Sulfur biogeochemistry in a constructed fen peatland in the Athabasca Oil Sands Region, Alberta, Canada

by

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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

In peatlands, increased sulfate (SO_4^{2-}) availability can stimulate dissimilatory SO_4^{2-} reduction (DSR), allowing it to become a prominent anaerobic carbon (C) mineralization process. In turn, methane emissions may be suppressed, but at the expense of potentially degrading peat accumulation processes if DSR dominates C mineralization pathways. Additionally, as a product of DSR, sulfide sequesters potentially toxic metals as insoluble precipitates. However, accumulation of dissolved sulfide may be toxic to wetland vegetation species. Peatlands are abundant in the Western Boreal Plain in Alberta, the majority of which are fens. Due to the nature of surface mining in the Athabasca Oil Sands Region (AOSR), these systems are removed from the landscape. Accordingly, oil sands companies are required to return their post-mined sites to equivalent pre-disturbed conditions. In an attempt to test the feasibility of fen creation in the AOSR, a fen peatland ecosystem, named Nikanotee Fen, has been constructed with water supply from an adjacent tailings sand upland aquifer and surrounding reclaimed hillslopes. In the fen peat deposit, pore water SO_4^{2-} concentrations are 1 to 2 orders of magnitude higher than in surrounding natural peatlands. Due to the nature of the materials used in the design of the system, and the management practices employed prior to construction, the sources that contribute to the elevated pool of SO_4^{2-} are not well understood. The purpose of this research was to investigate the main sources of SO_4^{2-} and identify hydrogeochemical controls on its dissolved pool in the pore waters of Nikanotee Fen.

Throughout the study period (2013-2016), pore water SO_4^{2-} concentrations were generally highest in the upland tailings sand aquifer, primarily derived from legacy gypsum ($CaSO_4{\cdot}2H_2O$) in process affected water, in addition to the marine origin of the sand which was reflected by $Ca:SO_4$ molar ratios less than 1 in the groundwater, especially in the eastern region. In the petroleum coke underdrain that was incorporated to control groundwater transport from the upland aquifer, pore water SO_4^{2-} concentrations increased over time. Dilution, due to freshwater inputs from precipitation and surface runoff generated by the reclaimed hillslopes, was the main mechanism controlling the dissolved SO_4^{2-} pool in the upland aquifer and petroleum coke underdrain. Additionally, the heterogeneity of the placed tailings sand likely contributed to the variability in pore water SO_4^{2-} distribution between the eastern and western regions of the upland.

Unexpectedly, the peat deposit in 2013 initially experienced substantially higher pore water SO_4^{2-} concentrations than the underlying petroleum coke underdrain in the western region of the fen, indicating a pre-existing source of SO_4^{2-} in the peat, possibly due to the prolonged drainage of the donor fen. However, lower average pore water SO_4^{2-} concentrations than in the underlying petroleum coke underdrain, $Ca:SO_4$ molar ratios exceeding 1, and elevated $HCO3^-$ concentrations in the eastern and western regions of the fen peat deposit indicated that SO_4^{2-} reduction was likely occurring in the layer at the end of the 2013 season and in the subsequent years.

To test the former hypothesis that the donor peat management practices may have led to elevated SO_4^{2-} concentrations in the peat deposit during the first year, a batch incubation experiment was conducted in which peat was treated with aeration (oxic conditions) and inundation (anoxic conditions) at 15 and 25°C, after a drying period of 7 days. Sulfate release was immediately evident 24 hours following re-wetting. At both incubation temperatures, further increases in $S\text{-}SO_4^{2-}$ concentrations were observed upon aerobic incubation of the dried and re-wet peat. Drying, instead of temperature sensitivity, was the primary mechanism controlling $S\text{-}SO_4^{2-}$ release due to oxidation of reduced inorganic sulfur (S) as well as enhanced mineralization of organic S. Following inundation of the formerly oxidized peat, a sharp decrease in $S\text{-}SO_4^{2-}$ concentration was seen at both temperature incubations, most likely due to SO_4^{2-} reduction. Further decreases in $S\text{-}SO_4^{2-}$ concentration were not pronounced at the end of the inundation period, possibly due to limitation by labile C since SO_4^{2-} apparently was not limiting for sulfate reducing bacteria.

This research provides insight into the sources of SO_4^{2-} and processes that control its dissolved pool in Nikanotee Fen. Additionally, the findings can be used to establish a general baseline for future reclamation projects that may mimic the design strategies of Nikanotee Fen. Based on the results, it is recommended that the time frame between drainage and extraction of donor peat is reduced as much as possible in the design of future fen systems in the AOSR.

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role in helping me stay motivated during times of doubt! I wish you and your family the best. Thank you Rubi😊.

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Dedication

To my loving family – Ibram, Sue and John: Thank you for everything.

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List of Abbreviations

AOSR	Athabasca Oil Sands Region
WBP	Western Boreal Plain
OSPW	Oil Sands Process Affected Water
SAGD	Steam Assisted Gravity Drainage
CSS	Cyclic Steam Stimulation
CT	Consolidated Tailings
NAs	Naphthenic Acids
PAHs	Polycyclic Aromatic Hydrocarbons
$CaSO_4 \cdot 2H_2O$	Gypsum
NaOH	Caustic (Sodium Hydroxide)
FeS_2	Pyrite
EC	Electrical Conductivity
MC	Moisture Content
OMC	Organic Matter Content
DO	Dissolved Oxygen
LOI	Loss on Ignition
IC	Ion Chromatography
E_h	Redox potential
TEAs	Terminal Electron Acceptors
K_{sp}	Solubility product constant
[ion]	Soluble concentration of an ion
Bgs	Below ground surface
C	Carbon
S	Sulfur
Fe	Iron
SO_4^{2-}	Sulfate
Ca^{2+}	Calcium
Mg^{2+}	Magnesium
Na^+	Sodium
HCO_3^-	Bicarbonate
$S\text{-}SO_4^{2-}$	Sulfur as sulfate
SRB	Sulfate Reducing Bacteria
DSR	Dissimilatory Sulfate Reduction
CBS	Carbon Bonded Sulfur
ESS	Ester Sulfate Sulfur
RIS	Reduced Inorganic Sulfur

1. Introduction

1.1 General introduction

Dissimilatory sulfate reduction (DSR) was believed to be an insignificant pathway of anaerobic carbon (C) mineralization in freshwater peatlands, owing to low dissolved sulfate (SO_4^{2-}) concentrations (Nedwell, 1984). However, evidence has emerged in support of a rather enigmatic sulfur (S) cycle in these systems, in which case DSR may become a prominent anaerobic C mineralization process despite an instantaneous small dissolved SO_4^{2-} pool (Wieder and Lang 1988, Wieder *et al.*, 1990). In view of the ramifications of DSR for C cycling in peatlands (Dise and Verry, 2001; Gauci *et al.*, 2002; Vile *et al.*, 2003a), recent research has further explored the potential mechanisms involved in sustaining the availability of SO_4^{2-} required for DSR to be an important contributor to C mineralization (Blodau *et al.*, 2007, Knorr *et al.*, 2009, Knorr and Blodau, 2009). In non-pristine systems, such as reclaimed landscapes in the Athabasca Oil Sands Region (AOSR), S biogeochemistry has only been investigated in tailings ponds and consolidated tailings (CT) deposits, due to their roles in reclamation technologies (Ramos-Padrón *et al.*, 2011; Warren *et al.*, 2016). However, peatland creation has recently been implemented in the AOSR and is the subject of ongoing research and monitoring (Pollard *et al.*, 2012). Presently, aside from the assessment of sulfide generation in a CT deposit undergoing fen reclamation (Reid and Warren, 2016), no information is available with respect to how current reclamation strategies and practices used in fen construction influence the dissolved pool of SO_4^{2-} in the pore water of these systems. Given that the intent of these projects is to mimic natural ecosystems and their respective functions, it is important to understand the implications of landscape reclamation practices on S biogeochemistry of target systems in the AOSR, such as fen peatlands.

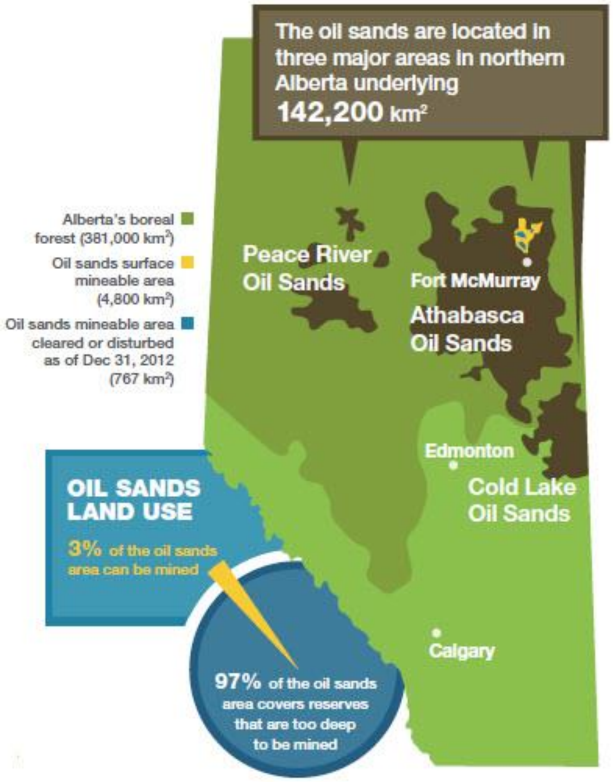

Figure 1-1: Map of Alberta's oil sands regions and disturbed area. From Alberta Government (2017).

