites. However, vascular vegetation plots at both reference sites had more significant correlations between quality indices and environmental variables.

At CF, DOC quality through the fen profile correlated with multiple environmental factors. Temperature had positive relationships with $SUVA_{254}$ ($F_{1,168}$=36.94, r^2=0.18, p<0.001), E2/E3 ($F_{1,54}$= 23.1, r^2=0.29, p<0.001), HIX ($F_{1,31}$=34.66, r^2=0.51, p<0.001), and had negative correlations with FI ($F_{1,31}$=15.18, r^2=0.31, p<0.001) and β/α ($F_{1,31}$=29.1, r^2=0.47, p<0.001). E2/E3 had a moderate ($F_{1,54}$= 23.1, r^2=0.29, p<0.001) and weak ($F_{1,168}$=26.3, r^2=0.13, p<0.01) positive association with pH and *EC*, respectively. In 2016, these relationships shifted across indices; $SUVA_{254}$ was negatively correlated with pH ($F_{1,136}$=71.05, r^2=0.34, p<0.001), while E2/E3 exhibited a positive relationship ($F_{1,136}$=42.8, r^2=0.23, p<0.001). Overall, the DOC quality through the fen profile varied with anticipated changes in environmental conditions, therefore they may be controlled by independent processes.

In 2015, EC represented a significant control on DOC quality at PF and CF, specifically as it pertains to E2/E3 (Appendix 3). Water table also displayed some control on $SUVA_{254}$ and E2/E3, producing smaller, less aromatic DOC as the *WT* became shallower. DOC quality at RF and SF exhibited no dependency on environmental conditions. All fluorescence spectroscopy indices across sites displayed no correlation with environmental variables. EC exhibited significant correlations with DOC quality at the CF in 2016; however, at PF, pH became a more important predictor of DOC quality. Again in 2016, RF and SF displayed no dependence on environmental conditions for determining DOC quality. As there are few similarities in DOC quality responses across sites to environmental variables, factors contributing to DOC quality may be unrelated. Correlations are also generally weak (Appendix 3), indicating alternative processes are impacting DOC quality at all sites.

2.5 Discussion

Environmental controls on DOC concentration and quality at the constructed and reference fens

DOC concentrations across all sites fit within the range measured in boreal peatlands and previously at these sites (Fraser et al., 2001; Moore, 2003; Khadka et al., 2016). This shows that DOC accumulation within the constructed fen has resulted in conditions similar to natural sites within the region. Electrical conductivity was the most consistent control on DOC concentration across sites, followed by temperature. Khadka et al. (2016) also found that *EC* and *T* had controls on DOC concentration at the CF. It was hypothesized that *EC* had a significant positive correlation because higher ion concentrations can saturate sorption sites within the peat, increasing DOC concentrations in solution (Kalbitz et al., 2000). Rastelli (2016) also observed a positive correlation between DOC concentration and *EC* at the Sandhill Fen, and suggested that an increase in sodium promoted microbial activity. An increase in *EC* can also be produced through increases in DOC concentration, due to a release of DOC with charged functional groups, and further mineralization that releases ions (Khadka et al., 2015). DOC dynamics at CF generally seem disconnected from interannual climate effects, and are internally controlled. At all reference sites, *T* increased and *WT* depth decreased from 2015 to 2016. This shift coincides with changes in DOC concentration, and decreases in E2/E3 values at reference sites. Increases in *T* have previously been linked to greater microbial activity (Boddy et al., 2014) that has been associated with decreases in E2/E3 values (Khadka et al., 2015). However, at the CF *T* decreased and *WT* depth increased over the study period, while DOC concentrations and quality remained consistent. Decreases in pH have historically been shown to lower DOC solubility (Clark et al., 2005), though the site which exhibits the lowest pH also has a moderate DOC concentration relative to other sites. Furthermore, the CF, which has the highest pH, had a significantly lower DOC concentration compared to SF. This indicates that environmental controls may have limited impacts on DOC production at the CF, despite observed correlations between environmental variables and DOC dynamics. Broader scale hydrological controls may also have a greater influence, such as flushing during precipitation events, which correlates with temperature and chemical variables.

Furthermore, there were few significant correlations between environmental variables and DOC quality at reference sites. Clark et al. (2005) determined that there are time lags between changes in *T* and pH with DOC concentration in a growing season of up to four weeks. Therefore, it may be more appropriate to use seasonal or inter-annual trends to explain changes in DOC concentration and quality, as opposed to using measurements taken on the day of sampling (Treat et al., 2007). However, when assessing plot-scale impacts, a greater number of correlations were observed. Specifically, at the CF, DOC concentration and E2/E3 were largely impacted by environmental variables at plots with vegetation, while bare plots exhibited few significant correlations. At reference sites, vascular plots also exhibited stronger correlations between environmental variables and DOC dynamics. Additionally, fluorescence spectroscopy indices displayed a greater dependence on *EC* at PF and SF. This indicates that the source of DOC is more influenced by environmental variables at reference sites, while at the CF, DOC structure may be indirectly impacted by *EC* and *T*. Indirect impacts may be attributed to the effect they have on vegetation, as plots with vascular plants were more impacted in DOC concentration and quality than bare or moss plots.

The fen profile at CF also displayed some relationship between DOC dynamics and environmental variables; however, this is likely related due to hydrochemical and physical evolution of the fen. Temperature will naturally decrease through the fen profile as heat transfer downwards is limited, and most *T* fluctuations occur within the rooting zone (Clymo, 1984). This coincides with the decrease in DOC concentration, and changes to FI, $SUVA_{254}$ and HIX at depths greater than 50 cm. An increase in concentration at the surface is likely due to a combination of greater production through vegetation inputs and evapoconcentration. The increase in HIX and $SUVA_{254}$ corresponds to an increase in both humic characteristics and aromaticity, but an increase in FI indicates a greater proportion of microbial sources are present. This indicates a more complex array of processes controlling DOC production are occurring within the rooting zone, compared to deeper in the fen profile where microbial degradation occurs more consistently, but is selective and limited in its effects. EC can also display a similar pattern, as evapoconcentration and movement of groundwater upwards through the peat profile will increase ion concentrations towards the surface of the peat (Kessel, 2016). Also, the pH will naturally develop a gradient through the peat profile as acids are released through organic soil degradation and DOC production (Shotyk, 1988; Bourbonniere, 2010). Therefore, it is more likely that the DOC and pH change are affected by similar processes resulting in the negative correlation, or the DOC production is increasing the acidity. It is unlikely that this correlation represents a direct effect of acidity on DOC solubility, as an increase in DOC concentration would be expected as pH increases.

In 2016, the Horse River Fire burned extensively across RF and SF. However, the severity of the fires was dissimilar between sites. SF is dominated by *J. balticus* and *Calamagrostis stricta*, and fire was only propagated across vascular vegetation and within the top 5 cm of the peat. In fact at plots adjacent to DOC sample locations, litter was still present at the surface of most plots. At RF, peat burn depths averaged 13 cm (Elmes et al., 2017), with dense, dry peat propagating smouldering deep into peat layers. The effects of the fire are reflected in the temperature increase seen at both sites, whereas PF and CF do not significantly increase in temperature. Although, this is not reflected in changes in DOC concentration at SF, RF does have a significant increase in DOC concentration in 2016; however, 2015 had the lowest DOC concentration measured from 2013 to 2016 (see also Khadka et al., 2016) and, therefore the concentration is falling back within expected values. *WT* was also significantly lower in 2015 at RF, and rewetting may mobilize DOC which has been produced and adsorbed to peat surfaces during the fire (Lundquist et al., 1999).

Overall, though EC does represent the most common control on DOC concentration and quality across sites, correlations were generally weak. All other variables have minimal influence on DOC concentration and quality. This indicates that there are alternative controls, outside of environmental variables measured within this study which have important controls on DOC dynamics, such as inputs from vegetation.

Impact of vegetation and microbial activity on DOC dynamics

Though DOC concentration at CF is comparable to reference sites, it is unlikely that it is sourced through comparable processes. All indices consistently indicated that DOC at the CF is smaller, more recently produced, terrestrially-sourced, and less recalcitrant compared to natural sites. Rastelli (2016) had similar DOC concentrations at the Sandhill Fen in 2015, compared to the CF in 2016. As the Sandhill Fen was completed in 2012, the development of the fen related to DOC dynamics is comparable. It was also determined that β/α was significantly higher at Sandhill Fen, while HIX and $SUVA_{254}$ were significantly lower compared to reference sites. FI was significantly different from both reference sites at Sandhill; however, RF had a higher value and PF was lower, relative to Sandhill fen. $SUVA_{254}$, HIX, and β/α all showed similar results in 2015, indicating that the development of DOC quality is comparable between constructed sites. A low $SUVA_{254}$ indicates DOC with a low degree of aromaticity dominates the DOC pool, while a high β/α suggests that the DOC is recently produced. This is characteristic of plant-sourced DOC, as root exudates and fresh litter will typically result in DOC with a less humic character than microbially-sourced DOC. In contrast, reference sites have DOC that appears to be sourced from both vegetation and peat. High concentrations at SF are likely a result of increased microbial degradation due to saline conditions (Kalbitz et al., 2000) and large root exudate input from a dominantly vascular vegetation community. To contrast, PF and RF are dominated by both vascular and moss species; moss has been shown to produce less DOC than vascular species (Khadka et al., 2015). Additionally, high nutrient availability at the RF may promote microbial cycling of DOC (Kelley et al., 1997), which may be why it has a lower DOC concentration than other reference sites. As microbial degradation of organic soils occurs in tandem with the production of peat, this is indicative that peat formation, and the introduction of a more diverse DOC pool is characteristic of natural peatlands.

Within the CF, DOC sources can vary in their quality. It was shown that commonly used evaulation techniques (i.e. $SUVA_{254}$, E2/E3) do not distinguish all differences in DOC sources, as they characterize all carbon contained within the sample. Alternatively, fluorescence spectroscopy measures a portion of the DOC pool (N. Shatilla, personal communication, 2017). HIX and β/α were significantly different in *Typha* plots on site compared to other treatments. Trinder et al. (2008) assessed DOC contribution in a tracer test using $^{13}CO_2$ at a cutover peatland, and found that up to 29% of ^{13}C was released beneath plants as root exudates. It was also found that DOC which contained ^{13}C varied significantly in concentration between the vascular plants studied. Crow and Wieder (2017) compared respiration from microbial degradation of root exudates and root respiration in a northern Canadian bog; CO_2 emissions from processing of root exudates accounted for up to 50% of CO_2 emissions in sedge plots. This was much higher than seen in shrub and moss plots. Conversely, Armstrong et al. (2012) observed higher DOC concentrations in shrub plots compared to sedge or moss plots. This indicates that the DOC pool can be substantially increased from root exudates, and has a non-aromatic, small, labile structure that is highly bioavailable. Furthermore, vegetation type can play an important role in determining the quality of the DOC pool. Currently, the CF is dominated by *Typha* and *C. aquatilus;* however, as the vegetation composition changes, DOC composition may also change, as shrub and moss cover may increase over time. *Typha* plots were commonly found in areas of open water, where DOC may have been affected by photodegradation, potentially reducing the presence of aromatic structures through mineralization (Obernosterer and Benner, 2004). However, as there was no concurrent decrease in DOC concentration, it is unlikely that this is the cause of the shift in quality. Though DOC quality at treatments within the CF did not vary, it is important to recognize that non-peatland species could also present important shifts in DOC quality, especially when they become a dominant vegetation type within the ecosystem.

Khadka et al. (2016) predicted that the DOC source within the fen would shift from microbially-produced to plant-sourced as vegetation productivity increased. Price et al. (2017) determined that net ecosystem exchange has increased from 2013 to 2015 within the CF, with a small increase from 2015 to 2016. This coincides with a large increase from 2013 to 2015 in DOC concentration, and large shifts in DOC quality (Khadka et al., 2016). From 2015 to 2016, DOC concentration and quality stayed consistent. This timeline suggests that inputs of root exudates are increasing as vegetation becomes more successful over time, and as NEE stabilized, changes in DOC dynamics within the fen were minimized. This is not uncommon to post-restoration responses observed in peatlands. Strack et al. (2015) detected higher E2/E3 and lower $SUVA_{254}$ values at a restored site relative to a nearby unrestored site. This too, was attributed to an increase in vascular plant cover, and an associated contribution to the DOC pool through root exudates. Microbial activity may also be promoted due to the rhizosphere priming effect (RPE) (Kuzyakov, 2002), and would explain why the DOC structure at the CF appears more plant-sourced, but indicates a mix of microbial and vegetation activity. RPE occurs when the input of labile carbon stimulates microbial activity, and can occur within a single season. Though microbial activity is the dominant source of DOC at reference sites, the total activity may be lower as the input of bioavailable DOC at the CF has shifted so dramatically over a short time period. The consistency in DOC quantity and quality within the CF may also be affected by microbes limiting a further accumulation of plant-sourced DOC. Unless the microbial community begins to offset the large input of fresh, labile DOC and produce peat that may offer a more complex, humic source of DOC, the biogeochemical function of the CF will not resemble that of reference peatlands. A large labile DOC input accompanied by a stimulated microbial community may promote shifts in biogeochemical processes. Martins et al. (2017) observed concurrent sulfate reduction and methanogenesis in the presence of high DOC concentrations, indicating that a large labile carbon substrate may reduce competitive inhibition of methane production. However, further investigation into microbial community characteristics is required to determine if this process may occur within constructed wetlands.

In this study, groundwater that discharges into the fen appeared smaller, less aromatic, and autochthonous. Groundwater beneath peatlands has been shown to contain DOC with low $SUVA_{254}$ and high E2/E3 (Olefeldt et al., 2013), which is likely due to microbial activity that has broken down all bonds providing energy to the microbial community. Zaccone et al., (2009) found that HIX decreased through the peat profile, particularly because vertical transport of DOC was limited, resulting in stratification within peat layers. However, this process would be limited in the CF due to a lack of layering. Fraser et al. (2001) determined that the FI increased through the peat profile into a groundwater source. They determined that this was due to increased microbial degradation of DOC sources, which break down DOC structures. This reduces the the amount of aromatic structures and decreases molecular size. Oxidative polycondensation may not have occurred within the mineral layers, limiting the humic character of DOC. However, within deeper peat layers the presence of suitable microbes for processing DOC may be present in greater concentrations, allowing for polycondensation to occur, increasing the humic character of DOC. This is further supported by the increase in $SUVA_{254}$ and decrease in E2/E3 into the peat profile. Polycondensation may occur once DOC enters the lower peat profile, increasing the aromaticity and size of DOC molecules. As water continues to move upwards through the peat profile, this signature then becomes dominated by vegetation inputs, shifting the structural characteristics of the DOC. This shift in size and aromaticity may also be due to the presence of naphthenic acids that are present on tailings sand as a by-product of oil sands production (Mackinnon et al., 2001).

As they do exist as DOC and, to our knowledge, have never been characterized using spectrophotometric and fluorescence spectroscopy methods, it is difficult to know what impact they will have on the indices used in this study. However, the general structure of naphthenic acids typically includes one to four benzene rings, and a carboxyl group (Hsu et al., 2000). Despite their small size and functional groups which may offer ideal locations for microbial degradation, naphthenic acids produced from oil sands process-affected water are largely recalcitrant, and therefore are persistent and unchanged within groundwater (Han et al., 2008). This may also explain why the DOC appears autochthonous, as it is sourced from the tailings sand as opposed to leaching from organic soils above the upland. Lab experiments have shown that naphthenic acids have a very low $SUVA_{254}$ and high β/α relative to DOC produced by vegetation and leached off of tailings sand (data not shown) and so their presence may be contributing to this appearance in the DOC quality, particularly as $SUVA_{254}$ represents an average of the aromaticity present within the sample (Weishaar et al., 2003). There has also been no previous work done on groundwater DOC quality using β/α index within peatlands, therefore it is difficult to compare to natural analogues. Regardless, it is important to develop a baseline for constructed environments, and data from the present study can be utilized for identifying organic sources within reclaimed areas when using tailings sand as a construction material.