The Western Boreal Plain (WBP) located in Alberta is home to the largest oil reserve in Canada, which trails only Venezuela and Saudi Arabia globally (Government of Alberta, 2017). Underlying ~142,200 km^2 of land (Figure 1 – 1), over 160 billion barrels (bbl) of recoverable oil currently make up the oil sands deposit in Alberta (Government of Alberta, 2017). This bituminous rich oil sand is covered by layers of overburden consisting of peat, till, sandstone and shale (Conly *et al.*, 2002; CEMA, 2014). To recover the bitumen, there are currently two techniques in practice. Open pit mining is used where the oil sands are closer to the surface, making up about 20% of the available oil sands reserves (NRC, 2016). For the deeper (exceeding 75 m below ground) and more abundant bitumen, *in-situ* drilling recovery technologies such as Cyclic Steam Stimulation (CSS) and Steam Assisted Gravity Drainage (SAGD) are used (Jiang *et al.,* 2010; NRC, 2016). There exist three major deposits in Alberta that comprise the oil reserve (Figure 1 – 1) including Athabasca, Cold Lake and Peace River (CAPP, 2016). The bitumen found in Cold Lake and Peace River is too deep to recover with open pit mining techniques (Government of Alberta, 2017). Therefore, surface mining is feasible only in the AOSR (Figure 1 – 1), which could disturb up to ~3% (total ~4,800 km^2) of the ~142,200 km^2 land area that cover the oil sands in Alberta (Weinhold, 2011). Wetlands within the AOSR (prior to disturbance) are reported to cover approximately half of the landscape, the majority of which are fen peatland systems (Vitt *et al.*, 1996). These systems are important natural landforms in the boreal forest. They are integral in sequestering C, and hence have significant roles in the regional and global C cycle (Blodau, 2002; Belyea and Malmer, 2004), can retain water essential for adjacent ecosystems (Devito *et al*., 2005), and can behave as transformers, sinks or sources of nutrients (Vile and Novák, 2006). Due to the nature of ongoing surface mining activities (i.e. 895 km^2 of land area disturbed as of 2013) (Government of Alberta, 2017), natural wetland ecosystems that overlay bitumen deposits are removed from the landscape (Rooney *et al.,* 2012). The aforementioned ecosystem services highlight the need for proper management strategies of disturbed peatlands. Accordingly, regulations have been implemented to require oil sands companies to return their post-mined sites to “equivalent land capability” after mining operations have halted (OSWWG, 2000). Equivalent land capability means that the land after reclamation has the ability to support land uses that are similar, but need not be identical, to those that existed prior to mining (CEMA, 2006). In the case of reclaiming peatlands (i.e. re-creation), equivalent land capability can be achieved by salvaging on-site mine waste materials and using known peatland restoration techniques (Price *et al.,* 2010; Pollard *et al.,* 2012).

1.2 Fen peatland reclamation

In an effort to reclaim disturbed peatlands in the AOSR, fen peatland creation in the region has recently been introduced (Pollard *et al.,* 2012). Peatland creation was previously considered impractical since peat accumulation is slow (Clymo, 1984; Moore and Basiliko, 2006). However, the novel work of Price *et al*. (2010), which used numerical modeling to test AOSR construction material's hydraulic properties and fen-upland geometry for potential fen creation, suggested that implementing known peatland restoration techniques essential for a vegetation community, along with the necessary hydrogeological conditions may result in successful fen creation.

Given that fen construction on the post-mined landscape is still at an experimental stage, there are knowledge gaps that result in a lack of a standard framework that can help in evaluating the success of fen reclamation. For instance, in the WBP, precipitation is typically less than potential evapotranspiration (Devito *et al.,* 2005). Therefore, to create a groundwater system that can sustain saturated conditions for peat accumulation and overall biogeochemical functioning of a fen, will require an understanding of the hydrogeological connectivity of the landscape and the required hydrophysical properties of the salvaged material. Additionally, the biogeochemical implications of management practices in using donor and mine waste materials need to be understood (Nwaishi *et al.,* 2015). For example, peatlands in the AOSR are typically drained prior to overburden removal (i.e. to expose the oil sands deposit beneath) and the peat is subsequently stripped and stockpiled for future use (CEMA, 2014), or directly transferred to target landscapes (Nwaishi *et al.,* 2015). Drained *in-situ* or stockpiled peat experiences frequent drying and wetting cycles (Lieffers, 1988), which results in higher decomposition rates of the peat, as aerobic decomposition occurs at a rate substantially higher than anaerobic decomposition (Clymo, 1984). It is known that accelerated decomposition is associated with enhanced mineralization of organic matter and further decay of organic structure (Macrae *et al*., 2013). Ultimately, the overall biogeochemical functioning of a constructed fen using drained donor peat may be different than that characteristic of natural systems depending on the peat quality.

Mine waste materials that are used in reclamation can have elevated salt concentrations, originating from natural marine shale (Purdy *et al.,* 2005; Kessler *et al.,* 2010; Holden *et al.,* 2011).

Moreover, oil sand extraction and tailings densification processes have previously introduced solutes into the reclamation material, originating from caustic (NaOH) to help dissociate the bitumen from the sand (Hadwin *et al.,* 2006), and gypsum ($CaSO_4 \cdot 2H_2O$) to accelerate the settling of fine solids in tailings ponds (Fedorak *et al.,* 2003). The released oil sands process affected water (OSPW) can contain elevated concentrations of SO_4^{2-}, sodium (Na^+), and calcium (Ca^{2+}), as well as considerable concentrations of heavy metals (e.g. Al, Hg, Mn) and organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and naphthenic acids (NAs) (Mackinnon *et al.*, 2001; Leung *et al.*, 2001; Li *et al.,* 2014, 2017). Although the use of NaOH and $CaSO_4 \cdot 2H_2O$ ceased after implementation of alternative technologies (J. Martin, personal communication, 2017), the recycling of OSPW in operations can introduce elevated concentrations of legacy Na^+, Ca^{2+} and SO_4^{2-} into reclamation material (Chalaturnyk *et al.,* 2002). Therefore, if such contaminated material is used for fen construction projects, elevated concentrations of the aforementioned solutes could be present in the pore water of the fen. This may affect the establishment of vegetation species (Rezanezhad *et al.*, 2012, Ketcheson *et al.,* 2016a), shifting the biogeochemical functioning of the system from target (i.e. pre-disturbed) performance.

To date, Nikanotee Fen and Sand Hill Fen are the only two pilot fen projects in operation (Ketcheson *et al.,* 2016a). Sandhill Fen was constructed on a consolidated tailings (CT) deposit overlain by a sand cap (Pollard *et al.*, 2012). The engineered system included underdrains to control elevated salinity levels in the fen (Pollard *et al.,* 2012; Ketcheson *et al.*, 2016a). Nikanotee Fen, which is the focus of this research, was designed based on the conceptual model of Price *et al.* (2010). Constructed on an overburden dump at a mine lease north of Fort McMurray, the fen-upland system comprises a tailings sand upland aquifer that supplies lateral groundwater flow into the adjacent fen, through a petroleum coke underdrain, that transmits the flow horizontally beneath the fen, then upwards into a 2 m peat layer. Reclaimed hillslopes overlying saline substrates surround the system, which have been found to contribute runoff to the lower lying upland and fen (Ketcheson *et al.,* 2016b, Ketcheson *et al.*, 2016c). Tailings sand contains elevated concentrations of Na^+, Ca^{2+}, SO_4^{2-} and NAs (Mackinnon *et al.*, 2001; Holden *et al.*, 2011). Petroleum coke contains elevated concentrations of vanadium (V) and nickel (Ni) (Squires, 2005; Simhayov, 2017). The donor peat topsoil was taken from a drained rich fen peatland in which enhanced decomposition and mineralization may have resulted in the release of elements such as S, that were locked within the organic complex of the peat (Simhayov *et al.*, 2017). However, this has yet to be investigated.

1.3 Research rationale

Previous hydrogeochemical research for the Nikanotee Fen project documented the potential of salt migration (Na^+) from the upland aquifer into the fen peat deposit (Kessel *et al.*, 2018), the availability and mobility of inorganic solutes within the system (Simhayov *et al.*, 2017, Kessel *et al.*, 2018) and the potential of heavy metal leaching from the construction materials (Simhayov, 2017). However, despite the abundance of SO_4^{2-} in the pore waters of the constructed fen-upland system (Simhayov *et al.*, 2017), there has been insufficient research targeted towards understanding its dynamics in the system. It is known that SO_4^{2-} availability is one of the main controls on DSR, a process that is responsible for sulfide production (Reddy and DeLaune, 2008). Dissolved sulfide can be toxic to wetland vegetation species at concentrations in the micromolar range (Lamers *et al.*, 1998a & 2013), potentially leading to suppressed growth and development by inhibition of nutrient uptake (Van der Welle *et al.*, 2007; Lamers *et al.*, 2013). Dissimilatory SO_4^{2-} reduction can also suppress CH_4 emissions from peatlands (Gauci *et al.*, 2002), which are known to be a natural source to the global CH_4 budget (~47 Tg annually) (Vile and Novák, 2006). Murray *et al.* (2017) found that CH_4 fluxes and concentrations in Nikanotee Fen were low compared to natural reference sites, due to significantly higher SO_4^{2-} concentrations in the pore waters of the constructed system's peat deposit. Abundant SO_4^{2-} thermodynamically favors SO_4^{2-} reducing bacteria (SRB) to outcompete methanogens for energy from organic compounds (Oremland and Polcin, 1982; Pester *et al.*, 2012). Thus, SO_4^{2-} reduction may account for a larger portion of total anaerobic C mineralization than methanogenesis (Wieder *et al.*, 1990), which may not favor peat accumulation at Nikanotee Fen. Furthermore, given that metals are present in the system inherent of mine waste materials (Simhayov, 2017), and that SO_4^{2-} reduction is expected to occur in the anaerobic zones of the fen (Simahyov *et al.*, 2017), this process would result in low aqueous concentrations of metals through the precipitation of metal sulfides (e.g. ZnS, NiS, CuS, CdS, etc.) of varying solubility (Simhayov, 2017). Ultimately, this may alter toxicity potential in the rooting zone.

In Nikanotee Fen, pore water concentrations of SO_4^{2-} in the peat profile are 1 to 2 orders of magnitude higher than in peat deposits of surrounding natural fen peatlands (Table 1 – 1), although they do not exceed those found in saline-spring fens in the region, which are fed by groundwater rich in ions from marine origin (Wells and Price, 2015). Given the nature of the reclamation material used, and the management practices employed pre-construction, the sources of SO_4^{2-} and its hydrogeochemical controls in Nikanotee Fen are not well understood. Investigating this uncertainty will help to assess how SO_4^{2-} dynamics might differ from those in natural peatland ecosystems, and how (or if) they might change over time. Moreover, as the goal of peatland reclamation is to return post-mined landscapes to have equivalent functions as pre-disturbed ecosystems, understanding the origins and dynamics of SO_4^{2-} in Nikanotee Fen will not only be crucial to allow for an assessment of the system's overall performance and implications, but the findings will also provide solid baseline information for future reclamation projects that may use strategies similar to those used in the construction of Nikanotee Fen.

Table 1 – 1: Mean, maximum and minimum pore water sulfate (SO_4^{2-}) concentrations, pH and Electrical Conductivity (EC) in the peat deposit of Nikanotee Fen compared to selected surrounding natural fens. Sampling was conducted in 2015 for all sites, except Saline Spring (2012). Sample size is denoted by *n*.

Type	*n*	SO_4^{2-} (mg L^{-1})			EC (µS cm^{-1})			pH		
		Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Nikanotee (Constructed)	27	684.7	1343.3	94.6	2557.3	3780	1692	7.2	7.7	6.8
Moderate Rich (Reference)**[a]**	51	8.1	31.7	0.1	428.2	728.7	103.2	6.8	7.5	4.2
Poor (Reference)**[a]**	12	1.9	7.0	0.5	20.7	39.3	12.5	4.5	5.2	3.9
Saline Spring (Reference)**[b]**	-	1561	3080	512	34550	-	-	6.40	-	-

a: unpublished data, University of Waterloo
b: data from Wells and Price (2015)

1.4 Research objectives

In view of the highlighted uncertainties, the aim of this research will be to examine the sources of SO_4^{2-} and identify controls on the dissolved pool in the pore waters of Nikanotee Fen Watershed. Specifically, the primary objectives are as follows:

1) characterize and assess the spatiotemporal pore water SO_4^{2-} distribution within Nikanotee Fen Watershed;
2) investigate the possible hydrogeochemical processes controlling the dissolved SO_4^{2-} pool within the fen-upland system; and
3) provide recommendations for donor material management and highlight essential future research.

1.5 Structure of thesis

This thesis is organized into 5 chapters, two of which are structured to meet the manuscript option at the University of Waterloo.

Chapter one provides a general introduction to the contents of the thesis, including background information for fen reclamation in the AOSR, rationale and primary objectives of the project.

Chapter two is a literature review, intended to provide the reader with a synthesis of S biogeochemistry in natural freshwater peatlands.

Chapter three and four are two independent manuscripts. The first manuscript investigates the sources of SO_4^{2-} and controls on its dissolved pool in Nikanotee Fen Watershed. The second manuscript attempts to simulate the donor peat management practices, to examine the impacts on SO_4^{2-} availability.

Chapter five summarizes the conclusions of the thesis, provides industry recommendations and suggests future research opportunities.

I, Fares Osman, conducted the experimental work, data analyses, and wrote the thesis. Dr. Jonathan Price and Dr. Richard Petrone provided guidance on the research, as well as editorial comments.

2. Sulfur biogeochemistry in peatlands

2.1 Overview

Peatlands sequester large amounts of C and are characterized by dynamic redox conditions due to aerobic and anaerobic zonation in the soil profile (Vile and Novák, 2006). Thus, they establish conditions that promote dynamic cycling of S, allowing it to play an integral role in plant growth, microbial energetics and regulation of redox chemistry (Vile and Novák, 2006; Reddy and DeLaune, 2008). Sulfur found in organic soils, such as peat, is an essential macronutrient for plants to use for the synthesis of proteins needed for their growth and survival (Kertesz and Mirleau, 2004; Hopkins and Huner, 2008). Amino acids like cysteine and methionine, the building blocks for proteins, are formed by microorganisms and plants, which use inorganic forms of S from soil and water (Leustek and Saito, 1999; Kessler, 2006; Reddy and DeLaune, 2008). Sulfur is also pivotal in the formation of vitamins and coenzymes, and enhances chlorophyll formation (Hopkins and Huner, 2008). Further, since S is highly reactive and has oxidation states ranging from -2 to +6 (Table 2 – 1), it participates in mineral precipitation and oxidation/dissolution reactions (Wieder and Lang, 1988; Lamers *et al.*, 1998b; Zak and Gelbrecht, 2007; Cirkel *et al.*, 2014), as well as biochemical transformations (Brown, 1985; Chapman and Davidson, 2001). In turn, this influences the aqueous speciation of S and the mobility of various metals in peatlands (Reddy and DeLaune, 2008).

Table 2 – 1: Selected S species in aqueous environments and their respective oxidation sates. **Bolded** species are those most common in wetlands. Modified from Keller-Lehmann *et al.* (2006) & Reddy and DeLaune (2008).

Sulfur Species	Oxidation State	Oxidation Product
SO_4^{2-}(Sulfate)	+6	-
SO_3^{2-} (Sulfite)	+4	SO_4^{2-}
$S_2O_3^{2-}$ (Thiosulfate)	+2	SO_4^{2-}
S^0 (Elemental Sulfur)	0	SO_4^{2-}
H_2S/HS^- (Sulfide)	-2	$S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}
R-S-H (Organic S)	-2	-

2.2 Distribution of sulfur in peatlands

Sulfate is the most oxidized state of inorganic S and is present in well aerated environments (Reddy and DeLaune, 2008). However, in peatlands, it can represent less than 5% of the total S pool (Novák *et al.,* 1994), and can even be a minor fraction of the inorganic S pool (Wieder and Lang, 1986 & 1988, Urban *et al.,* 1989). Dissolved pore water SO_4^{2-} concentrations in peatlands are typically in the range of 10-500 µM (Wieder and Lang, 1988; Kemmers and Jansen, 1988, Koretsky *et al.,* 2007; Mitchell *et al.,* 2008a,b; Wieder *et al.,* 2016). However, pore water SO_4^{2-} concentrations can increase in peatlands experiencing frequent water table fluctuations (Bayley *et al.,* 1986; Evans *et al.,* 1997; Reiche *et al.,* 2009; Coleman-Wasik *et al.,* 2015). The reduced inorganic S (RIS) pool also makes up a small fraction of the total S pool (Brown, 1985; Wieder and Lang, 1988, Gauci *et al.,* 2004). Iron sulfides (FeS, FeS_2), elemental sulfur (S^0) and sulfide make up the RIS pool in peat (Wieder *et al.,* 1987; Novák and Wieder, 1992, Chapman and Davidson, 2001). Dissolved sulfide in freshwater peatlands can be in the form of H_2S or HS^-, depending on the pH. Dihydrogen monosulfide (H_2S) is stable in ombrotrophic bogs, which are acidic (pH < 5), whereas HS^- is stable in more neutral systems (pH 7-8), such as minerotrophic fens (Reddy and DeLaune, 2008). It is believed that S^{2-} is never a pronounced species in aqueous systems (Schoonen and Barnes, 1988; Reddy and DeLaune, 2008). Nonetheless, because sulfide is known to react with organic matter (Brown, 1985; Wieder and Lang, 1988, Chapman and Davidson, 2001), and participate in the formation of metal sulfides (Koretsky *et al.,* 2006), its dissolved concentration in peatlands is lower than SO_4^{2-} (Wieder, 1985, Wieder and Lang, 1988). While there is potential for some sulfide to be lost to the atmosphere as it diffuses upward into the surface layer, sulfide emissions from peatlands are typically low (Vile and Novák, 2006).