2.6 Conclusion

Vegetation appears to be the dominant input of DOC within the CF, through a combination of root exudates and fresh litter inputs. This source dominates the DOC pool, more so than at natural sites that appear to source DOC from both vegetation and microbial inputs. Traditional indices that are used throughout literature indicate that DOC within the constructed fen is smaller, less aromatic, and sourced from vegetation as opposed to microbial production. Spectrophotometric and fluorescence indices indicate a greater microbial contribution deeper in the peat profile, however, this signature is lost as plant-sourced DOC dominates the DOC pool near the surface. Though previous work indicates that the constructed fen is functioning hydrologically and from a carbon storage perspective, biogeochemically it does not resemble natural analogues. Peat accumulation may be required to promote biogeochemical cycling that mimics reference sites within the region, though this will occur on a much longer time scale than is currently being analyzed. The microbial community may begin to increase as the amount of bioavailable DOC increases; however, it is unlikely this will transform the DOC quality such that it resembles reference sites over a short time scale. As these ecosystems will likely be incorporated into a larger reclaimed landscape, it is important to keep this long-term biogeochemical evolution in mind, as wetland-sourced DOC has been shown to have significant impacts on downstream water chemistry and quality. It will also be important to monitor the system long term, to determine if the quantity of DOC within the fen will remain consistent, increase, or decrease as DOC sources evolve through time. As one distinct shift in DOC concentration and quality has already been observed within the first decade post-construction, it is reasonable to assume further shifts will occur as plant communities shift, and peat accumulation occurs. Therefore, ecosystems which have the capacity to adapt to shifting water quality would be a good choice to construct directly downstream of constructed fens.

Chapter 3: Flux of dissolved organic carbon through a constructed fen watershed in the Athabasca Oil Sands Region, Alberta

3.1 Introduction

Within the Western Boreal Plain (WBP), dissolved organic carbon (DOC) transport has been shown to be higher in watersheds dominated by wetlands (Eimers et al., 2008). However, disturbance can alter DOC transport across the landscape (Saari et al., 2009; Schelker et al., 2012). Within the WBP, specifically, the Athabasca Oil Sands Region (AOSR), peatlands have been removed for bitumen extraction. Soils that are stripped from the surface, including peat and the litter-fibric-humic (LFH) materials soil layer of upland forests are sometimes stockpiled, and applied to the surface during reclamation activities (Ketcheson et al., 2017). Additionally, tailings sand, which is a by-product of bitumen extraction, can be used in construction of new ecosystems. A fen watershed has been constructed near Fort McMurray, Alberta using such materials. Early post-construction DOC dynamics have been quantified within the fen; however, the importance of DOC inputs from external sources (i.e., runoff, groundwater, precipitation) to the fen have not been quantified. Additionally, it is unknown whether these fluxes are important for export DOC quantity and quality. As DOC can represent up to 25% of the carbon exchange within a peatland (Roulet et al., 2007), it is important to understand the sources of DOC within a constructed watershed, and how each source may impact DOC exported to downstream ecosystems.

DOC can be transported in any water that comes in contact with organic material, including groundwater (Waddington et al., 1997), precipitation (Fraser et al., 2001) and surface runoff (Hongve, 1999; Strack et al., 2011). Since there are multiple sources of DOC within aquatic and terrestrial ecosystems, this can result in a large diversity in DOC quality. Historically, precipitation has not contributed significantly to the DOC budget of peatland ecosystems (Fraser et al., 2001).

Surface runoff typically represents a significant contribution of DOC to downstream ecosystems from both forestlands (Hongve, 1999; Schelker and Bishop, 2009) and wetlands (Laudon et al., 2004). Groundwater can have limited or large DOC contributions to wetlands and forestlands depending on its point of origin, with export from organic-rich soils typically having high concentrations of DOC (Olefeldt et al., 2013). Agron et al. (2008) assessed the quantity and quality of DOC in surface runoff across boreal catchments, and determined that peatland-dominated catchments contributed greater amounts of DOC to export. Additionally, the DOC that was sourced from forestlands had a less aromatic, more bioavailable structure and had a larger impact on downstream DOC biodynamics. However, the relative importance of each contribution within a peatland watershed has not been well documented for quantity and quality simultaneously; therefore, it is difficult to predict what importance the hydrological transport of DOC may represent in a constructed system.

DOC export can vary between hydrological sources, but it will also change within each source depending on the volume of water transported and DOC structure. Large precipitation events that result in large volumes of surface runoff, have been shown to represent a significant portion of the DOC output in boreal ecosystems (Eimers et al., 2008), and can mobilize a greater array of DOC compounds. However, snowmelt and the spring freshet can have highly variable contributions across upland and wetland environments, as snowmelt had a greater contribution to DOC export in forestlands compared to wetlands (Laudon et al., 2003). This relationship has also been shown to vary inter-annually; Jager et al. (2009) determined that snowmelt represented a larger proportion of DOC export in dry years, compared to wet years when the contribution to runoff through rainfall increases. Though there is strong evidence that dry conditions increase degradation of organic material (Strack et al., 2008), this also results in less surface runoff, and an overall decrease in DOC export (Jager et al., 2008). Drier conditions can create small hydraulic gradients, that do not transport large, aromatic compounds effectively. Smaller, aliphatic compounds are typically mobile under all conditions and may represent a large portion of the exported DOC (Boddy et al., 2014).

In the constructed fen watershed, all materials have been produced or collected elsewhere, and placed within the watershed. Organic soils that were extracted and placed within constructed landscapes may exhibit an increase in DOC production and export because the physical movement of organic soils can increase DOC export (Blodau & Moore, 2003). For example, Blodau and Moore (2003) found that incubation experiments resulted in higher DOC production in extracted samples, compared to undisturbed soils, suggesting that physical disturbance during peat collection enhanced DOC production. Dewatering, transportation, and placement of peat also eliminates systematic layering within the peat profile at the constructed fen. This can result in a greater distribution of small pores as the pore structure typical of the upper layer in undisturbed peatlands is not present (Nwaishi et al., 2015), limiting water and DOC transport through the fen (Rezanezhad et al., 2016), and compounding the effect of limited mobility for larger DOC molecules. However, systems that promote surface runoff reduce the amount of water interacting with the soil, reducing dissolution of large, complex DOC compounds (Strack et al., 2011). Therefore, it is important to determine which process is dominant, surface flow or groundwater flow, during outflow events in the constructed watershed.

The relative contribution of each DOC source is difficult to predict when working in natural systems, and may be more unpredictable when assessing disturbed, restored or constructed environments. Assessing DOC dynamics can become more complex when considering hydrological inputs and outputs from wetlands, the magnitude of which may have significant impacts on the DOC budget of a system. Waddington et al., (2008) found that cutover peatlands release greater amounts of DOC than restored cutover systems. However, both types of peatlands resulted in greater DOC export than natural sites within the region. When assessing DOC quality, Strack et al. (2011) found that there was no difference in DOC quality between cutover and restored sites, and quality was largely controlled by hydrological, rather than biogeochemical conditions. However, they found that there were significant seasonal impacts on DOC quality. Disturbances within forestlands may also alter DOC dynamics; Schelker and Bishop (2009) found that harvested boreal forestlands had increased DOC export due to greater surface runoff. Although deforestation impacts on DOC quantity have been studied, the changes to DOC quality have not been assessed in detail.

Nwaishi et al. (2015) have stated that constructed fens in the AOSR may develop into novel ecosystems. Therefore, it is important to determine what components of this system may contribute to variability in export DOC quantity and quality. Within the constructed watershed, runoff, groundwater inputs, and fen discharge have been quantified in initial post-construction conditions. The east slope of the catchment has been shown to produce very little runoff, compared to the west and southeast slopes due to a shallower slope, greater infiltration rate, and potentially more retention and interception from greater vegetation establishment (Ketcheson and Price, 2016). In 2014, the groundwater and surface runoff directed to the fen was 177 and 67 mm, respectively, while discharge out of the fen totalled 127 mm. However, runoff and discharge are largely dominated by snowmelt and the spring freshet; therefore, groundwater and surface runoff may represent a small DOC input through the growing season. The fen has high DOC concentrations, with production primarily occurring as root exudates by vascular vegetation (Chapter 2). Construction materials may also play an important role in determining DOC export. Khadka et al.

(2015) determined that the LFH-mineral mix used as a cover soil in construction of the upland, produced small amounts of DOC in an incubation experiment, much less than was sourced from the fen through both peat and undecomposed vegetation (*J. balticus. C. aquatilus*, moss). The LFH-mineral mix produced more DOC per unit mass than only tailings sands or petroleum coke (the latter being a buried layer meant to distribute flows beneath the fen). However, assessments of concentration and quality have not been measured in the field within water that is directly transported through these materials. Therefore, it is important to understand how the hydrology and biogeochemistry interact to affect DOC dynamics. This study aims to quantify hydrological DOC fluxes into a constructed fen, relative to internal DOC production, and will assess the potential importance of each source for DOC export using DOC quantity and quality.

3.2 Study Site

The study was conducted on a constructed watershed (56°55.944'N, 111°25.035'W) approximately 40 km north of Fort McMurray, Alberta. It consists of an upland-fen system surrounded by three previously reclaimed hillslopes and one natural hillslope. The constructed fen is ~3 ha, while the entire watershed encompasses 32 ha (Figure 3-1).

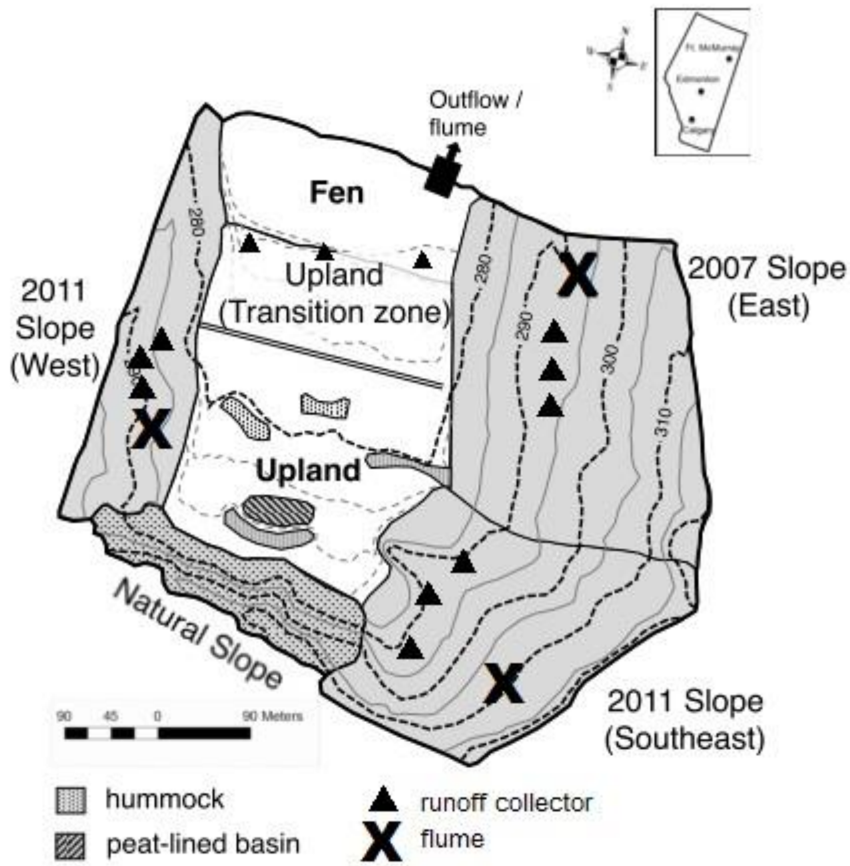

Figure 3-1. Design of upland and hillslopes, including hummock landforms. Runoff collector and flume locations on the west, southeast, east hillslopes, and the upland are indicated in the diagram (adapted from Ketcheson et al., 2016).

The fen is composed of 2 m of peat, collected from a fen dewatered for two years prior to extraction, placed on 50 cm of relatively permeable petroleum coke, and 50 cm of tailings sand (Daly et al., 2012). Construction was completed in January 2013, while vegetation planting did not finish until July 2013. Vegetation planted on site includes *Carex aquatilis*, *Juncus balticus*, moss layer transfer (Quinty and Rochefort, 2003), and bare control cover types, with *Typha* spp. spontaneously colonizing between one quarter to one third of the fen area by 2016. Seedlings used for vascular establishment were propagated in a commercial nursery (Borkenhagen, unpublished).

Donor material used for the moss layer transfer was collected from a rich fen and applied in July 2013 at a 1:10 area ratio of donor to constructed site (Quinty and Rochefort, 2003).

At the north-east edge of the fen is a spillbox that conducts surface flow in the fen to a storage pond down-gradient of the fen (Figure 3-1). South of the fen is a transition zone between the fen and upland, delineated by the presence of the petroleum coke layer that extends approximately 100 m beyond the margin of the fen at the base of the tailings sand. Both the transition zone and the upland further to the south act as a recharge zone are covered with 30-50 cm of LFH-mineral mix, overlying up to ~3 m of tailings sand. The tailings sand and, closer to the fen, the petroleum coke layer conduct water towards the fen; a geosynthetic clay liner underlies the fen and tailings sand upland (Daly et al, 2012; Ketcheson et al., 2017). The upland has a ~3% basal grade to direct water towards the fen (Price et al., 2010). In the fall of 2013, the surface of the LFH-mineral mix was furrowed perpendicular to the direction of slope to detain surface water, and thereby increase infiltration and reduce surface runoff. Recharge basins (LFH-mineral layer removed, 400-1500 m^2) located south (upgradient) of hummock landforms were also incorporated into the southern upland to promote water retention and infiltration in tandem with the furrows (Kessel, 2016). The upland vegetation comprises primarily forbs and grasses, of which 66% were native species (Gingras-Hill, 2016). Water percolates through tailings sand, producing a relatively saline groundwater source (average 2013-2016 electrical conductivity (EC) =2700 $\mu S\ cm^{-1}$) (Kessel, 2016). Kessel (2016) showed that recharged groundwater mobilized salts through the tailings sand, towards the underdrain and upwards into the fen peat. Because of the essentially impermeable geosynthetic clay liner all water losses from the system are represented through evapotranspiration and surface outflow from the spillbox. Surrounding the fen and upland are three reclaimed slopes comprising 50 cm of peat/mineral mix, on 100 cm of a secondary capping layer (low sodic soil) (Ketcheson and Price, 2016). The peat/mineral mix is created using a combination of peat that has been over-stripped, and mixed with the underlying glacial mineral sediments (Meiers et al., 2006). The east slope (8.1 ha) was reclaimed in 2007, and revegetated in 2008. The southeast (8.2 ha) and west (2.4 ha) slopes were reclaimed in 2011, and revegetated in 2012 (Ketcheson and Price, 2016). Consequently, vegetation establishment on the east slope was more extensive, consisting mostly of white spruce (*Picea glauca)*, aspen (*Populus tremuloides*), white birch (*Betula papyrifera*), green alder (*Alnus crispa*), and an assortment of shrubs (e.g., Saskatoon berry (*Amelanchier alnifolia*), pincherry (*Prunus pensylvanica*) and chokecherry (*Prunus virginiana*)). Trees were up to 3 m tall, and the groundcover was mostly complete. The west slope was planted with white spruce, aspen, white birch, green alder, and has been colonized by similar shrubs as the east slope. The southeast slope has a similar plant community to the west slope, and has been colonized by jack pine (*Pinus banksiana*) and blueberry (*Vaccinium* spp.). The west and southeast slope have been spontaneously colonized by multiple forb and grass species. Vegetation on the west and southeast slope did not exceed 1 m in height, and groundcover is less extensive than the east slope (Figure 3-2).

Figure 3-2. An enclosed runoff collector, located on the west slope, used to collect DOC samples in 2015, and estimate runoff depth in 2015 and 2016. Vegetation cover is limited, and vegetation height in this photo does not exceed 0.5 m.

3.3 Methods

In 2015, measurements were taken from May 1st to August 20th. However, in 2016 the Horse River Fire in and around Fort McMurray, began on May 1st, limiting access to the field site; therefore the measurement period was July 1st to August 18th.