The majority of S (>80%) in peatlands is bound to the organic S pool of the peat matrix (Brown, 1985; Wieder *et al.,* 1987; Wieder and Lang, 1988; Novák and Wieder, 1992). Carbon-bonded S (CBS) and ester sulfate S (ESS) compounds constitute the organic S pool in peat, with CBS being more abundant (Spratt *et al.,* 1987, Wieder *et al.,* 1987, Wieder and Lang, 1988). Carbon-bonded S compounds are mainly S-containing proteins and amino acids such as cysteine and methionine (Reddy and DeLaune, 2008), while the ESS pool comprises compounds in which

S is bound to oxygen instead of C (-C-O-S), such as phenolic sulfates (Germida *et al.*, 1992; Ghani *et al.*, 1992, Sokolova and Alekseeva, 2008).

2.3 Cycling of sulfur in peatlands

Since S is highly reactive, it goes through both oxidation and reduction reactions over an eight-electron transfer (Reddy and DeLaune, 2008). As such, it has many transformations as it cycles through the organic and inorganic S pools of peat via immobilization, mineralization, oxidation and reduction processes (Figure 2 – 1).

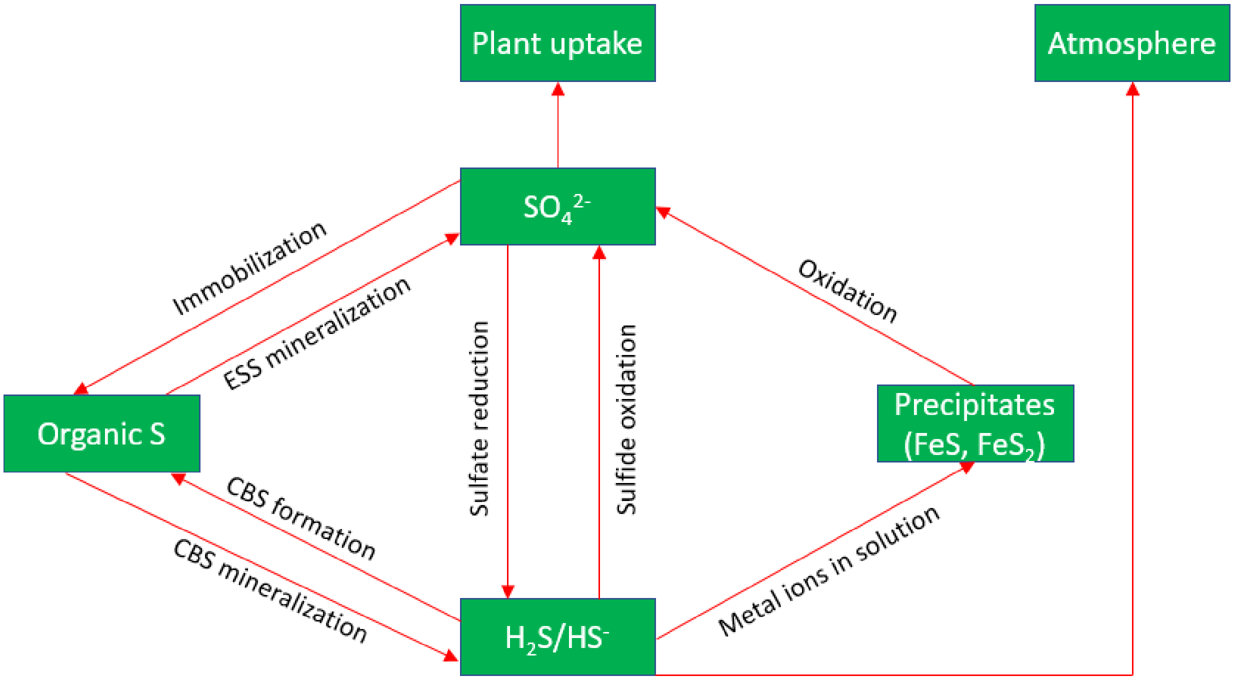

Figure 2-1: Simplified schematic of S cycling in peatlands. CBS stands for Carbon Bonded S, ESS stands for ester sulfate S. Modified from Edwards (1998).

2.3.1 Mineralization and Immobilization

Mineralization of organic S (Figure 2 – 1) in soils is the biogeochemical process that converts organic S into inorganic forms such as SO_4^{2-} (Germida *et al.*, 1992). Immobilization (Figure 2 – 1), through assimilatory SO_4^{2-} reduction, is carried out by microbes. In this process, assimilated SO_4^{2-} is reduced and directly used in the biosynthesis of cell metabolites containing S (Reddy and DeLaune, 2008). This S eventually becomes incorporated into the organic S fractions of peat after microbial biomass turnover (Chapman and Davidson, 2001). In organic soils, adsorption of SO_4^{2-} is inhibited due to high organic matter content (Johnson and Todd, 1983). Therefore, immobilization serves as a more dominant sink for SO_4^{2-} in peatlands. However, at least in peatlands, apparently this pathway of organic S formation is relatively minor in comparison with dissimilatory (e.g. Vile *et al.,* 2003b), in which large quantities of expelled sulfide can rapidly react with organic matter to form CBS end products (Brown, 1986). Notwithstanding, given that the ultimate end-product of organic S mineralization is SO_4^{2-}, immobilization occurs concurrently with mineralization (Sokolova and Alekseeva, 2008).

Given that the majority of S in peat is locked into the organic matter complex, mineralization is a prominent process in controlling inorganic S availability in peatlands. Mineralization of organic S in peatlands can occur through biochemical or biological pathways (Wieder and Lang, 1988). The latter occurs when organic matter is used as an energy source for heterotrophic microbial communities through organic C decomposition (McGill and Cole, 1981). As peat decomposes, CBS is mineralized to sulfide and under aerobic conditions becomes oxidized to SO_4^{2-} (equation 2.1, Figure 2 – 1) (Reddy and DeLaune, 2008). The mineralization of ESS is a biochemical reaction that does not require microbial activity (McGill and Cole, 1981). This process is regulated by enzymes referred to as sulfatases (e.g. arylsulfatases) that exist extracellularly and hydrolyze SO_4^{2-} esters, releasing dissolved SO_4^{2-} in the process (equation 2.2, Figure 2 – 1) (McGill and Cole, 1981; Reddy and DeLaune, 2008). For net mineralization of S to occur, it is necessary that mineralization exceeds immobilization (Germida *et al.,* 1992). This means as long as microbial energy (from CBS) and nutrition needs (from ESS) are met, S will be excreted (Sokolova and Alekseeva, 2008).

$$\text{(cysteine) } HSCH_2NH_2CH\text{–}COOH \rightarrow H_2S + NH_3 + CH_3COOH \qquad [2.1]$$

$$\text{(organosulfate) } R \cdot OSO_3^{-} + H_2O \rightarrow R \cdot OH + H^{+} + SO_4^{2-} \qquad [2.2]$$

2.3.2 Factors affecting mineralization

Several factors influence mineralization of CBS in peatlands. Given that the process is directly related to decomposition of organic C (Schroth *et al.,* 2007), water table elevation largely controls the amount of S mineralized (Coleman-Wasik *et al.,* 2015). A near-surface water table constrains aerobic decomposition to the surficial peat layer (Belyea, 1996), and below this zone oxygen is depleted which favors anaerobic decomposition (Moore and Basiliko, 2006). It has been established that anaerobic decomposition of organic matter in peatlands occurs at a rate substantially slower than that under aerobic conditions (Clymo, 1984), thus mineralization of CBS would likely be limited in such state. For example, Urban *et al.* (1989) found that mineralization of organic S in a bog was restricted to the surficial peat layer but decreased substantially at depth. Bayley *et al.* (1986) suggested one of the mechanisms generating SO_4^{2-} following water table drawdown in an experimental fen was enhanced activity of heterotrophic decomposers (i.e. mineralization of CBS) in the near surface aerobic peat. In contrast, if moisture is below the optimal for microbial activity (i.e. due to severe droughts), then mineralization of S will be reduced (Germida *et al.,* 1992). Recent studies examining S cycling in peat have largely focused on simulating water table drawdowns in peatlands via drying and re-wetting of peat and examining attendant impacts on SO_4^{2-} generation (e.g. Blodau *et al.*, 2007, Goldhammer and Blodau, 2008, Knorr and Blodau, 2009, Knorr *et al.*, 2009, Estop-Aragonés *et al.*, 2013). The general consensus is that drying and re-wetting generates large pulses of SO_4^{2-}, likely due to stimulated aerobic decomposition of peat (and therefore enhanced mineralization of CBS) as well as oxidation of RIS compounds in the peat such as FeS and FeS_2 (Eimers *et al.*, 2003, Whitfield *et al.*, 2010, Coleman-Wasik *et al.*, 2015). Temperature is also known to influence mineralization of organic matter, as it stimulates microbial activity (Kong *et al.,* 1980; Eimers *et al.*, 2003). However, perhaps the most important factor that determines whether mineralization of CBS will occur is microbial needs for C as a source of energy (McGill and Cole, 1981; Germida *et al.*, 1992; Edwards, 1998). Essentially, if there are significant quantities of S containing C substrates, and if microbes need C, then S will be released (McGill and Cole, 1981).

In soil biochemistry, it is known that ESS mineralization does not require microbial activity (McGill and Cole, 1981), since the process is regulated by the activity of extracellular sulfohydrolase enzymes (sulfatases) that are largely dependent on S supply (Edwards, 1998; Scherer, 2009). Factors that affect sulfatase enzyme synthesis, activity and kinetics play key roles in regulating ESS mineralization (Germida *et al.,* 1992). Abundant CBS (Fitzgerald, 1976 & 1978), as well as high SO_4^{2-} availability may inhibit microbial sulfatases' production and activity (Press *et al.,* 1985; Jarvis *et al.,* 1987), thereby reducing the mineralization of organic S from the ESS pool. Wieder *et al.* (1987) suggested high SO_4^{2-} availability was an inhibitor to ESS mineralization in a bog peatland. Additionally, CBS pool of the peat in their study was ~8 and ~3 times higher than ESS pool in the surface and subsurface peat, respectively.

While the majority of total S is stored in the organic form, the cycling of S typically occurs at greater quantities through the inorganic fractions. Wieder and Lang (1988) found that the amount of S that cycled through the RIS pool was ~4 times higher than the amount that cycled through the organic S pools in peat. This makes dissimilatory SO_4^{2-} reduction an important C mineralization process in peatlands under certain hydrogeochemical conditions, despite the general belief that the process was not prominent in SO_4^{2-} limited freshwater systems.

2.3.3 Dissimilatory Sulfate Reduction

Peatlands are considered to have a diplotelmic soil structure (Vasander and Kettunen, 2006), consisting of an acrotelm that overlies the catotelm (Ingram, 1978). The acrotelm is the uppermost layer of a peat profile, and is characterized by having high hydraulic conductivity, a fluctuating water table (pre-dominantly oxic conditions), and growing plants and their roots (Ingram, 1978). Since this layer is well aerated, respiratory activity is aerobic (Kuder and Kruge, 2001) and occurs at a fast rate. The underlying layer is the catotelm, in which hydraulic conductivity is much lower than the acrotelm, and permanently saturated conditions make this zone anoxic (Ingram 1978). As such, respiration occurs via anaerobic pathways (Kuder and Kruge, 2001), so decomposition rates are much slower than in the acrotelm (Blodau, 2002). The existence of such redox zonation allows S to cycle dynamically in these systems (Vile and Novák, 2006).

In peatlands, oxygen is consumed by microbial communities in the acrotelm to oxidize organic matter and meet their energy needs (Vile and Novák, 2006). As oxygen is the most favorable electron acceptor (i.e. highest free energy yield; Table 2 – 2), it quickly becomes exhausted beyond the oxic zone, after which microbial communities use alternative terminal electron acceptors (TEAs; such as SO_4^{2-}) under thermodynamically favorable conditions for anaerobic degradation of organic compounds (Inglett *et al.*, 2005) (Table 2 – 2).

Table 2 – 2: Thermodynamic redox sequence for reduction of inorganic electron acceptors at pH 7 and 25°C in wetland soils. Note decreasing redox potential (E_h) and Gibbs free energy yields (ΔG) from aerobic respiration → methanogenesis. Values of E_h are reported in volts (V) while ΔG is Kcal mol^{-1} per e$^-$. Adapted from Schlesinger (1997).

Pathway	Half reaction	E_h	ΔG
Aerobic respiration	$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	0.812	-29.9
Denitrification	$2NO_3^- + 6H^+ + 6e^- \rightleftarrows N_2 + 3H_2O$	0.747	-28.4
Mn(IV) reduction	$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	0.526	-23.3
Fe(III) reduction	$Fe(OH)_3 + 3H^+ + e^- \rightleftarrows Fe^{2+} + 3H_2O$	-0.047	-10.1
Sulfate reduction	$SO_4^{2-} + 10H^+ + 8e^- \rightleftarrows H_2S + 4H_2O$	-0.221	-5.9
Methanogenesis	$CO_2 + 8H^+ + 8e^- \rightleftarrows CH_4 + 2H_2O$	-0.244	-5.6

Dissimilatory SO_4^{2-} reduction (DSR) is an anaerobic respiration process (equation 2.3) mediated by many bacterial groups (Rooney-Varga *et al.*, 1998; Reddy and DeLaune 2008) in wetland environments. The process is different than assimilatory SO_4^{2-} reduction because it excretes the produced sulfide, instead of immobilizing it to synthesize S containing metabolites by microbes (Chapman and Davidson, 2001). During DSR, simple organic compounds (e.g. acetate and alcohols) are oxidized for energy needs by bacteria capable of using SO_4^{2-} as an electron acceptor in the anaerobic zone to produce sulfide and increase alkalinity (Reddy and DeLaune, 2008; McLaughlin and Webster, 2010).

$$\text{(acetate) } CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \qquad [2.3]$$

The produced sulfide can undergo several biogeochemical reactions and therefore has different fates (Vile and Novák, 2006). It can react with organic matter to form CBS (Altschuler *et al.,* 1983; Brown, 1985, Vile *et al.,* 2003b). If metals are present in the pore water, such as Fe, insoluble FeS and FeS_2 precipitates form (Brown, 1985; Koretsky *et al.,* 2007), and become subject to re-oxidation to SO_4^{2-} if the water table drops (Lamers *et al.,* 1998b), or in anaerobic conditions, can be re-oxidized using nitrate (NO_3^-) (Cirkel *et al.,* 2014), or ferric iron (Fe^{3+}) (Wieder *et al.,* 1990) as electron acceptors. If aqueous concentrations of metals are insufficient for formation of metal sulfides, the produced sulfide can diffuse upwards through the acrotelm and re-oxidize to

SO_4^{2-} or leave the system through degassing (Vile and Novák, 2006). Below are equations showing end products from the oxidation of FeS_2 using O_2, Fe^{3+}, and NO_3^- as electron acceptors.

$$FeS_{2(s)} + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow Fe(OH)_{3(s)} + 4H^+_{(aq)} + 2SO_4^{2-}{}_{(aq)} \qquad [2.4]$$

$$FeS_{2(s)} + 14Fe^{3+}{}_{(aq)} + 8H_2O \rightarrow 15Fe^{2+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 16H^+_{(aq)} \qquad [2.5]$$

$$FeS_{2(s)} + 3NO_3^-{}_{(aq)} + 2H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-}{}_{(aq)} + \frac{3}{2}N_{2(g)} + H^+_{(aq)} \qquad [2.6]$$

2.3.4 Controls on Dissimilatory Sulfate Reduction

The continuity of DSR in peatlands is strongly dependent on the local redox conditions, SO_4^{2-} availability, and organic matter quality. Anoxic conditions are necessary for DSR to occur (Brown and Macqueen, 1985), as they favor the growth and activity of SRB (Gibson, 1990; Tokarz and Urban, 2015). The availability of SO_4^{2-} is an important regulator for DSR in peatlands; a sufficient pool must be present for SRB to utilize organic compounds as substrates for energy sources in anaerobic respiration (Reddy and DeLaune, 2008). Given that freshwater systems such as peatlands are typically limited in SO_4^{2-} availability (Pester *et al.,* 2012), DSR has not been considered as a prominent anaerobic C mineralization in these systems (Nedwell, 1984). However, pioneering work provided evidence of high SO_4^{2-} reduction rates occurring in peatlands experiencing pore water SO_4^{2-} concentrations in the micromolar range (Wieder and Lang 1988; Wieder *et al.,* 1990; Nedwell and Watson, 1995). Wieder and Lang (1988) showed their estimated SO_4^{2-} reduction rates in peat were comparable to or greater than coastal marine sediments, and similar to the lower range of SO_4^{2-} reduction rates experienced by salt marshes. Apparently, despite the small dissolved SO_4^{2-} pool, alternating SO_4^{2-} reduction and oxidation of RIS compounds (e.g. FeS and FeS_2) resulted in rapid recycling of dissolved SO_4^{2-} (Wieder and Lang, 1988). The authors ascribed this phenomenon to the rapid turnover of the RIS pool in comparison with the organic S pool, meaning that SO_4^{2-} reduction end-products that are incorporated into the organic S fractions (i.e. CBS) are much more stable to re-oxidation (Vile *et al.,* 2003b). More recent studies examining S cycling in peatlands reported similar findings, whereby high SO_4^{2-} reduction rates were observed despite a small instantaneous SO_4^{2-} pool (Blodau *et al.*, 2007; Knorr and Boldau, 2009). The recycling of this SO_4^{2-} pool in peatlands may be maintained by various biogeochemical mechanisms, some of which include (1) aerobic oxidation of reduced S in oxic-anoxic interface of the peat column where anaerobic microsites are present (Knorr *et al.*, 2009, Knorr and Blodau, 2009), (2) oxidation of reduced S by other TEAs such as Fe^{3+} (Wieder *et al.*, 1990), and/or NO_3^- (Cirkel *et al.*, 2014), (3) aerobic oxidation of the peat (and reduced S) following water table drawdowns (Wieder *et al.*, 1990; Reiche *et* al., 2009), (4) oxidation by dissolved organic matter (DOM) to thiosulfate, which is either directly used by SRB (if SO_4^{2-} is not present) to carry out DSR (Heitmann and Blodau, 2006), or subsequently disproportionated into SO_4^{2-} and sulfide (Elsgaard and Jørgensen, 1992; Habicht *et al.*, 1998) thus regenerating the required SO_4^{2-} pool, and (5) through ESS mineralization when the SO_4^{2-} pool is depleted (Jarvis *et al.*, 1987; Mandernack *et al.*, 2000). Temperature is known to serve as a control on SO_4^{2-} reduction; warmer temperature stimulates SO_4^{2-} reduction rates (Reddy and DeLaune, 2008). This relationship has been widely observed in peatlands (Wieder and Lang, 1988; Spratt and Morgan, 1990; Watson and Nedwell, 1995; Groscheova *et al.*, 2000). Several studies have shown that the relative quality of organic compounds (i.e. labile forms) is crucial in driving anaerobic C mineralization processes in peatlands (Updegraff *et al.*, 1995; Watson and Nedwell, 1998; Fisk *et al.*, 2003; Hoyos-Santillan *et al.*, 2016). Lability of organic C is largely controlled by the degree of decomposition of the peat, whereby older and deeper peat is of more recalcitrant C than that of recently formed peat near the surface (Hogg *et al.*, 1992). Therefore, in the deeper peat layer, labile fermentation products may not be present in sufficient quantities for DSR and other anaerobic mineralization processes to proceed (Shannon and White, 1996; Vile *et al.*, 2003b; Hahn-Schofl *et al.*, 2011), ultimately resulting in depth-variable SO_4^{2-} reduction potential (Wieder and Lang, 1988; Novák and Wieder, 1992; Hahn-Schofl *et al.*, 2011). However, changes in hydrological regimes (i.e. drainage) can cause depletion of labile C fractions even in the surficial peat layers due to enhanced decomposition of organic matter (Urbanová *et al.*, 2018), leaving behind recalcitrant residues that may not be adequate for anaerobic C mineralization pathways to proceed (Blodau, 2002; Zak *et al.*, 2009; Leifeld *et al.*, 2012; Kononen *et al.*, 2016). Following restoration (i.e. inundation) of these drained peatlands and the re-establishment of vegetation (Glatzel *et al.*, 2004), inputs of fresh labile C from root exudates and litter (Strack *et al.*, 2015; Jauhiainen *et al.*, 2016), would reactivate microbial processes such as SO_4^{2-} reduction (Hahn-Schofl *et al.*, 2011). Clearly, changes in local geochemical conditions, SO_4^{2-} availability, and substrate quality make the dynamic nature of S cycling in peatlands highly complex.