Precipitation

Precipitation was measured using a tipping bucket rain gauge located within the upland. One manual gauge was placed on each of the north end of the fen, the west and east slopes, and two in the upland. Manual gauges for measuring precipitation were used to collect water samples from each rain event. When sufficient sample was available, water from the manual gauge in the fen was used. Otherwise, samples from the east and west slope gauges were combined to create one sample. Gauges were flushed with de-ionized water (DI) between events to limit algae and microbial growth. However, concentrations occasionally exceeded of the expected range (1-3 mg/L, Fraser et al., 2001), due to algal growth. In this case, DOC concentrations from precipitation samples at the nearby Poplar Fen (8.4 km) were used instead. Spectrophotometric indices were collected for precipitation samples; however, fluorescence spectroscopy was not measured due to limited water available for sampling.

Surface Runoff

One flume was placed on each of the east, west, and southeast slopes (Figure 3-1). The east and west flumes were placed mid-slope, while the southeast flume was placed at a higher position due to limitations from erosion through the peat/mineral mix, caused by excessively high flows from that hillslope. In addition, three enclosed runoff collectors (Figure 3-1) were placed mid-slope in 2016, to mimic slope positions of the respective flumes; their placement was outside the catchment boundary of the flumes (Figure 3-1). Enclosed runoff collectors were also placed in the transition zone within the upland, in an east-west transect. Flumes and collectors were constructed using metal siding, which was dug into the ground ~5 cm and cemented in place using Quikrete® hydraulic water-stop cement (Figure 3-3). The flumes drained into a 23 litre bucket that had a V-notch outflow (Figure 3-4). A calibration curve was created, and used to estimate discharge based on the height of water above the notch. A well with a pressure transducer (Schlumberger Mini-Diver) or an Odyssey capacitive water level logger was placed in each flume bucket to monitor within-event runoff at a 15-minute time interval. Runoff collectors from enclosed plots drained into 23 L buckets; following runoff events the volume of water within each bucket was measured. Buckets were covered with an opaque tarp to limit the impacts of ultra-violet radiation on DOC structure and concentration, and to prevent changes in volume through direct precipitation inputs (Figure 3-3). DOC samples were collected within 24 hours, following the end of the precipitation event. Contributing area to flumes was estimated by completing topographic surveys on each hillslope using a Topcon (Tokyo, Japan) HiPER GL RTK GPS system. Issues with pressure transducer function resulted in large portions of the seasonal runoff being missed in both 2015 on the west slope, and west and east slope in 2016. As such, the west, east, and upland runoff was estimated using runoff collectors in 2016. To estimate runoff in 2015, a multiple linear regression was used, in which runoff depth was plotted against precipitation (P) size, and maximum P intensity (west slope) or average P intensity (upland) for runoff collectors in 2016 (Appendix 4). These relationships were then used to estimate runoff depth on contributing areas in 2015 (west, upland). DOC samples were collected from flumes and runoff collectors in 2016, and average DOC concentration for each event was applied to runoff volume across each contributing area to estimate total DOC mobilized. In 2015, buckets below flumes consistently contained algae, introducing potential error to DOC concentration measurements. Therefore, the average seasonal DOC concentration in 2016 on hillslopes and the upland was used to estimate 2015 DOC fluxes, as there was no correlation between concentration and runoff depth across all contributing areas.

Figure 3-3. An enclosed runoff collector, located on the east slope, used to collect DOC samples and estimate runoff depth in 2016. Vegetation cover was extensive, and tree height within this photo was ~1.5 m.

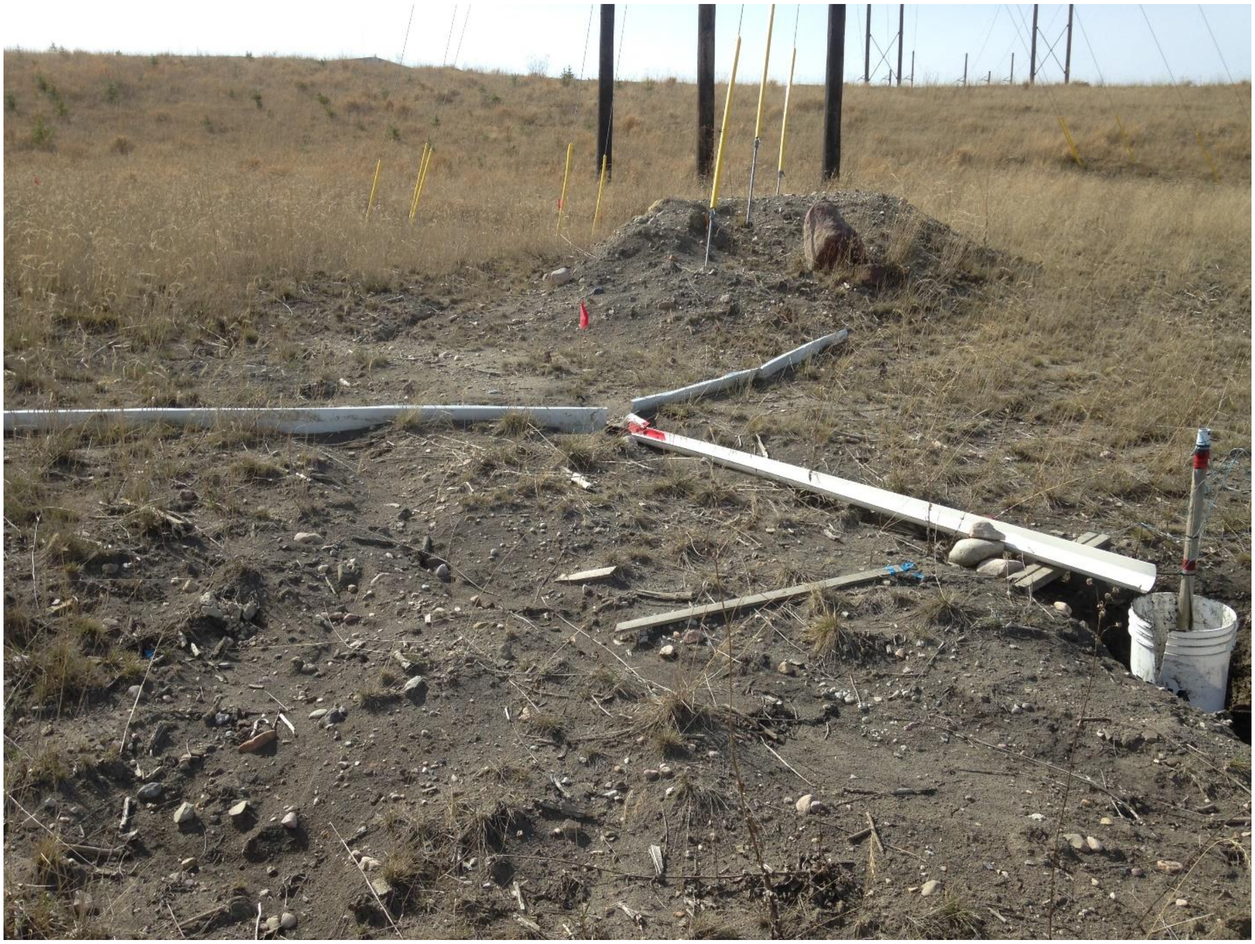

Figure 3-4. Flume open to the southeast hillslope used to estimate runoff depth and collect DOC samples. Bucket contains a well with a Schlumberger Mini- Diver pressure transducer.

Groundwater

Ten piezometer nests were sampled from across the constructed fen, targeting the layers within peat (30, 50, 90, 150 cm), and the petroleum coke layer (275 cm) that conducts groundwater to the fen (Figure 2-3). All piezometers were constructed from PVC pipe (2.54 cm inner diameter), with a 20 cm slotted intake, and wrapped with filter sock.

Groundwater flux was calculated using Darcy's Law:

$$q = \frac{Q}{A} = -K_{sat}\frac{dh}{dL} \tag{3-1}$$

where q is the specific discharge (m s^{-1}), Q is the volumetric discharge (m^3/s), A is the cross-sectional area of the flow face (m^2) and dh/dl is the hydraulic gradient (i.e., the change in head, dh, divided by the change in length, dl, between the measurement points; unitless). Specific discharge fluxes to the CF through the petroleum coke underdrain were estimated using the vertical hydraulic gradient between the piezometers installed in the coke layer beneath the fen and the water table in the fen, for each nest in the fen, on each measurement date (~ once weekly), using Equation (3-1) (Ketcheson et al., 2017). Fluxes were calculated on a weekly basis, then averaged for each date of measurement. Groundwater entering the fen in the transition zone from tailings sand directly to peat (i.e. horizontal flow) was estimated to be 4.6 mm in 2014, or 1.5% (O. Sutton, personal communication, 2017) of the total groundwater input, and therefore was considered negligible. Hence, the flow face used for flux calculations is the fen area, and total distance is fen peat depth.

Nwaishi et al. (2015b) reported that the peat displayed isotropic K_{sat}, but had layered heterogeneity through the profile, so the equivalent vertical hydraulic conductivity through the system of layers within the peat deposit (K_z) was estimated at each nest according to the weighted influence of each layer (Freeze and Cherry, 1979),

$$K_z = \frac{d}{\sum_{i=1-4}^{n} \frac{D_i}{K_i}} \qquad (3\text{-}2)$$

where d is the total thickness of the peat deposit (2.0 m), and D_i and K_i are the thickness and saturated hydraulic conductivity of each peat layer, respectively. Field measurements of K_{sat} were conducted using bail tests within piezometers in the fen, following the hydrostatic time-lag method (Hvorslev, 1951). All nests had triplicate manual measurements of K_{sat} at 50, 90 and 150 cm depths in 2015, with a 30 cm depth added in 2016. Piezometer slots represented the center of each peat layer used to estimate K_z. Refer to Ketcheson et al. (2017) for more details regarding hydraulic conductivity and groundwater flux calculations.

Water samples were extracted from piezometers once each month during the growing season, in June-August (2015) and July-August (2016) for DOC concentration and spectrophotometric samples. In July 2015, piezometers within the tailings sand below the fen were sampled for fluorescence spectroscopy. All piezometers were purged (minimum three well volumes) 24 hours prior to extraction. All samples were extracted using a 12V peristaltic pump with vinyl tubing, and each soil type had designated tubing to minimize contamination. All tubing was flushed with de-ionized water prior to sampling. Samples were taken from 10 nests, that covered the central E-W transect through the fen, and the peripheral N-S transects along the East and West hillslope (see chapter 2).

DOC Export

Discharge from the site was monitored using a Teledyne Isco 2110 Ultrasonic flow module that logged water level every 30 minutes. The outflow point was a 30^{o} v-notch weir ~3 m upstream of the spillbox. Water samples were collected daily when surface flow occurred; however, when discharge rates were high (≥0.5 L/s), multiple samples were taken throughout the day.

Fen DOC Storage

Total DOC stored within the fen was calculated using average DOC concentration within each layer in the peat as delineated by piezometer depths. The middle point between each piezometer determined the boundaries of the depth over which each DOC concentration was applied. As such, the ranges for DOC mass calculations were 0-40, 40-70, 70-120, 120-200 cm. Porosity as determined by Ketcheson et al. (2017) was used to calculate the volume available for water storage; porosity from 0-50 cm (0.92) was used for piezometer depths of 30 and 50 cm, porosity determined for 50-200 cm (0.87) was used for all other depths. Average DOC concentration from each sampled depth at all piezometers was used, as there was no observed spatial relationship of DOC concentration across the fen.

DOC Balance

To determine the contribution of DOC production within the fen compared to external inputs, the fen DOC production was determined using:

$$Net\ Fen\ DOC\ Prodution = \Delta\ Fen\ Storage - DOC_P(P) - DOC_R(R_{slope}) - DOC_{GW}(GW) + DOC_Q(Q) \qquad (3\text{-}3)$$

where DOC_x is the DOC concentration at each sampling location, P is precipitation, R_{slope} is runoff from constructed hillslopes and uplands, GW is groundwater flow into the fen, and Q is outflow from the v-notch weir. The water table was assumed to be at the peat surface for all calculations, as the water table did not vary from this value by more than 10%, and to limit bias of water table on budget estimates.

DOC Concentration and Chemistry Analysis

For water samples collected from all study locations, a volume of water (~50 mL) was collected into a clean reservoir for in-field measurements of environmental variables (electrical conductivity, pH, temperature). An electrical conductivity (*EC*) and temperature (*T*) probe (Thermo Scientific™ Orion™ Conductivity and Temperature probe) and a pH probe (Thermo Scientific™ Orion™ Economy Series pH Combination Electrode) were inserted into the collected volume. *EC* probes were calibrated monthly to 1413 µS/cm, and pH probes were three-point calibrated to a pH of 4, 7, and 10 before every daily use. After the above procedures, another water sample was taken in a clean 60 mL high density polyethylene vial and 40 mL amber borosilicate vial, and stored in a cooler until they were returned that day to the laboratory, where they were stored at 4°C. For samples collected on hillslopes, if a secondary volume was not available, the initial collected volume was used for DOC analysis. Samples were filtered within 24 hours through 0.45 μm nitrocellulose filters, then decanted into 60 ml vials for DOC concentration and spectrophotometric analysis, and 40 mL borosilicate vials for fluorescence spectroscopy analysis.

Samples were analyzed using a PerkinElmer UV/VIS Spectrophotometer Lambda 35 to measure absorbance at 250 nm, 254 nm, and 365 nm wavelengths. The concentration of DOC was determined using a Shimadzu TOC analyzer (Environmental Sciences Program, University of Calgary) by the Non-Purgeable Organic Carbon (NPOC) method. As TOC was determined on filtered samples, this represents DOC. In 2015, a 20% subset of samples was selected to measure DOC, and values were then correlated with absorbance at 250 nm (a250) to estimate DOC for all samples (Peacock et al., 2014; Appendix 1). In 2016, all water samples were analyzed for DOC concentration. See chapter 2 for further details regarding sample analysis.

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:

At an excitation of 370 nm: $$\frac{Emission\ at\ 470\ nm}{Emission\ at\ 520\ nm} \qquad (3\text{-}4)$$

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:

At an excitation of 310 nm: $$\frac{Emission\ at\ 380\ nm}{\substack{Maximum\ emission\ between \\ 420\ nm\ and\ 435\ nm}} \qquad (3\text{-}5)$$

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:

$$\frac{Sum\ of\ emission\ from\ 435\ nm\ to\ 480\ nm}{(Sum\ of\ emission\ from\ 300\ nm\ to\ 345\ nm) + (Sum\ of\ emission\ from\ 435\ nm\ to\ 480\ nm)} \tag{3-6}$$

$SUVA_{254}$ (Weishaar et al., 2003) was used to indicate the relative amount of aromatic carbon present, in which a high $SUVA_{254}$ correlated to higher aromatic carbon. $SUVA_{254}$ was calculated using equation 5:

$$\frac{UVA\ (cm^{-1})}{DOC\ concentration\ (mg/L)} * (\frac{100cm}{m}) \tag{3-7}$$

E2/E3 (Helms et al., 2008) was used to assess the relative molecular weight of the organic structure present, in which a high E2/E3 value indicates a low molecular weight. E2/E3 was calculated using equation 6:

$$\frac{a250}{a365} \tag{3-8}$$

Data Analysis

R (R Core Team, 2016), was used for all statistical analyses. All variables were tested for normality using the Shapiro-Wilks test prior to analysis. Linear mixed effect model (function “lme”, package “nlme”, Pinheiro et al., 2015) was used to test the effect of runoff source on DOC concentration and quality, where the sampling cycle was treated as a random factor to account for repeated measures. When there was a significant effect, a Tukey post-hoc analysis (function “glht”, package “multcomp”, Hothorn et al., 2008) was used to assess differences between locations. Multiple linear regressions were used to model runoff depth based on precipitation intensity (average for upland, maximum for hillslopes), and precipitation size. A significance of $p \leq 0.05$ was used for all analyses.

3.4 Results

Precipitation

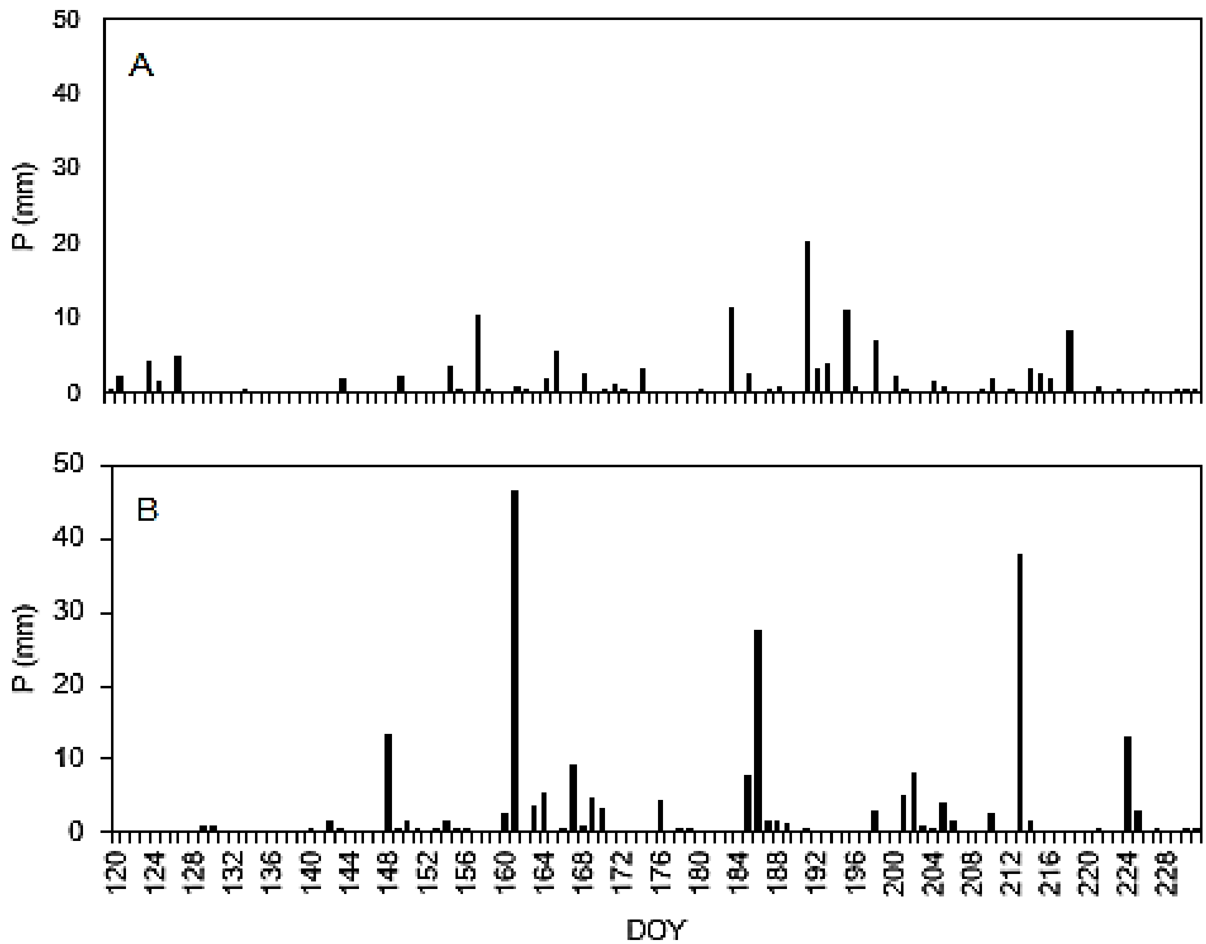

Figure 3-5. Precipitation that has fallen within the constructed watershed in (A) 2015 and (B) 2016, collected from the tipping bucket within the upland.

During the study period in 2015 (May 1st-August 20th), the depth of rainfall was 107 mm (Figure 3-5), which is less than the average amount of 245 mm for this time period (1981-2010;

Fort McMurray A station, Environment Canada, 2017). Average (standard deviation) DOC concentration in rain was 4.67 (1.5) mg/L, thus the amount of DOC that fell on the fen over the study period was 0.5 g/m^2. In July and August of 2016, precipitation totalled 103 mm. Average DOC concentration was 4.41 (0.78) mg/L, thus the DOC which entered the fen through rainfall was 0.45 g/m^2. In 2015 and 2016, the $SUVA_{254}$ of DOC in precipitation was 3.3 (1.03) and 2.97 (0.72) L/mg m, and E2/E3 values were 3.65 (1.85) and 2.93 (0.49), respectively.

In 2015, the maximum precipitation intensity measured was 8.6 mm/hr, while in 2016, the maximum value was 9.4 mm/hr (Figure 3-6). Additionally, though the exceedance curves follow a similar pattern, there were a greater number of total observed events in 2016. Therefore, there were a higher total number of high intensity precipitation events in 2016.

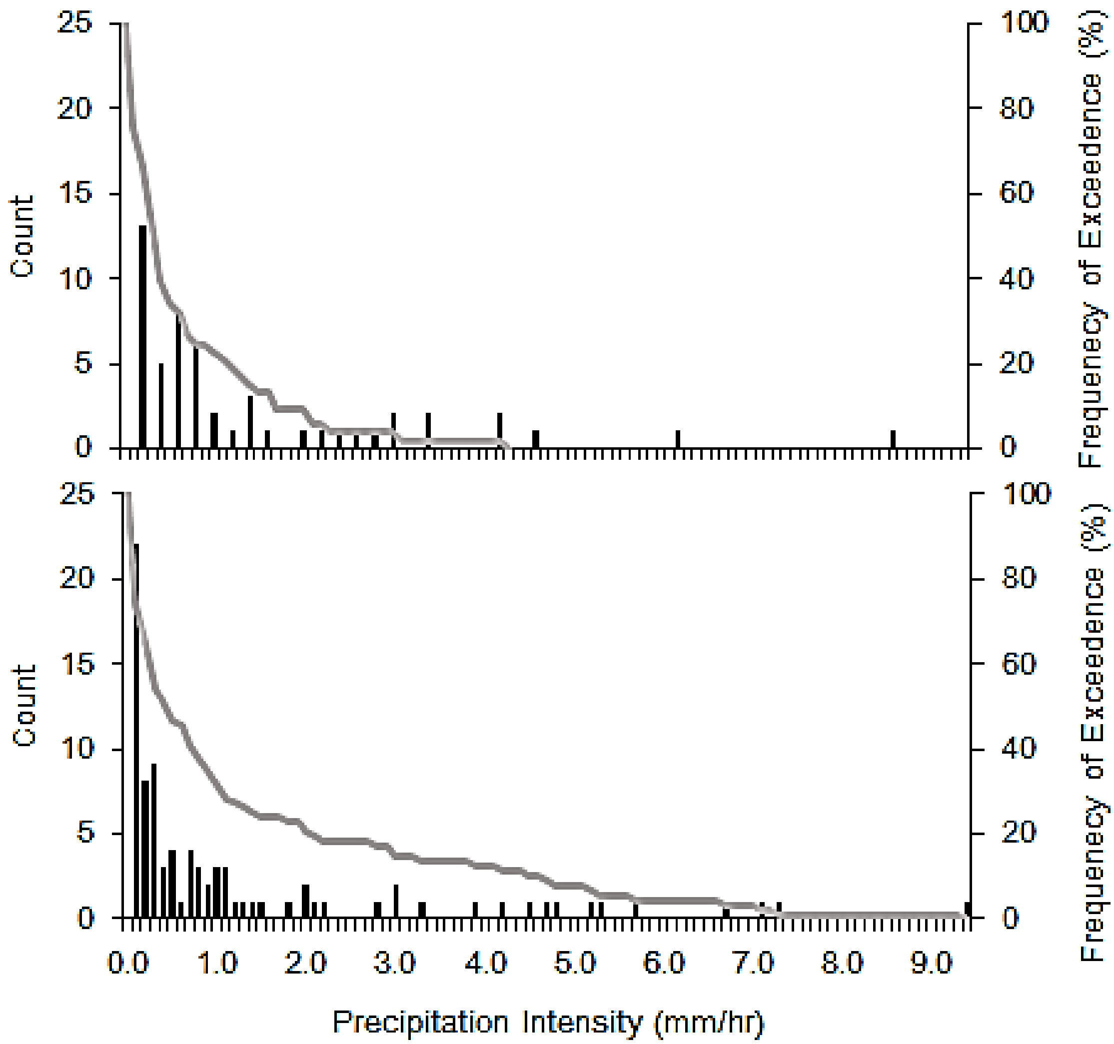

Figure 3-6. Precipitation intensity (black bars) and frequency of exceedance (grey line) for 2015 (top) and 2016 (bottom). Count indicates the number of events for which a precipitation intensity was observed.

Groundwater

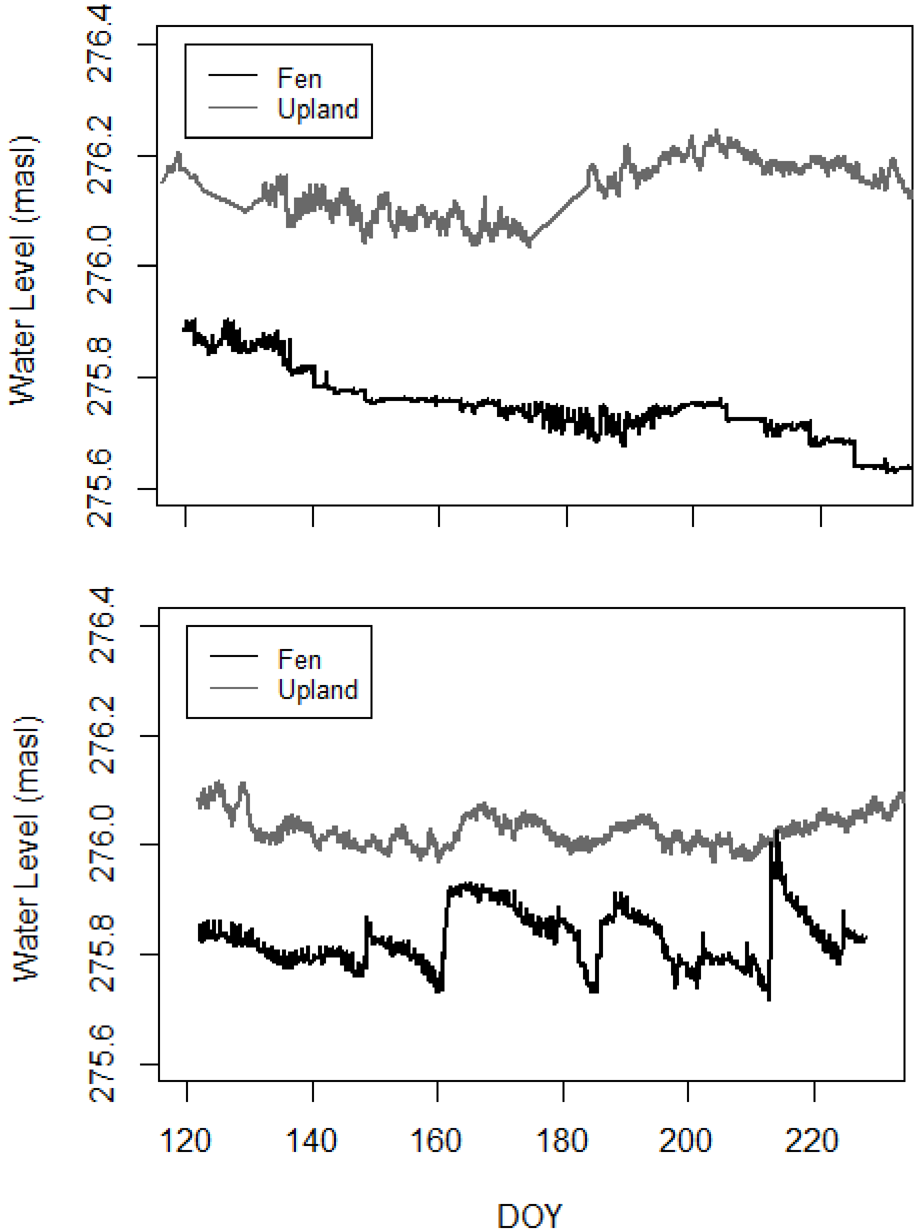

Figure 3-7. Water table (masl) in 2015 (top) and 2016 (below) in the upland and fen. Pressure transducers were installed prior to the fire, therefore data were collected within a central fen and upland well in May and June of 2016. Upland and fen surface elevation are 278.7 and 275.8 masl, respectively.

Data for manual piezometer measurements in 2016 were not collected before July 1st, therefore groundwater flux estimates in 2016 are restricted to July and August. Groundwater inputs to the fen were still larger in 2015 compared to 2016 through July and August. In 2015, the water table was at least 25 cm higher, within the upland than in the fen at the beginning of May, reaching a maximum of 55 cm by day 230 (Figure 3-7). This is reflected in the vertical hydraulic gradients seen within the fen (Figure 3-8). Following ground-ice melt, the gradient between the upland and fen increased (Figure 3-7); therefore, the vertical hydraulic gradient increased upwards through the fen (Figure 3-8). Increased vertical gradients coincided with an increase in upland water table after day 180. However, in July and August of 2016, the difference in water table between the fen and upland was smaller, and was more variable (Figure 3-7). Following a precipitation event on day 213, the water table increased within the fen, and was at the same level as that observed in the upland. This small difference in water tables was reflected in the small vertical hydraulic gradients measured in 2016 (Figure 3-8); values measured centered around zero, limiting groundwater inputs to the fen through July and August.

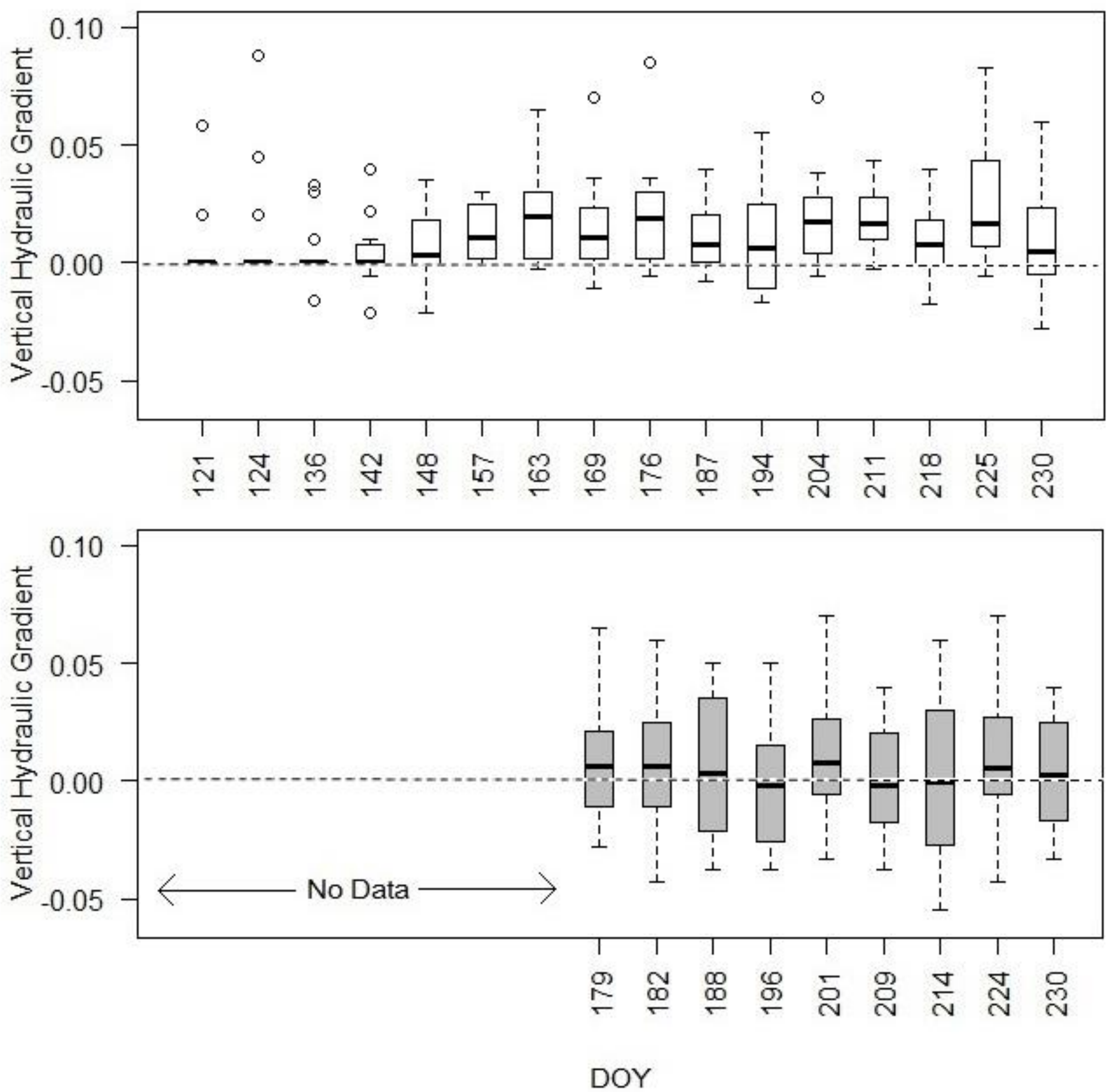

Figure 3-8. Vertical hydraulic gradients in the constructed fen in 2015 (top) and 2016 (bottom). A positive value indicates an upward gradient from petroleum coke to peat surface.