2.3.5 Significance of Dissimilatory Sulfate Reduction

Numerous studies examining S dynamics in wetlands have focused on investigating the role of DSR in controlling the mobility of heavy metals (e.g. Webb *et al.,* 1998; Moreau *et al.,* 2013), some of which include manganese (Mn), nickel (Ni), zinc (Zn), iron (Fe), cadmium (Cd), copper (Cu), lead (Pb), and mercury (Hg) (Shotyk, 1988, 1996; Shotyk *et al.*, 2005; Oswald and Carey, 2016). As the solubility of most sulfides are low (Reddy and DeLaune, 2008), potentially toxic metals become sequestered in systems that favor SRB; these systems are anoxic, rich in labile organic substrates, and supplied with sufficient SO_4^{2-} (Debusk *et al.*, 1996; Sheoran and Sheoran, 2006). Thus, peatlands, provided SO_4^{2-} availability is not limiting, offer the aforementioned conditions to limit aqueous metal concentrations through precipitation of metal sulfides (Koretsky *et al.,* 2006; Van Der Welle *et al.*, 2007; Yoon *et al.,* 2012; Smieja-Krol *et al.*, 2010 & 2015). For example, Koretsky *et al.* (2007) found that dissolved porewaters concentrations of trace metals such as Zn, Pb, Cu, Ni, Co in a minetrophic fen were either low or below detection. Based on solid phase analyses, they suggested precipitation of the aforementioned metals as sulfides in the reducing zones of the peat profile limited their aqueous concentrations in the fen pore water.

Although Hg can be immobilized via DSR, due to the accumulation of sulfide (e.g. to precipitate insoluble $HgS_{(s)}$) (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Gilmour *et al.,* 1992; Orem *et al.,* 2011), numerous studies in the available literature have linked DSR as a mechanism to the production of methylmercury (MeHg) in peatlands (e.g. Mitchell *et al.*, 2008b, 2009; Coleman-Wasik *et al.,* 2012, 2015; McCarter *et al.*, 2017). MeHg is a known neurotoxin that bioaccumulates in aquatic organisms (Morel *et al.*, 1998). Therefore, its export from peatlands may have detrimental effects on downstream ecosystems (Branfireun *et al.,* 1996). Sulfate reducing bacteria are known to methylate Hg as a byproduct of DSR in peatlands (Branfireun *et al.,* 1999), therefore the presence of MeHg is indicative of DSR. For example, Mitchell *et al.* (2008a) examined hot spots of methylmercury production in peatlands that are surrounded by run-off supplying forested uplands. They found that pore waters at or near the upland-peatland interface (i.e. where upland runoff and peatland waters mix) had higher %MeHg values than porewaters farther away from upland-peatland interface. They suggested that increased SO_4^{2-} loading from the upland run-off water likely stimulated SO_4^{2-} reduction in the upland-peatland interface, and in turn partially resulted in increased MeHg production. The fact that sulfide limits methylation of Hg is in part due to increased SO_4^{2-} availability. Gilmour and Henry (1991) speculated that SO_4^{2-} concentrations in the range of 200-500 µM are optimal for MeHg generation in sediments, and below this threshold SO_4^{2-} reduction would be SO_4^{2-} limited, leading to limited MeHg production. However, they acknowledged that this threshold would differ from system to system due to other limiting factors (e.g. labile organic C availability).

In peatlands, the suppression of methanogenesis by stimulated DSR has long been recognized (Dise and Verry, 2001; Gauci *et al.*, 2002). This inhibition occurs because SRB effectively outcompete methanogens for simple organic compounds (e.g. hydrogen, acetate) in anaerobic respiration pathways (Kristjansson *et al.*, 1982; Schonheit *et al.*, 1982; Kristjansson and Schonheit, 1983). As long as SO_4^{2-} is abundant in peatlands, via recycling and/or groundwater and atmospheric inputs, DSR can be a substantial anaerobic C mineralization pathway provided labile C is not limiting (Wieder *et al.*, 1990; Pester *et al.*, 2012). As a result, methanogenesis becomes significantly suppressed, but at the expense of potentially degrading peat accumulation processes (i.e. anaerobic C mineralization exceeds organic matter inputs into the anaerobic zone) (Wieder *et al.*, 1990), and possible buildup of dissolved sulfide. Sulfide is known to be a phytotoxin to vegetation species in freshwater wetlands (Van Der Welle *et al.*, 2007; Geurts *et al.*, 2009)

2.4 Biogeochemical implications for constructed fens

Our general understanding of S biogeochemistry in natural peatlands is based on studies conducted in bogs and fens that do not have porewater SO_4^{2-} concentrations in the range of constructed Nikanotee Fen. Presently, the implications for S biogeochemistry from incorporating reclaimed AOSR construction materials and drained peat in constructed fen landscapes are unknown. In such systems, where SO_4^{2-} is likely to be more abundant than natural fens, the controls on SO_4^{2-} availability may behave differently from those in natural systems. Thus, dissolved SO_4^{2-} pools may persist for a prolonged period, potentially driving DSR to become a dominant anaerobic C mineralization process (Wieder *et al.*, 1990), which is not typical in natural peatlands. It is then imperative to understand if and what processes may cause SO_4^{2-} availability dynamics in constructed fens to be different from those in targeted reclamation landscapes.

3. Sources of sulfate in a constructed fen in the Athabasca Oil Sands Region

3.1 Context

Surface mining activities to recover bitumen from shallow oil sands deposits located in the Athabasca Oil Sands Region (AOSR) have disturbed upwards of ~900 km^2 of land area as of 2013 (Government of Alberta, 2017). Over 50% of the region comprises wetlands, of which the majority are reported to be fen peatlands (Vitt *et al*., 1996). Due to the nature of surface mining techniques, peatlands are removed from the landscape (Rooney *et al.,* 2012). Therefore, their associated ecosystems services, such as water storage and cycling (Devito *et al.*, 2005), habitat support for numerous plant species (Desrochers and van Duinen, 2006), and storage of carbon and nutrients (Blodau, 2002, Limpens *et al.,* 2009, Wang *et al.,* 2015), are lost. As per mine closure plans, Alberta oil sands industries are required to return their post-mined sites to "equivalent land capability" after mining operations have ceased (OSWWG, 2000). Equivalent land capability means that the land uses sustained by the reclaimed landscape have to be similar, but need not be identical, to those that existed prior to disturbance (CEMA, 2006). Fen reclamation is a new concept currently being tested in the AOSR (Ketcheson *et al.,* 2016), which requires creation of the necessary conditions for a self-sustaining ecosystem that is carbon-accumulating and able to support appropriate vegetation species (Daly *et al.,* 2012). Fen creation was considered impractical until two pioneering projects began to address this uncertainty using known wetland restoration techniques (Pollard *et al*., 2012, Ketcheson *et al.,* 2016). One of these is the Nikanotee Fen Watershed, a constructed fen-upland system that was engineered from mine waste materials including tailings sand and petroleum coke, with targeted hydrophysical properties and geometry necessary to sustain saturated conditions in a 2 m thick placed fen peat deposit (Price *et al.*, 2010; Daly *et al.,* 2012).