Hydraulic conductivity did not significantly change from 2015 to 2016 at 50, 90, and 150 cm (Figure 3-9), and therefore, groundwater flux into the fen was dependent on the vertical hydraulic gradients. Total groundwater inputs over the study periods in 2015 and 2016 was 38 (112 days) and 8 (51 days) mm, respectively.

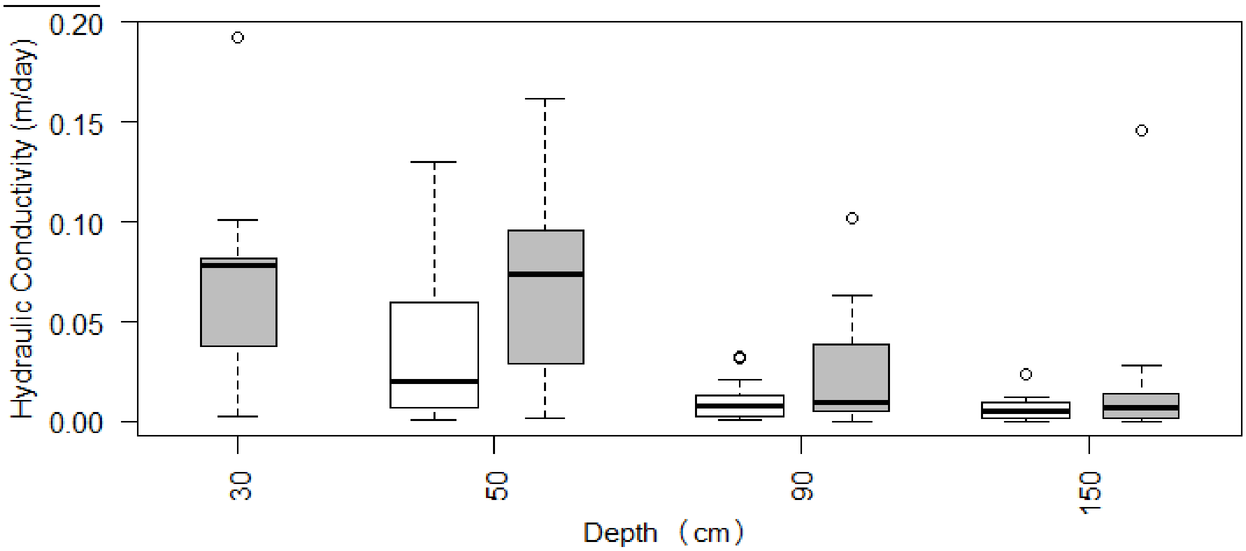

Figure 3-9. Saturated hydraulic conductivity measured at piezometers in 2015 (white) and 2016 (grey) within the peat at the constructed fen.

DOC concentration in the petroleum coke layer in 2015 and 2016 did not significantly differ, though concentrations were generally higher in 2016 (Figure 3-10). Total DOC inputs through groundwater were 1.3 and 0.6 g/m^2 in 2015 and 2016, respectively. E2/E3 also did not change seasonally or between years, though $SUVA_{254}$ decreased in 2016, indicating less aromatic DOC was transported towards the fen (Figure 3-10). When measured in July, average (standard deviation) values for FI, β/α, and HIX in groundwater samples were 1.72 (0.02), 1.23 (0.03), and 0.58 (0.01), respectively.

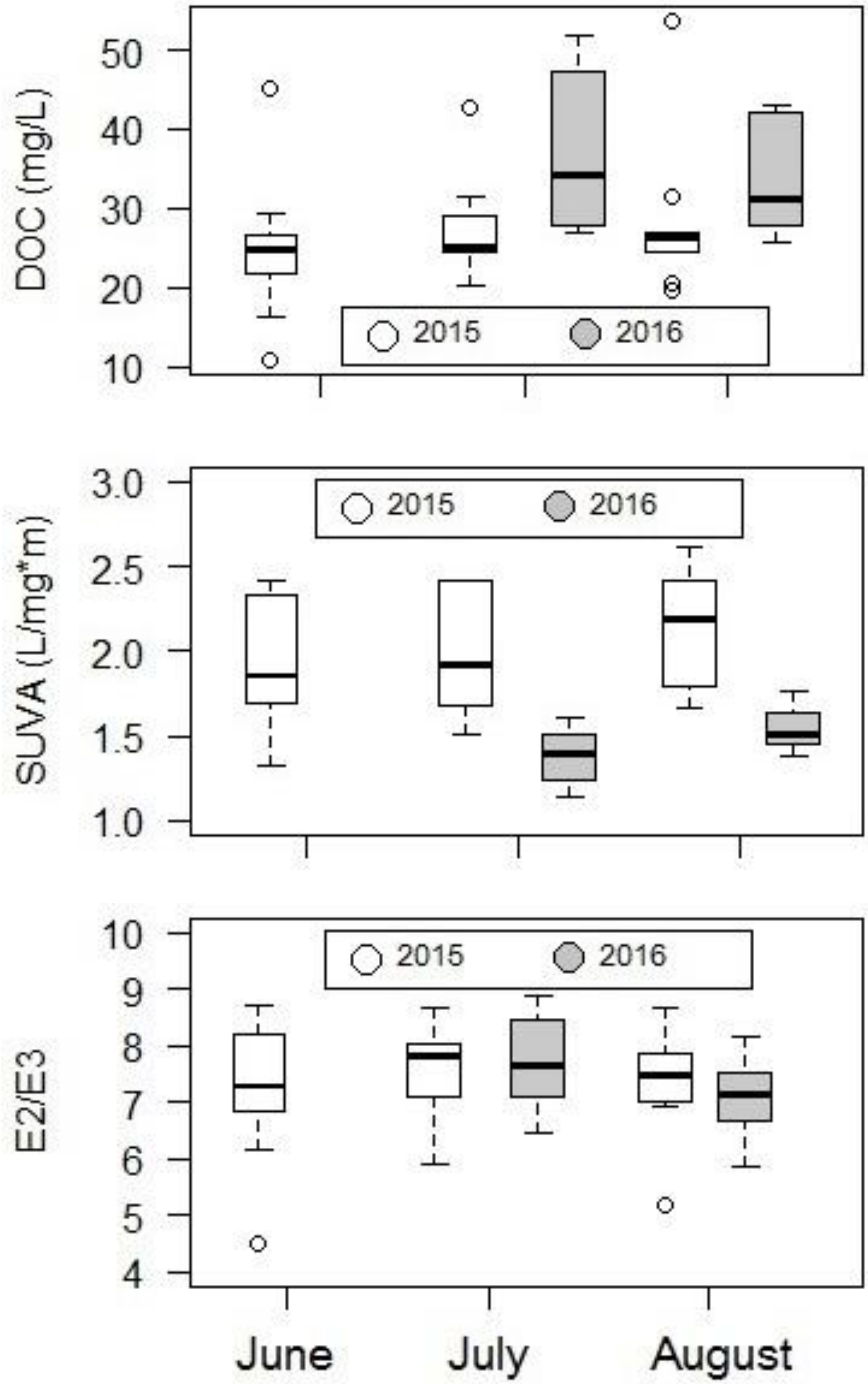

Figure 3-10. DOC concentration (top), $SUVA_{254}$ (centre), and E2/E3 (bottom) in 2015 and 2016 within the petroleum coke below the fen.

Surface Runoff

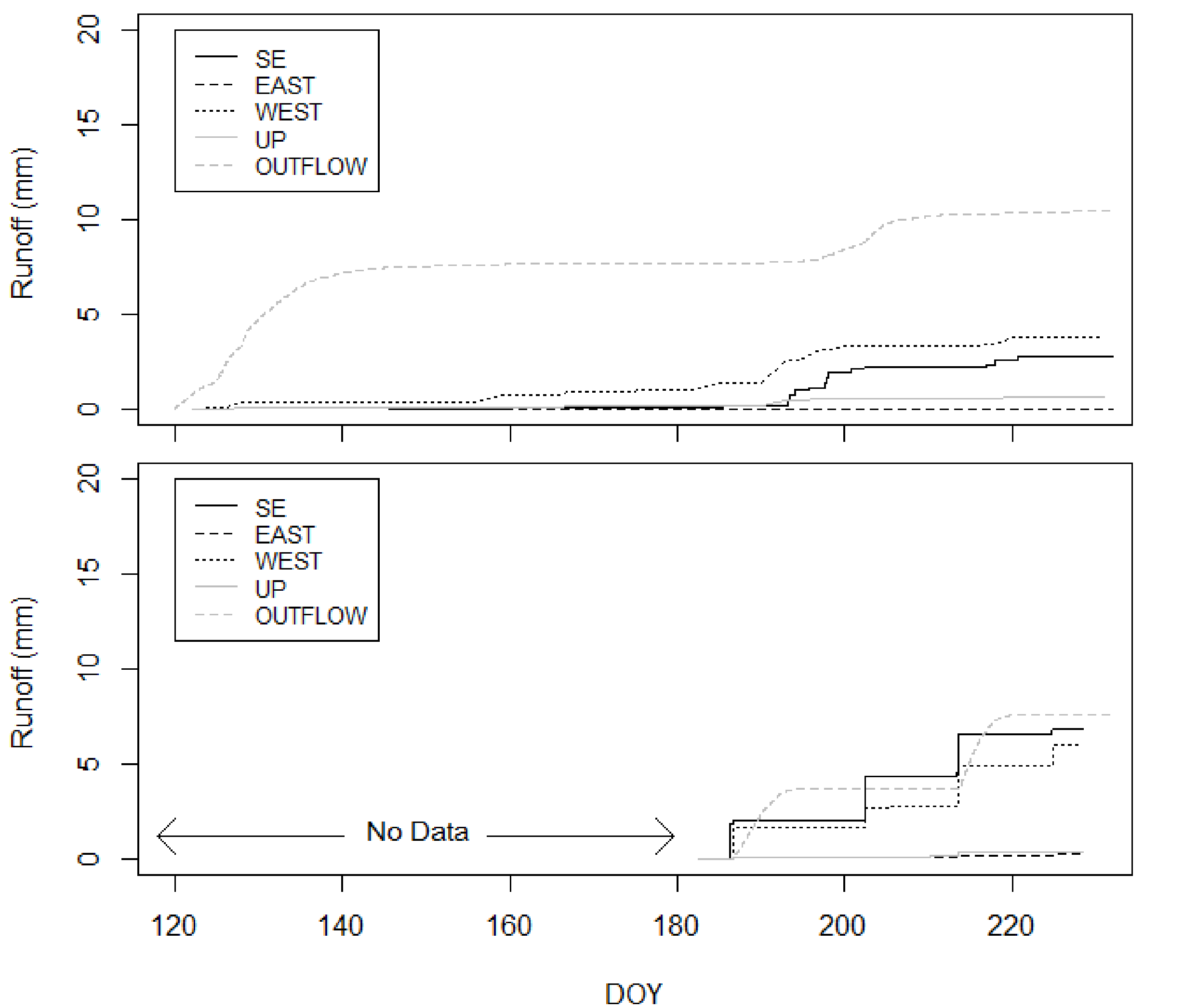

Figure 3-11. Depth of surface runoff on the southeast, east, west hillslopes, upland, and v-notch in a) 2015 and b) 2016. No data were collected from day 120 to 180 of 2016 due to the Horse River Fire.

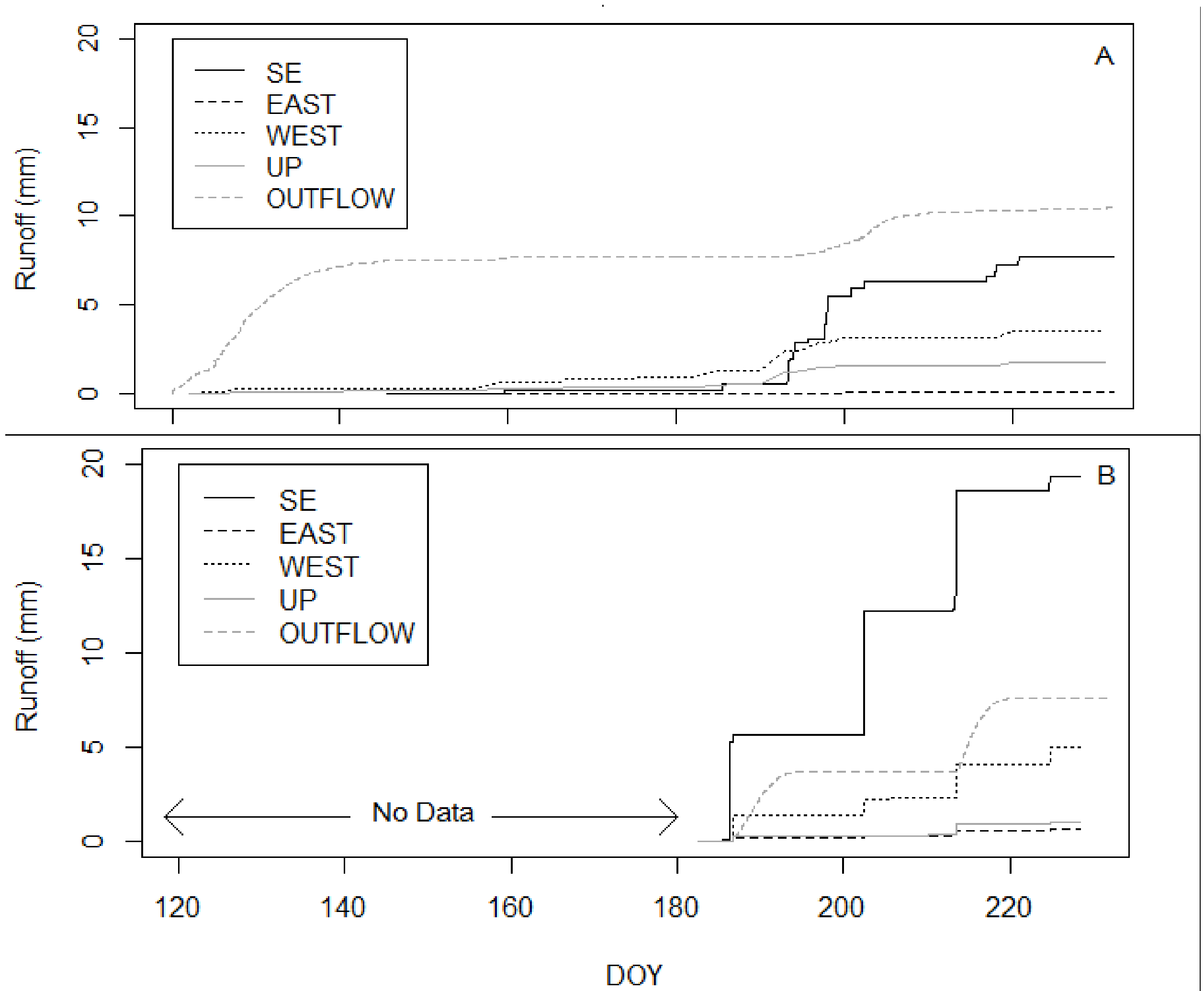

Figure 3-12. Depth of surface runoff normalised to fen area on the southeast, east, west hillslopes, upland, and v-notch in a) 2015 and b) 2016.