Within the peat deposit of the constructed fen-upland system, sulfate (SO_4^{2-}) concentrations are 1 to 2 orders of magnitude higher than in surrounding natural fen peatlands (Chapter 1). In Alberta's rich fen peatlands, it has been shown that porewater aqueous sulfur (S) concentrations can be below 1 mg L^{-1} (Vitt and Chee, 1990; Vitt *et al.*, 1995). Only saline-spring fens in the region deriving groundwater from saline substrates of marine origin, are known to have dissolved SO_4^{2-} concentrations in the range of Nikanotee Fen (Wells and Price, 2015). In peatlands, increased pore water SO_4^{2-} availability is known to stimulate dissimilatory SO_4^{2-} reduction (DSR) (Vile *et al.,* 2003a; Pester *et al.,* 2012). Enhancement of DSR is known to suppress methane (CH_4) emissions from peatlands (Dise and Verry, 2001; Gauci *et al.,* 2002, 2005; Dowrick *et al.,* 2006), as SO_4^{2-} reducing bacteria (SRB) outcompete methanogens for utilization of labile carbon (C) substrates (Kristjansson and Schonheit, 1983). Thus, peat accumulation might degrade if DSR dominates anaerobic C mineralization pathways (Wieder *et al.,* 1990). Furthermore, DSR produces sulfide which regulates heavy metal mobility in peatlands (Koretsky *et al.,* 2006, 2007; Smieja-Krol *et al.,* 2010, 2015). However, dissolved sulfide is also known to be toxic to wetland plants (Lamers *et al.,* 1998a; Geurts *et al.,* 2009; Lamers *et al.,* 2013). In view of the aforementioned ramifications, it is important to understand the origins of SO_4^{2-} and its availability dynamics in these pioneering constructed landscapes; this has not been extensively explored in the available literature (Reid and Warren, 2016).

To date, hydrogeochemical research in Nikanotee Fen Watershed has documented the release and transport of sodium (Na^+) from the tailings sand upland aquifer to the fen (Kessel *et al.,* 2018). It was determined that Na^+ has been progressively flushed from the aquifer, into the petroleum coke underdrain beneath the fen, and entering the basal layers of the peat profile (Kessel *et al.,* 2018). Additionally, based on laboratory derived soluble and solid-phase concentrations of solutes within all construction materials, it was shown that the upland is the biggest reservoir of Ca, Na, S and Mg (Simhayov *et al.,* 2017) Therefore, as with Na^+, the upland aquifer is expected to deliver SO_4^{2-} to the fen via transport. Moreover, surrounding the fen-upland system are three reclaimed slopes that contribute snowmelt surface run-off during the spring freshet, which recharges water to the upland aquifer that ultimately feeds the fen (Ketcheson and Price, 2016a). Also, surface run-off discharges to the fen surface directly, since the fen is the lowest lying landform within the constructed system (Ketcheson and Price, 2016a). These slopes are built upon overburden substrate from the Cretaceous Clearwater Formation and thus may have high concentrations of Na^+, Ca^{2+} and SO_4^{2-} (see Table A-20; Appendix A). Surface runoff could transport SO_4^{2-} that accumulates at the surface of the ~50 cm peat-mineral mix that overlies the Clearwater substrate (Ketcheson and Price, 2016b), to the lower lying fen. Furthermore, since the donor peat was drained for 2 years prior to placement (but without windrowing and stockpiling) mineralization of organic matter could increase soluble concentration of ions, including SO_4^{2-} (Nwaishi *et al.,* 2015; Simhayov *et al.,* 2017). It is well understood from studies that the drainage of fen peat is associated with increases in porewater SO_4^{2-} concentrations upon saturation (Heathwaite, 1990,1991; Zak and Gelbrecht, 2007). Due to the aforementioned confounding sources, it is uncertain if the high SO_4^{2-} concentrations in the fen pore water are a result of the peat salvaging practices, or from transport mechanisms operating on the reclaimed slopes and in the upland aquifer, or a combination of both.

Therefore, the primary objectives of this study are to: 1) characterize the spatiotemporal distribution of SO_4^{2-} in the constructed system; and 2) suggest the main source(s) of SO_4^{2-}, and hydrogeochemical controls on its dissolved pool in the fen-upland system.

3.2 Study Site

Construction of Nikanotee Fen Watershed finished in January 2013. It is a constructed fen-upland system situated on a mine lease ~30 km north of Fort McMurray, Alberta (56°55.944'N 111°25.035'W). The system includes a fen peatland (2.9 ha) supplied by shallow groundwater from the constructed upland aquifer (7.7 ha) and surface run-off inputs from surrounding reclaimed slopes of varying age (24.4 ha) (Ketcheson *et al.*, 2017). Nikanotee Fen Watershed includes a small, steep natural slope to the south that does not contribute to surface water runoff or groundwater recharge to the fen system (Ketcheson *et al.*, 2017). The constructed fen and upland aquifer were underlain by an engineered geosynthetic clay liner to minimize water losses via deep drainage (Ketcheson *et al.,* 2017). The upland (3% slope towards fen) was constructed from tailings sand collected from a dry tailings pond (Simhayov *et al.,* 2017). The upland aquifer is capped with a thin (30-50 cm) LFH-mineral mix soil cover which is commonly used in reclaiming AOSR's landscapes (Naeth *et al.,* 2013), with the intention of promoting water infiltration and storage in the aquifer (Daly *et al.*, 2012). In 2013, to further promote recharge to the aquifer, four small depressions (referred to as "recharge basins"; 100-700 m^2 in area) were implemented by exposing the tailings sand behind pre-existing constructed "hummock" landforms situated within the upland (Figure 3 – 1) (Kessel *et al.,* 2018). These features played an integral role in providing freshwater recharge to the aquifer and consequently diluted the leachable solutes, ultimately reducing peak concentrations received at the fen (Kessel *et al.*, 2018). The fen was constructed with 2 m of moderately decomposed peat, taken from a rich fen donor peatland (Nwaishi *et al.*, 2015). The donor fen (maximum peat thickness 255 cm, average 145 cm), was located south of Nikanotee Fen (56°54.258'N 111°19.610'W), which had been drained in early 2010 (Nwaishi *et al.*, 2015). Peat was then excavated and transferred to the constructed site between December 2012 and January 2013 (Nwashi *et al.*, 2015). Beneath the placed peat and overlying 50-cm of tailings sand, a 50-cm layer of raw petroleum coke was placed as an "underdrain" layer; this extends approximately 100 m into the upland (referred to as "transition zone"), where it is covered with tailings sand (Kessel *et al.*, 2018) (Figure 3 – 1). The intent of this underdrain was to more evenly distribute water pressure beneath the fen and promote upwards flow through the peat profile (Figure 3 – 1). Surrounding the constructed fen-upland system are three reclaimed hill slopes (Figure 3 – 1). The east slope (8.1 ha) was reclaimed in 2007 and vegetated in 2008, while the west (2.4 ha) and south-east slopes (8.2 ha) were reclaimed in 2011 and vegetated in 2012 (Ketcheson and Price, 2016b; Ketcheson *et al.*, 2017). These hill slopes overlie reclaimed overburden substrate of marine origin having a chemical composition rich in salt constituents (Appendix A, Table A-20). Peat-mineral mix reclamation soil (~50 cm thick) covers a ~100 cm capping layer that has a pH and sodium adsorption ratio of less than 8, consistent with guidelines (Ketcheson, 2015). Planting of the fen began in July 2013 after the donor peat was placed. This procedure followed an experimental plot design approach to help evaluate the most appropriate re-vegetation strategy. Freshwater and salt tolerant species (*Carex aquatilis* and *Juncus balticus*) dominate the vegetation in the fen. A detailed description of planting strategies can be found in Nwaishi *et al*. (2015) and Murray *et al.* (2017).