In 2015, the west slope produced the largest depth of runoff at 3.8 mm (Figure 3-11), followed by the southeast slope. However, in 2016 the southeast slope had the largest runoff depth at 6.9 mm. In both years, the upland and east slope produced very little runoff (<2 mm). When runoff depth was normalised to fen area in 2015, the southeast slope produced the most runoff at 7.4 mm (Figure 3-12). The normalised values for upland and east slope runoff were 1.7 and <0.1 mm, respectively. The 95% confidence intervals for the upland and west slope runoff estimates in 2015 are shown in Appendix 5. In 2016 this pattern continued, as the southeast slope had the largest runoff depth when normalised to the fen area, and the east slope produced the smallest amount of runoff. As DOC concentrations did not vary between contributing areas (Figure 3-13), the southeast slope had the largest DOC flux, followed by the west slope, upland, then east slope, in both years (Figure 3-14). However, as the southeast slope is located at the south end of the system, and the east and west slopes have portions of their delineated border shared with the fen (Figure 3-1), it is difficult to quantify the total amount of DOC that reaches the fen from each area.

Though DOC concentration did not vary between contributing areas, DOC quality was significantly different between locations, specifically between upland and hillslopes. For spectrophotometric indices, $SUVA_{254}$ and E2/E3 were significantly lower and higher, in the upland compared to southeast and west slopes, respectively. E2/E3 was significantly lower on the east slope, and though not significant, still $SUVA_{254}$ was also higher, compared to the upland. Fluorescence spectroscopy indices also display differences across locations; FI and β/α were greater in the upland, relative to values on the west and southeast slopes (Figure 3-14).

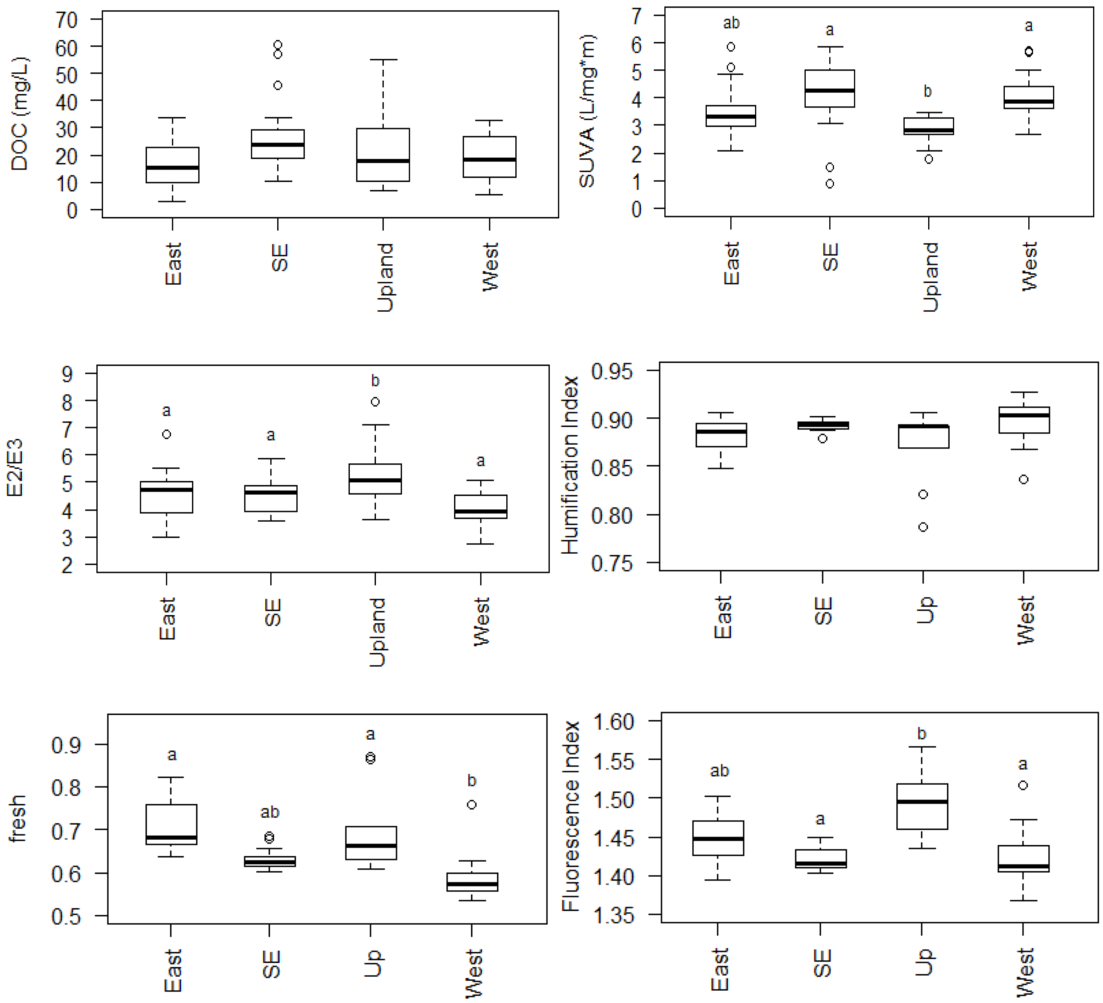

Figure 3-13. DOC concentration and quality across the upland, east, southeast (SE), and west hillslopes in July and August of 2016, across all runoff events. Different letters indicate a significant difference between locations.

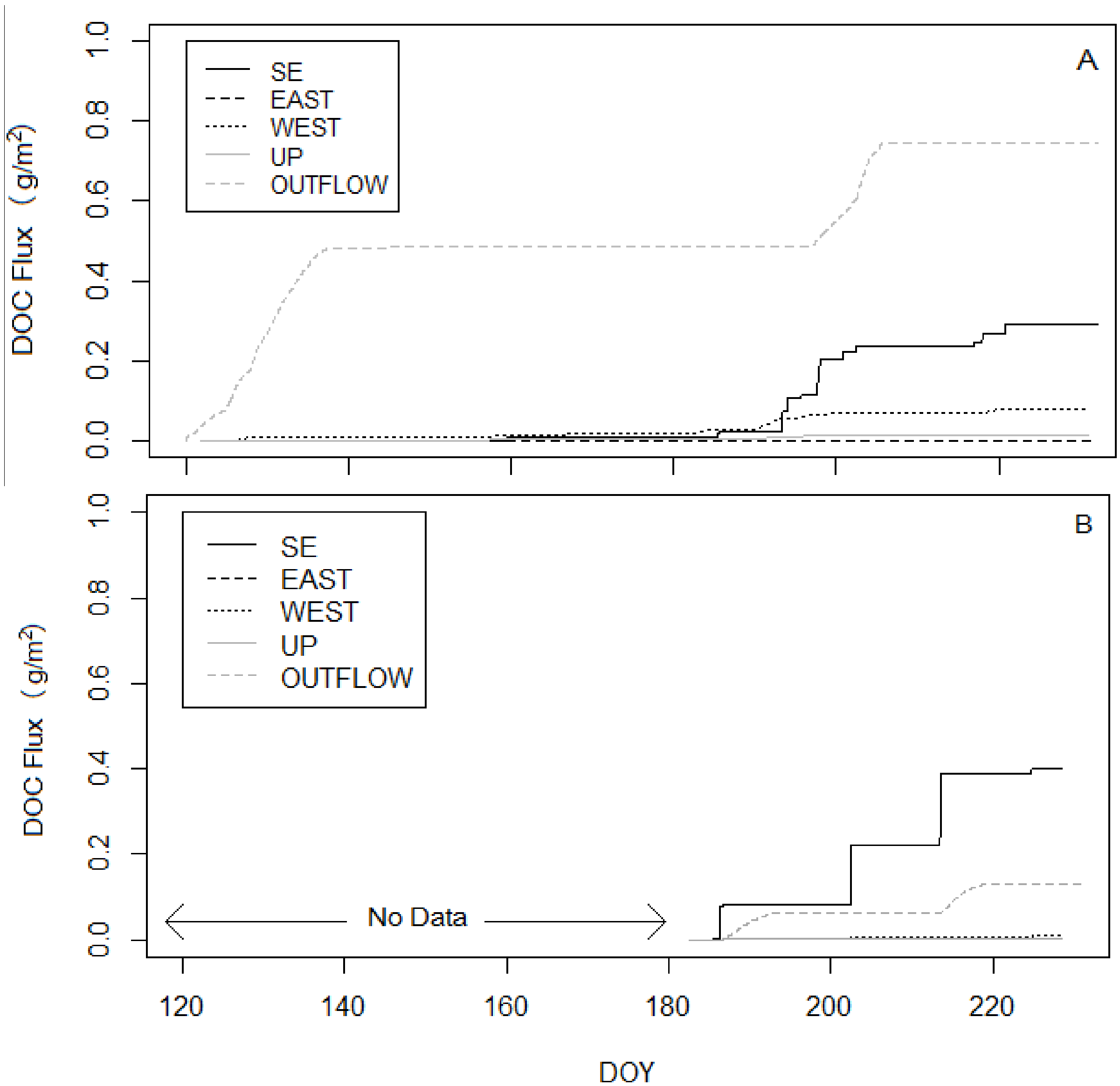

Figure 3-14. Cumulative DOC export from each contributing area, and outflow from the fen in a) 2015 and b) 2016. No data were collected from day 120 to 180 of 2016 due to the Horse River Fire.

Outflow

In 2015, the majority of discharge occurred during the first two weeks of the field season, coinciding with the post-snowmelt freshet, culminating in 7 mm of surface runoff lost through the v-notch weir (Figure 3-15). DOC concentrations ranged from 20-77 mg/L, and there was no significant correlation between discharge rate and DOC concentration. However, within the spring freshet, DOC concentration was generally higher during low-flow events. The majority of DOC lost through the study period was exported during spring freshet, transporting ~0.5 g/m^2 of DOC out of the system. There was a secondary discharge event at the end of July that coincides with a large precipitation event. This resulted in the remaining DOC exported, totalling 0.7 g/m^2 released during the 2015 growing season. In 2016, as the spring freshet had been missed, there were limited outflow events captured. However, two were observed, at the end of July and mid-August. Maximum discharge rate was ~0.4 L/s, with both occurrences of outflow corresponding to large precipitation events (Figure 3-15). During these events, DOC concentration increased as discharge rate decreased (Figure 3-15), although there were comparable DOC concentrations observed during the 2015 spring freshet. The total DOC exported during July and August (51 days) was only ~0.1 g/m^2, less than observed (0.26 g/m^2) over the same time period in 2015.

DOC quality in discharge exhibited no trends in 2015; $SUVA_{254}$ consistently ranged from 2-3 L/(mg m), regardless of discharge rate. E2/E3 also exhibited the same pattern, as it ranged 7-8, despite changes in discharge. Only three samples were run for fluorescence spectroscopy analysis; one sample, collected on May 29th, had a HIX value of 0.68, FI of 1.6, and β/α of 0.99. The two remaining samples were obtained July 23rd and 24th; the average (standard deviation) HIX increased to 0.80 (0.01), while FI and β/α decreased to 1.51 (0.02), and 0.76 (0.01), respectively. In contrast, in 2016 as discharge decreased following precipitation events, E2/E3 and $SUVA_{254}$ decreased and increased, respectively. The range of values for $SUVA_{254}$ also increased to 3-5 L/(mg m), and E2/E3 decreased to ~5. This indicates that exported DOC increased in size and aromaticity from 2015 to 2016. Alternatively, fluorescence spectroscopy indices displayed minimal variability during both outflow events. Seasonal values for HIX, FI, and β/α were 0.85 (0.04). 1.48 (0.02). and 0.69 (0.04), respectively.

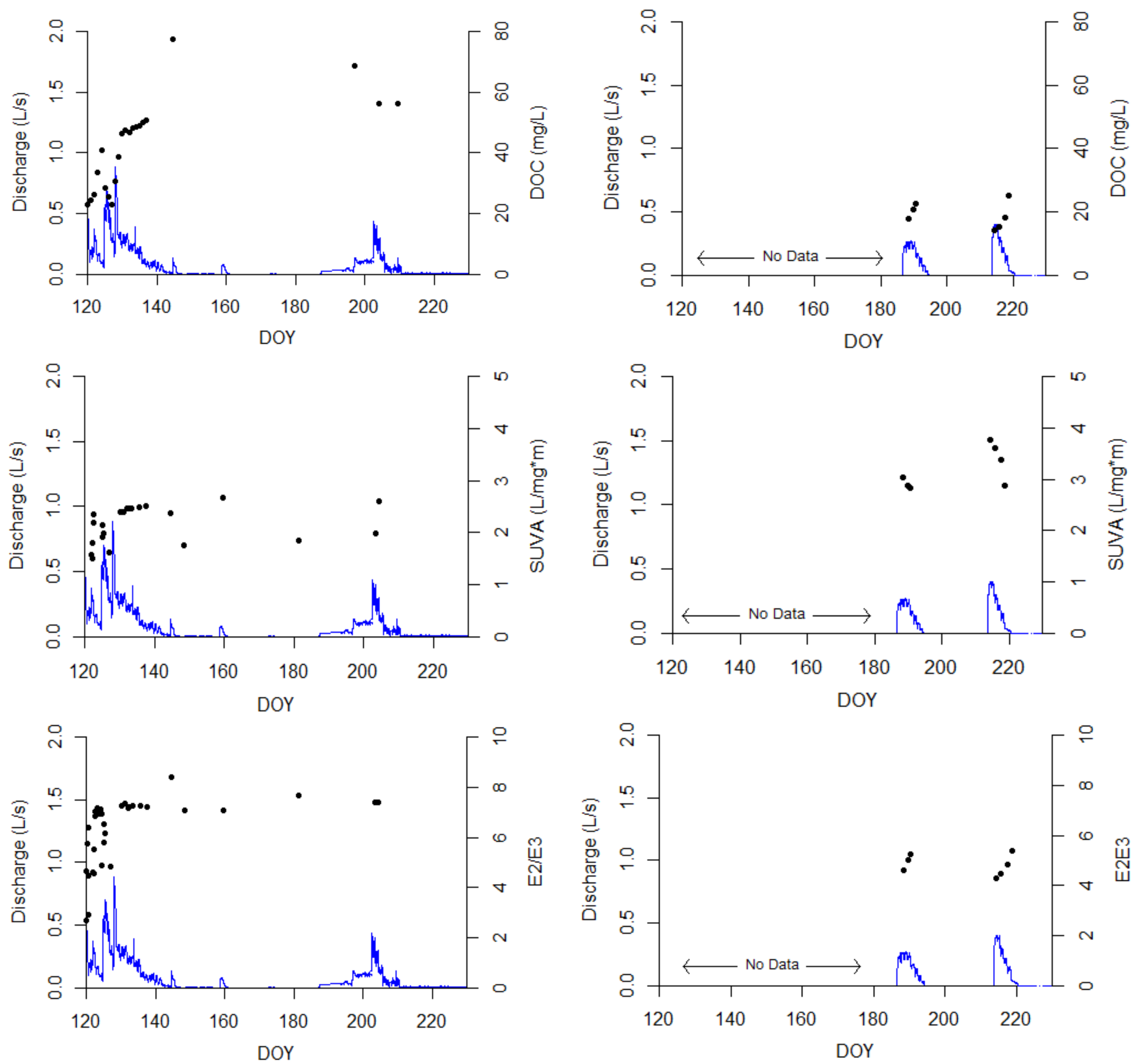

Figure 3-15. Discharge, DOC concentration, $SUVA_{254}$, and E2/E3 values during outflow events in 2015 (left) and 2016 (right).

DOC Balance

Table 3-1. DOC balance in 2015 (left) and 2016 (right), including groundwater (GW), runoff (RO), precipitation (P), outflow, fen storage, and net DOC production. Average seasonal DOC concentration are shown; however, for runoff, groundwater, precipitation, discharge, fen storage, and net production were not used for total flux estimates. Monthly average was used for groundwater, fen storage, and net production, while event-specific DOC concentration was used for runoff, precipitation, and discharge, therefore there is no error value associated with precipitation or discharge. Data are shown as averages (standard deviation) for DOC concentration and calculated water depth. As DOC concentration for runoff was only collected in 2016, there are no values for 2015, and the same concentration (standard deviation) is assumed for 2015 and 2016.

	2015						2016					
	GW	RO	P	Q	Fen Storage	Net Production	GW	RO	P	Q	Fen Storage	Net Production
Water Depth (mm)	38 (54)	13 (6)	107	10.5	2000	-	8 (23)	26 (3)	103	7.6	2000	-
Avg. DOC Conc. (mg/L)	26.8 (8.4)	21.4 (11.8)	4.67 (1.5)	37.4 (14.6)	38.2 (7.7)	-	35.6 (8.9)	21.4 (11.8)	4.41 (0.78)	24.9 (11.9)	35.4 (7.4)	-
Total DOC Flux (g/m^2)	1.2 (0.5)	0.4 (0.1)	0.5	0.75	22.3 (3.4)	20.9 (5.0)	0.3 (0.2)	0.4 (0.03)	0.5	0.13	20.66 (3.8)	19.6 (4.1)

Net DOC production (standard deviation) in 2015 and 2016 was 20.9 (5.0) and 19.6 (4.1) g/m^2, or 23.9 and 20.7% error, respectively. Overall, inputs to the fen decreased in 2016 due to the limited groundwater inputs, as runoff and precipitation were comparable to 2015. Outflow also decreased, though inputs and outputs had little effect on the total DOC within the fen, as the dominant DOC input was through internal production (Table 3-1). Net DOC production did not vary between years, as the seasonal increase in DOC concentration through the fen profile did not change significantly from 2015 to 2016. However, it is important to note that the net DOC production in 2016 was calculated based on data for only July and August, and excluded May and June. Therefore, it is likely that net DOC production in 2016 was actually greater than in 2015. However, as all other inputs and outputs would also have increased if May and June were included, the proportional change was likely minimal.

3.5 Discussion

Hydrological inputs of DOC to the constructed fen

DOC concentration in precipitation was close to the range (1-3 mg/L) previously reported for boreal ecosystems (Fraser et al., 2001; Moore, 2003) in 2015 (4.67) and 2016 (4.41). Therefore, DOC loading from precipitation fell within the expected range, although within the lower end of this spectrum due to the lower than average precipitation that fell within the constructed watershed in 2015. In 2016 the loading was also within the expected range, though the total for July and August was at the high end of this range. Precipitation had comparable $SUVA_{254}$, and low E2/E3 values relative to what is seen in the fen (Appendix 6), indicating that DOC in precipitation is dominated by large, non-aromatic compounds. This is comparable to findings by Likens and Galloway (1983), who determined that DOC in precipitation is dominated by macromolecular organic carbon, but the majority of DOC had a non-aromatic structure. However, though the size of DOC compounds differs in precipitation compared to the fen, individual inputs of precipitation are unlikely to change fen DOC quality, as the mass of DOC within the fen is dramatically larger than the addition through precipitation (Table 3-1).

Surface runoff also followed this temporal trend between years, as DOC exports from hillslopes and runoff were much larger in 2016 compared to 2015. This is likely due to the difference in the precipitation intensity between years. As precipitation intensity was higher in 2016, and the total number of high-intensity events was greater (Figure 3-6), there was more overland flow. Overland flow was also observed within this watershed in 2013 and 2014 (Ketcheson and Price, 2016); the east slope produced <1 and 6 mm, compared to 52 and 73 mm on the west slope in 2013 and 2014, respectively. Within the present study, surface runoff on the southeast and west slope also exceeded that on the east slope. This was likely due, in part, to differences in infiltration rates; Ketcheson and Price (2016) determined that infiltration rates were highest on the east slope, followed by west and southeast slopes. Additionally, vegetation cover was more extensive and mature on the east slope, which may contribute to the promotion of infiltration. Thompson et al. (2010) observed greater infiltration capacity as aboveground tree biomass increased, specifically in regions with limited precipitation input. Furrowing and hummock features, instead of infiltration capacity, likely played a larger role in limiting runoff in the upland by retaining surface water, which was visually confirmed in 2016 (Figure 3-16). Devito et al. (2017) also observed that surface runoff was limited in hummocky, forestland terrain, and that these features acted as water sinks.

DOC concentration did not vary between slope locations, though runoff depth varied between contributing areas, indicating that construction materials and/or time post construction do not impact DOC in solution, but has an overall impact on DOC transported to the fen. However, DOC quality was affected by post-construction conditions. DOC on the west and southeast slopes appeared terrestrially-sourced due to low FI values. Johnson et al. (2006) observed limited interaction of water with soil components during overland flow, particularly as runoff increases, decreasing dissolution of DOC from soils. Therefore, DOC from the southeast and west slope is more characteristic of DOC terrestrially-produced at the surface, rather than those produced from sub-surface processes. The upland and east slope displayed values closer to 1.6, indicating a mix of terrestrial and microbial influences. This may be due to the longer time frame the east slope has had since reclamation, relative to other slopes and the upland, allowing greater establishment of microbial communities, and greater soil-water interaction through macropores created by rooting systems (Wilcox et al., 2015). The upland had the highest FI values, indicating the largest proportion of microbially- sourced DOC. As the upland has had the shortest time post-construction to establish, the vegetation community has also had the least amount of time to develop, and therefore may have produced a less terrestrial signature. Though all runoff is assumed to reach the fen from all contributing areas in the fen DOC budget, it is not likely the case, and a large portion of the runoff will be directed through the upland. While this limits the direct contribution from those slopes, their DOC may also take on a quality closer to that of the upland.

Figure 3-16. Water retained by furrows in the upland following a large precipitation event on August 1, 2016. The slope from upland to fen is from bottom to top of photo.

Groundwater represented the largest hydrological input of DOC to the constructed fen in 2015 (Table 3-1). However, the amount of water entering the constructed fen in 2015 and 2016 (38, 8 mm, respectively) was much smaller than reported by Ketcheson et al. (2017) in 2014 (177 mm), thus displaying important inter-annual variability. Groundwater DOC concentrations were comparable to other boreal peatlands (Waddington and Roulet, 1997). Though not significant, there was an overall increase in DOC concentration in 2016, which is likely due to the lower water table compared to 2015. This indicates that the DOC flux towards the fen is more dependent on the volume of groundwater discharge to the fen than variability in DOC concentration. Smerdon et al. (2008) found that climate variation 1-2 years before measurement determined aquifer recharge in sub-humid boreal environments. As the watershed received less than average seasonal precipitation in 2015, groundwater recharge may have been limited, and subsequently, groundwater input to the fen. In 2016, the difference in water table between upland and fen became smaller (Figure 3-7), causing the vertical gradient within the fen to decrease (Figure 3-8), reducing groundwater DOC inputs.

Khadka et al. (2015) found that very little DOC was produced from the upland tailings sand; however, as a large mass of tailings sand is present within the upland, it is possible that dissolution into percolating water may cause accumulation of DOC in groundwater. During an incubation experiment by Khadka et al. (2015), tailings sand placed in DI water produced DOC with a high $SUVA_{254}$ (~4) and low E2/E3 (~1.5); however, $SUVA_{254}$ significantly decreased (~2.5) once incubated in saline water. $SUVA_{254}$ in the saline incubation had values comparable to those observed in groundwater (1.5-2.5), though E2/E3 values were lower in the incubation. Alternatively, DOC within the groundwater may be partly sourced from infiltration from surface runoff, which had higher E2/E3 values than those observed the tailings sand incubation. Freeze-thaw and root development increases infiltration into the reclaimed soils in the upland (Ketcheson, 2015) that may enhance both DOC percolation to groundwater and transport to the fen. Kessel (2016) outlined how recharge basins within the upland promote infiltration from direct precipitation inputs and hillslope runoff. As these features are important hydrologically, they may also represent an important biogeochemical control on constructed systems; future reclaimed sites that use similar construction materials should be aware of the implications of recharge, and how this will direct DOC transport within a watershed. However; no source of DOC monitored in the study at the constructed watershed produced E2/E3 values similar to that observed in groundwater, indicating alternative processes (i.e. microbial activity) are impacting DOC dynamics.

Impacts of inputs on DOC export from the fen

Within both natural (Jager et al., 2008) and restored (Shantz and Price, 2006) peatlands, precipitation events during the growing season have been shown to promote significant DOC export. Jager et al. (2008) determined that precipitation events coupled with high water tables significantly increased outflow, thus DOC export; however, dry conditions became more important once the discharge from snowmelt had dissipated. This was also the case in the constructed fen, as outflow events from June-August of both years were a result of large precipitation events, whereas almost all outflow in May 2015 was due to the spring freshet. The water table from June to August of 2015 commonly fell below the height of the v-notch, and precipitation had less of an impact on discharge, compared to that in a wet year. This trend was amplified in 2016; despite a greater precipitation input in 2016, there was less outflow due to depleted water storage within the fen from 2015 to 2016. This has been observed in other boreal peatlands, where there is a lag between annual precipitation inputs, and changes in water storage (Devito et al., 2012).

Groundwater can be an important vector for export of DOC from peatlands (Waddington and Roulet, 1997; Olefeldt et al., 2013). However, the constructed fen is designed to isolate the system from groundwater losses; groundwater movement occurs upward through the fen peat and thus contributes to surface water discharge. The small groundwater input from the upland was insufficient to raise the water level within the fen to generate DOC export for much of the 2015 and 2016 study period. As groundwater input was limited to 38 mm in 2015, it is unlikely that the DOC brought into the fen from groundwater impacted DOC export. This is supported by DOC quality data; $SUVA_{254}$ and E2/E3 values in groundwater samples were comparable to DOC quality observed in the outflow in 2015 (Appendix 6), though all fluorescence spectroscopy indices differ markedly between groundwater and outflow samples. Groundwater DOC quality also differed from that at the outflow in 2016 (Appendix 6); $SUVA_{254}$ values decreased from 2015, indicating a lesser degree of aromaticity, reinforcing DOC transport data that suggests groundwater transport represents a small portion of the fen DOC budget, and subsequently has little impact on DOC export. Therefore, although DOC is transported to the fen via groundwater, the small volume of groundwater results in it contributing very little to the DOC that is exported. It will likely take multiple years for DOC from groundwater to reach the outflow, and any specific quality signature will be lost by mixing with the large pool of DOC produced within the fen.

When comparing DOC quality at the outflow to runoff, all indices fall within comparable ranges. As samples on hillslopes were only collected in 2016, this is the only year being used for comparison to outflow. $SUVA_{254,}$ E2/E3, FI, HIX, and β/α values from runoff (Figure 3-13) were all similar to values observed at the outflow (Figure 3-15). Specifically, surface runoff also represented a negligible input of DOC to the fen, relative to the net DOC production within the fen (Figure 3-16). This is in part due to the alternative potential pathways for runoff prior to its arrival at the fen. As the southeast slope has no direct contact with the fen, and is directly upstream of a recharge basin, most of its surface runoff percolates to groundwater storage (Kessel, 2016). On the east and west slope, only a small portion of their boundary is shared with the fen, so much of their surface runoff was directed through the upland, where it was detained by furrows, eventually recharging the upland aquifer. Consequently, the volume of runoff, thus DOC, from the upland and hillslopes was small, and it is unlikely that any runoff has a significant impact on DOC export.

The outflow DOC quality may have changed from 2015 to 2016 due to the volume of discharge, as opposed to the actual DOC quality within the fen. In 2015, the majority of export occurred during the spring freshet, during which time the surface was largely frozen. Additionally, vegetation had not started to grow; both factors would limit the variability in DOC quality over this period. Hood et al. (2006) determined that the aromatic, humic fraction of DOC in export increased during storm events increased relative to baseline flow. Export of humic compounds was attributed to the flushing of more DOC through the system. This favoured the transport of larger, more aromatic compounds during peak flow, which was evident during the two outflow events in 2016; DOC became smaller and less aromatic as discharge decreased.

DOC dynamics within the fen are primarily dominated by vegetation sources (Chapter 2). Despite multiple hydrological DOC sources within the catchment, net DOC production from root exudates and microbial production represents the largest DOC input to the fen (Table 3-1). Associated error in the production estimate is comparable to the mesocosms experiment conducted by Blodau et al. (2004); standard deviation represented 25% of the net DOC production. As the fen is also in proximally closest to the spillbox relative to other study areas within this catchment, water is channeled directly from the fen to the outflow point. As such, export is dominated by vegetation growth in the fen 3-4 years post construction. However, the proportion of each DOC input may change over time, particularly as vegetation growth or changes in community structure stabilize. The importance of temporal changes in vegetation community has also been suggested in restored peatlands; snowmelt and shifts in increases in vascular plant cover have been shown to promote hydrophilic acid export in restored sites (Strack et al., 2011). Hence, monitoring DOC export can be used to assess changes in DOC inputs in the fen over longer time scales. It will also be important to account for changes in discharge; the magnitude of outflow has been shown to directly impact export DOC quality (Figure 3-15). Therefore, implications of export to downstream ecosystems can be estimated by assessing discharge rate and fen DOC dynamics.

3.6 Conclusion

In natural sites, hydrologic fluxes of DOC can represent significant inputs of DOC to wetlands, but this is not the case within this constructed watershed. Precipitation provided the smallest input of DOC hydrologically, but it was only a marginally smaller input than surface runoff or groundwater. DOC concentrations did not vary notably between the soils or time post-construction in the upland or hillslopes, though there were significant differences in DOC quality. Therefore, as surface runoff into the fen represents a small amount of the DOC flux within this system, the variability in DOC quality from the various sources will likely have little impact on overall DOC dynamics within the fen or downstream ecosystem. However, in systems that are solely forestland, and are composed of peat/mineral mix or LFH-mineral mix, the impact of changes in quality should be taken into consideration as these may dominate the DOC input to downstream ecosystems.

Groundwater represented the largest hydrologic input of DOC in 2015; however, this was relatively small compared to the amount of DOC produced in the fen. It does not appear that any of the hydrological DOC inputs have a significant influence on the outflow DOC, as runoff and groundwater inputs have different values for almost all DOC quality indices. This is expected, as the DOC budget clearly shows that the fen produces a much larger proportion of DOC within the system than any other source, and channels water and DOC directly to the outlet. The design of the system limits DOC output, as the only discharge point is through the single outflow point. This must be taken into account when considering what will be incorporated into the landscape downstream, as DOC can represent an important organic source for microbial communities, but may also transport contaminants, particularly metals, bound to its structure. This study has not addressed the important time periods outside the growing season, such as during the snowmelt period, which can also generate significant outputs of DOC from natural wetland ecosystems. Therefore, this should be considered an important component to address in future studies.

Currently, the hydrology, not biogeochemistry, seems to control the mass of DOC mobilized within the constructed watershed, although the biogeochemistry controls the mass of DOC within the fen. Moving forward, the wetland should be the most intensively monitored aspect of this watershed for DOC dynamics. This is due to the large net DOC production within the fen, and direct impact DOC production has on DOC export from the system, in terms of both quantity and quality. Therefore, the physical design must be taken into account when expanding this assumption into other watersheds, particularly if the wetland is not in direct contact with the outflow point, or groundwater is released from the system. Additionally, the relative proportion of DOC fluxes may change as the vegetation community in the upland and hillslopes develops, changing the soil structure, altering both runoff and groundwater transport as well as DOC production.

Chapter 4: Recommendations and implications for fen construction

Work within the constructed fen and reference sites has demonstrated that the biogeochemical function of the Nikanotee Fen does not yet resemble natural analogues. Rather, the DOC pool is dominated by vascular plant inputs, specifically through root exudates, 3-4 years post-construction. This creates a DOC pool that is highly bioavailable, and can stimulate downstream microbial activity. Moreover, DOC-metal complexation can occur, especially as high metal concentrations have been observed within the constructed watershed (Simhayov, 2017). Labile DOC is more successful at transporting metals, less likely to be stored within sediments, and has a greater chance of being broken down and re-releasing metals relative to recalcitrant DOC. Therefore, a shift to vegetation-sourced DOC is important to monitor. Over longer time periods, plant litter in the fen will accumulate and cause peat formation. As recently produced peat can release large amounts of DOC, quality will shift to appear more recalcitrant, and therefore less bioavailable than the root exudates currently being produced. Therefore, long-term shifts in water quality must be taken into account for landscape-scale reclamation to understand the function they may provide within larger watersheds. Specifically, ecosystems integrated downstream should be adaptable to variability in metal and organic substrate inputs if export exhibits inter-annual variability.

One distinct shift in DOC quality has been observed within the constructed fen in four-year period post-construction, as vegetation success has promoted root exudate production, increasing DOC concentration and bioavailability. It is likely at least one more shift will occur, as peat accumulates. Furthermore, DOC quality may shift as invasive species become established within fens. This may alter DOC dynamics within constructed peatlands if management strategies do not adequately promote fen vegetation success. As the sample size of *Typha* spp. within this study was small, further work should be done to quantify DOC quality across potential invasive species on constructed wetlands in the WBP. This will help to assess whether invasive species can alter DOC quality enough to change DOC export quality. Hence, it is important to monitor fen and discharge DOC concentration and quality continuously until significant peat accumulation has occurred, and vegetation communities become established, such that DOC concentration and quality have stabilized. Within-site monitoring efforts should be most intensive during changes in vegetation community composition, and when peat begins to accumulate.

Hydrological inputs of DOC inputs to the fen are negligible relative to the internal net DOC production within the fen. Between all hydrological fluxes of DOC, groundwater represents the largest input to the fen when there is sufficient recharge to the upland aquifer. However, following dry conditions, precipitation represented the largest input. Across the watershed, DOC fluxes to the fen are largely dependent on the hydrology of the site, rather than the biogeochemistry. The export of DOC from the fen is dominated by DOC produced within the fen, rather than external sources. Additionally, DOC export quantity and quality is primarily dependent on the discharge rate, rather than seasonal shifts. This is due to the geometry of the site, where surface flow through a small discharge point is the only opportunity for DOC to be lost from the system hydrologically. However, low discharge occurred due to limited precipitation inputs through the summer. DOC export will likely play a more important role in downstream biogeochemistry following snowmelt, and when water table within the fen rises. Therefore, though total DOC export within this study is small, continued monitoring of DOC export is important, as it is influenced by shifts in net DOC production within the fen, and may have direct impacts on downstream water quality. If future reclamation sites feature a similar site design, monitoring should be focused within the fen, and at the outflow in early years post-succession. Should greater connectivity between the fen watershed and the surrounding landscape occur, groundwater DOC monitoring may become important, to account for potential metal transport, and organic inputs to downstream watersheds. Ecosystems that can adapt to shifts in DOC quality should be constructed directly downstream of fens to ensure long-term success of reclamation attempts.

Though decreasing DOC export may limit metal mobility, this would come at the expense of reducing discharge. As this may come in conflict with alternative peatland function within the landscape, it is proposed that DOC can still be used as a metric of fen biogeochemical function. Therefore, DOC can represent a fast and inexpensive method for assessing fen biogeochemical processes between larger monitoring efforts. This study employed a wide range of indices to assess DOC quality. As spectrophotometric indices integrate the entire DOC sample, and $SUVA_{254}$ inherently requires DOC concentration be determined, these indices are recommended for use on a broader scale when monitoring within-fen DOC dynamics. Fluorescence spectroscopy can be limited to outflow samples, which may highlight the need for intensive monitoring within the fen. Shifts in DOC quality or concentration observed in outflow samples, particularly when observed with changes in vegetation community or peat accumulation indicate that intensive sampling within the fen should be conducted to capture variations in DOC sources. Consistent sampling at the outflow may also be a useful indicator for further changes in DOC quantity or quality within the fen.

This study has also illustrated important biogeochemical differences between DOC produced on varying contributing areas. Specifically, DOC concentration does not vary on LFH-mineral and peat-mineral mix areas, while the DOC quality varied significantly. Within watersheds which use LFH-mineral or peat-mineral mixes on a large scale, this is an important study for providing early-successional data on DOC quality across construction materials. It will be important to take this quality data into consideration for sites which may be built using only these materials, and when planning for reclamation projects downstream. Additionally, it is likely that the organic material in peat/LFH-mineral mix soils are a large source of DOC for groundwater recharge, it is important to be cognizant of the shift in DOC quality once surface water percolates to the tailings sand aquifer. Though this study has highlighted potential sources of DOC in peat/LFH-mineral soils and tailings sand, processes that transform and shift DOC quality between these areas are still poorly understood. Specifically, future studies should address microbial activity and identify DOC compounds within reclamation materials, further improving the ability to predict downstream impacts of DOC export from reclamation projects.

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Appendix

Appendix 1. DOC correlations with absorbance at 250 nm (a250) used to estimate DOC concentration in 2015.

Location	**Equation**	**DF**	**F-value**	**R^2**	**p value**
Saline Fen	TOC=0.03(a250)+0.48	1,8	132.9	0.94	<0.001
Poor Fen	TOC=0.037(a250)+0.18	1,14	54.03	0.78	<0.001
Rich Fen	TOC=0.031(a250)+0.97	1,14	23.68	0.7	<0.001
Constructed Fen Peat	TOC=0.023(a250)+0.21	1,41	172.9	0.8	<0.001
Constructed Fen Mineral	TOC=0.01(a250)+0.23	1,24	96.83	0.79	<0.001

Appendix 2. Correlations between all measured DOC characteristics (dependent variables/DV) and environmental variables (independent variables/IV). Rows which are bolded were shown to be significant ($p<0.05$), and those not bolded represented potentially important relationships ($p<0.1$).

Site	Treatment	DV	IV	F value	R^2	p value
CF	**B**	**DOC**	**pH**	**5.59**	**0.28**	**0.037**
CF	**B**	**DOC**	***EC***	**4.65**	**0.23**	**0.05**
CF	B	SUVA	*EC*	4.38	0.22	0.06
CF	B	SUVA	*WT*	3.91	0.2	0.07
CF	**B**	**E2/E3**	***WT***	**5.43**	**0.27**	**0.04**
CF	**B**	**E2/E3**	***EC***	**94.4**	**0.89**	**<0.001**
CF`	B	HIX	*WT*	7.21	0.55	0.055
CF	B	FI	*EC*	7.39	0.56	0.053
CF	B	β/α	*WT*	6.3	0.51	0.066
CF	***C. aquatilus***	**DOC**	***T***	**7.28**	**0.3**	**0.017**
CF	***C. aquatilus***	**DOC**	***EC***	**32.13**	**0.67**	**<0.001**
CF	***C. aquatilus***	**E2/E3**	**pH**	**5.26**	**0.22**	**0.038**
CF	***C. aquatilus***	**E2/E3**	***EC***	**15.61**	**0.49**	**0.001**
CF	***C. aquatilus***	**HIX**	***T***	**7.46**	**0.37**	**0.021**
CF	***C. aquatilus***	**HIX**	***EC***	**12.84**	**0.52**	**0.005**
CF	**CM**	**DOC**	***WT***	**8.97**	**0.3**	**0.008**
CF	**CM**	**DOC**	***T***	**6.1**	**0.21**	**0.024**
CF	**CM**	**SUVA**	***EC***	**5.01**	**0.17**	**0.038**
CF	**CM**	**SUVA**	***T***	**4.65**	**0.16**	**0.045**
CF	**CM**	**E2/E3**	***EC***	**15.08**	**0.42**	**0.001**
CF	CM	HIX	*T*	3.8	0.18	0.075
CF	**CM**	**HIX**	***EC***	**5.03**	**0.24**	**0.045**
CF	CM	FI	*EC*	3.79	0.18	0.075
CF	***J. balticus***	**DOC**	***T***	**14.51**	**0.46**	**0.002**
CF	***J. balticus***	**DOC**	***EC***	**24.09**	**0.59**	**<0.001**
CF	***J. balticus***	**E2/E3**	***EC***	**75.28**	**0.82**	**<0.001**
CF	**JM**	**DOC**	***WT***	**8.87**	**0.29**	**0.008**
CF	**JM**	**DOC**	***T***	**4.63**	**0.16**	**0.044**
CF	**JM**	**SUVA**	***WT***	**6.1**	**0.21**	**0.024**
CF	**JM**	**E2/E3**	***EC***	**46.85**	**0.71**	**<0.001**
CF	**JM**	**HIX**	***T***	**5.77**	**0.28**	**0.035**
CF	**JM**	**β/α**	***WT***	**6.67**	**0.32**	**0.025**
CF	**JM**	**β/α**	***EC***	**10.17**	**0.43**	**0.009**
CF	**moss**	**DOC**	***T***	**4.63**	**0.14**	**0.043**
CF	**moss**	**DOC**	***EC***	**21.16**	**0.47**	**<0.001**
CF	**moss**	**SUVA**	***EC***	**7.75**	**0.23**	**0.011**
CF	**moss**	**SUVA**	***T***	**4.48**	**0.13**	**0.046**
CF	**moss**	**E2/E3**	***EC***	**24.87**	**0.51**	**<0.001**
CF	**moss**	**FI**	***EC***	**4.41**	**0.13**	**0.047**
CF	**moss**	**FI**	***WT***	**6.37**	**0.19**	**0.019**
SF	**B**	**DOC**	**pH**	**4.83**	**0.21**	**0.048**

SF	B	SUVA	*T*	4.01	0.18	0.066
SF	B	E2/E3	*EC*	3.76	0.16	0.074
SF	**B**	**β/α**	***EC***	**7.57**	**0.29**	**0.015**
SF	***J. balticus***	**DOC**	***EC***	**18.06**	**0.59**	**0.001**
SF	***J. balticus***	**E2/E3**	***EC***	**5.98**	**0.29**	**0.033**
SF	***J. balticus***	**FI**	***EC***	**82.43**	**0.86**	**<0.001**
SF	***J. balticus***	**FI**	***WT***	**10.54**	**0.42**	**0.007**
SF	***J. balticus***	**β/α**	***WT***	**5.31**	**0.25**	**0.04**
SF	***J. balticus***	**β/α**	***EC***	**41.47**	**0.76**	**<0.001**
PF	moss	DOC	*EC*	3.93	0.12	0.06
PF	**moss**	**β/α**	***T***	**4.97**	**0.17**	**0.039**
PF	***C. aquatilus***	**DOC**	***T***	**5.94**	**0.22**	**0.026**
PF	***C. aquatilus***	**SUVA**	***EC***	**5.43**	**0.2**	**0.032**
PF	***C. aquatilus***	**HIX**	***EC***	**13.76**	**0.38**	**0.001**
PF	***C. aquatilus***	**FI**	***EC***	**14.54**	**0.39**	**0.001**

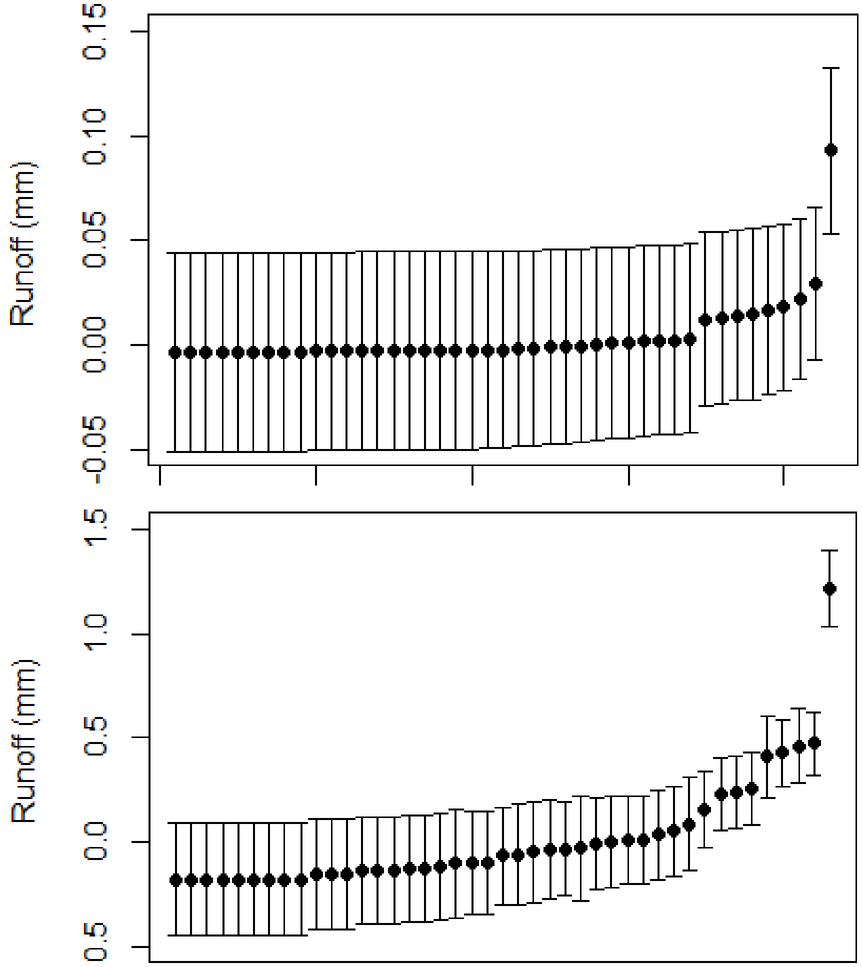
Appendix 3. Correlations between all measured DOC characteristics (dependent variables/DV) and environmental variables (independent variables/IV) across monitored sites at 50 cm piezometers.

Site	**Year**	**DV**	**IV**	**F-value**	**R^2**	**Slope**	**p-value**
CF	2015	DOC	T	11.34	0.28	1.41	0.002
CF	2015	DOC	EC	5.59	0.15	0.0044	0.026
CF	2015	$SUVA_{254}$	WT	5.61	0.15	0.012	0.026
CF	2015	E2/E3	EC	33.16	0.55	$4.65*10^{-4}$	<0.001
CF	2016	DOC	WT	13.08	0.33	-1.19	0.001
CF	2016	DOC	T	12.92	0.32	-1.08	0.001
CF	2016	DOC	EC	45.61	0.64	0.0072	<0.001
CF	2016	$SUVA_{254}$	WT	7.12	0.20	0.035	0.013
CF	2016	$SUVA_{254}$	EC	6.61	0.18	$-1.52*10^{-4}$	0.017
CF	2016	E2/E3	WT	5.72	0.16	-0.051	0.025
CF	2016	E2/E3	EC	10.87	0.28	$2.9*10^{-4}$	0.003
RF	2015	DOC	EC	10.22	0.35	0.058	0.006
SF	2015	DOC	T	17.54	0.43	4.27	<0.001
SF	2015	DOC	EC	4.34	0.12	0.0035	0.05
PF	2015	DOC	EC	23.99	0.5	0.020	<0.001
PF	2015	$SUVA_{254}$	EC	7.4	0.22	$-4.6*10^{-6}$	0.012
PF	2015	E2/E3	EC	57.11	0.71	0.0030	<0.001
PF	2016	DOC	pH	4.86	0.26	-17.60	0.05
PF	2016	$SUVA_{254}$	pH	8.45	0.40	-1.23	0.016
PF	2016	$SUVA_{254}$	WT	6.88	0.35	0.040	0.025
PF	2016	E2/E3	pH	5.64	0.30	-0.46	0.039

Appendix 4. Regression models for the west slope and upland from data collected in 2016 used to estimate runoff depth in 2015. Int_{max} and Int_{avg} are the maximum and average precipitation intensity, respectively, observed during a rainfall event.

Location	**Model**	**DF**	**F value**	$\mathbf{R^2}$	**p value**
West	$R=P*Int_{max}$	1,17	67.86	0.91	<0.001
Upland	$R=P:Int_{avg}$	1,18	13.42	0.4	0.002

Appendix 5. 95% confidence intervals for all modelled runoff events in 2015 on the upland (top) and west slope (bottom). Points indicate actual values used for runoff estimates, prior to being normalised to fen area.



Appendix 6. Summary of DOC quality across hydrologic inputs and outputs in the constructed fen in 2015 and 2016. The seasonal average is presented for all quality indices. Average fen values are used from 50 cm piezometers.

	2015					2016				
	$SUVA_{254}$ (L/mg m)	E2/E3	HIX	FI	β/α	$SUVA_{254}$ (L/mg m)	E2/E3	HIX	FI	β/α
Precipitation	3.30	3.65	-	-	-	2.97	2.93	-	-	-
East Slope	-	-	-	-	-	3.52	4.50	0.88	1.45	0.71
West Slope	-	-	-	-	-	4.05	4.04	0.90	1.42	0.59
Southeast Slope	-	-	-	-	-	4.23	4.57	0.89	1.42	0.63
Upland	-	-	-	-	-	2.83	5.40	0.87	1.5	0.70
Groundwater	2.03	7.39	0.58	1.72	1.23	1.46	7.47	-	-	-
Fen	2.58	5.96	0.88	1.58	0.63	2.84	6.06	-	-	-
Discharge	2.04	6.25	0.76	1.54	0.84	3.19	4.84	0.85	1.48	0.68