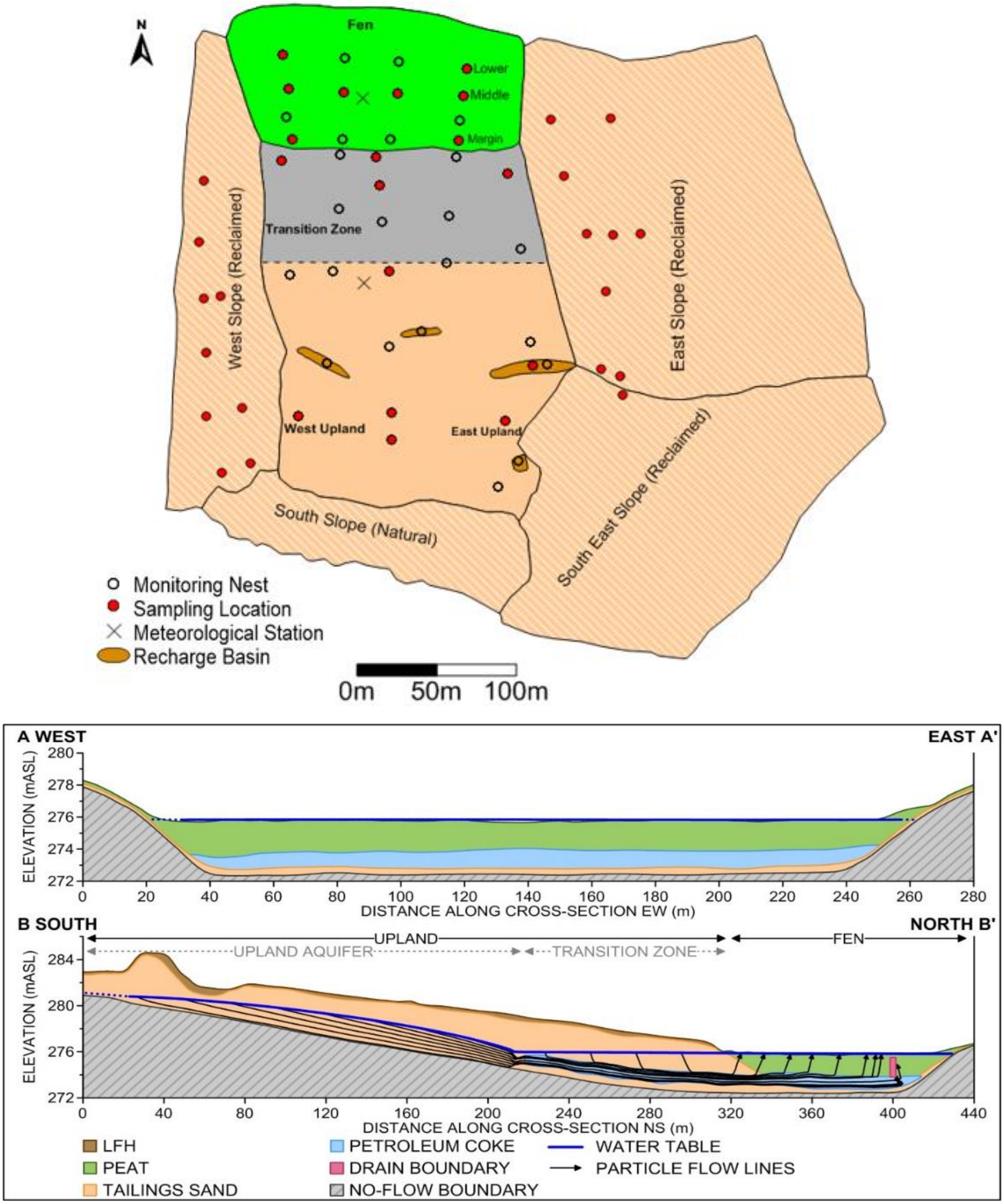

Figure 3 – 1: Map of the Nikanotee fen-upland system and contributing reclaimed slopes with monitoring network and transects (top) and cross-sectional diagram of groundwater flow in layers from upland tailing sand → petroleum coke → peat (bottom). Source: Kessel (2016); Ketcheson *et al.* (2017)

3.3 Methods

3.3.1 Monitoring network, water sampling and chemical analyses

A hydrological monitoring network of 2.5 cm inside diameter PVC piezometers and wells (referred to as monitoring nests) were installed in 2013 within the upland and fen. The depths and locations of each piezometer and well varied, as the purpose was to capture variability in pore water chemistry from each construction layer. In the central, east and west side of the upland, wells were installed in the tailings sand layer (275 cm below ground surface; bgs). In 2014, another well was installed (372 cm bgs) in the central region of the upland where the water table was deeper than 275 cm bgs (Kessel, 2016). Within the east, central and west regions of the transition zone, monitoring nests included a well and two piezometers that were installed in the tailings sand (225 cm bgs) and petroleum coke (275 cm bgs) (Kessel, 2016). In the fen, wells and piezometers were installed in the upper marginal (margin), middle, and lower marginal transects (lower) of the fen (see Figure 3 – 1). Piezometers in the fen were installed at depths of 50, 90 and 150 cm bgs in the peat layer, 225 cm bgs into the petroleum coke and 275 cm bgs centered into the tailings sand beneath the fen (Kessel *et al.,* 2018). Wells and piezometers in all regions were purged 24 hours prior to retrieval of water samples. For on-site measurements of pH, temperature (T) and electrical conductivity (EC), water samples (~50 mL) in each area of the fen-upland system were extracted from wells and piezometers with care to avoid cross-contamination between material types, and measurements were determined using a portable multiparameter meter (Thermo Scientific™ Orion Star™ A329). Another set of samples were extracted, transferred to polyethylene vials and stored at 4°C. These samples were filtered within 24 hours using 0.45 µm nitrocellulose filters, and then water inserted into 60 mL vials and stored in a freezer for subsequent analyses of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}). Concentrations of cations and anions were measured by a Dionex ICS-1600 (Method EPA 300.0) at the Biotron Experimental Climate Change Research Facility at University of Western Ontario, Canada. Analytical precision for cations and anions was either ±1 mg L^{-1}, or less (±0.01-0.1 mg L^{-1}) (Kessel *et al.,* 2018). Alkalinity was measured only in 2016. It was determined by automated colorimetry (Bran Luebbe AutoAnalyzer III system, Seal Analytical Ltd, Method G-148-95 Rev. 2) at the Biogeochemistry Laboratory at University of Waterloo, Canada. Values were reported as "Alkalinity as $CaCO_3$". To convert from $CaCO_3$ to HCO_3^-, $CaCO_3$ values (in mg L^{-1}) were multiplied by a factor of 1.22

(Richter and Kreitler, 1993). All values of cations and anions are presented in mg L^{-1}. Groundwater from the east, south east and west slopes was collected from a series of monitoring wells located at the upper, middle and lower regions of the slopes (Figure 3 – 1). In addition, surface run-off collectors were installed on each slope (Irvine, 2018), from which water samples were extracted. Analyses of major cations and anions for groundwater and run-off water (snow melt and summer run-off) of the slopes were treated using the same procedure described above. Water sampling from the fen and the upland followed a monthly campaign (from 2013-2016) covering May (2013 only), June (all years except 2016), July (all years), August (all years) and October (all years except 2016). *In-situ* groundwater samples from the slopes were only taken in 2013 (August), and 2014 (June, August), whereas snow melt (Ketcheson and Price, 2016b) and summer runoff samples were only taken in 2013 (April), and 2016 (July, August), respectively. Throughout the sampling campaign, blanks containing deionized water were taken for quality assurance. A more detailed explanation of the instrumentation was reported by Kessel *et al.* (2018).

3.3.2 Data analyses

To characterize the spatiotemporal distribution of dissolved SO_4^{2-} in each of the construction material's layers in Nikanotee Fen, measured pore water SO_4^{2-} concentrations from the eastern and western regions of the upland and fen were included. Additionally, scatterplots of Ca:SO_4 ratios in each region were used to suggest potential mechanisms that may influence the chemical composition (SO_4^{2-} concentration in this case) of the groundwater in each of the layers (Markel *et al.*, 1998; Li *et al.*, 2015; Yuan *et al.*, 2017). Full groundwater chemical composition used in this analysis, including *in-situ* environmental parameters (pH, EC and T), of all layers in the western and eastern regions of the system (2013-2016) is found in Appendix A. Note HCO_3^- was only available in 2016.

All statistical analyses were completed using the R statistical software version 3.4.2 (R Core Team, 2017) and applying a significance level of $\alpha = 0.05$. To test for normality, Shapiro-Wilk test was conducted as well as producing and inspecting normal Q-Q (quantile-quantile) plots and histograms. In general, it was found that the data was not normally distributed. Additionally, in some instances, log transformation of the data did not meet the normality conditions for parametric tests. Therefore, a non-parametric approach was used for significance testing (Gilbert, 1987). Mann-Whitney-Wilcoxon (MWW) test was used to compare differences in pH and temperature data of construction materials from year to year. The same test was applied to detect differences in Ca^{2+} and SO_4^{2-} porewater concentrations for each respective construction material from year to year, and if any statistical difference in Ca^{2+} and SO_4^{2-} pore water concentrations existed between eastern and western regions of a construction material. P values less than 0.05 were interpreted as statistically significant differences existed between compared groups. Data from 2016 for the eastern and western regions of the upland sand were excluded in statistical testing due to very low sample size ($n \leq 4$), which is not sufficient to detect differences at the applied significance level (Fay and Proschan, 2010).

3.4 Results

3.4.1 Annual pH and temperature in construction materials

In 2013, the pore water of the upland tailings sand and petroleum coke underdrain experienced the lowest and highest mean pH values, respectively, and remained so for the entire study period. Consistent pH increases in construction materials were seen in 2014, wherein the highest values for all, except the upland tailings sand, were observed. Statistical testing showed 2014 pH values of all construction materials, except coke, to be significantly different from those in 2013 ($P < 0.05$; Table 3 – 1). Except for the upland tailings sand, all construction materials experienced lower pH in 2015, wherein significant differences relative to 2014 were detected for all construction materials, except for sand beneath the fen ($P < 0.05$; Table 3 – 1). In 2016, the upland tailings sand experienced noticeable decrease in pH (~0.6 units; $P > 0.05$), while all other construction materials were in the same range as 2015. In the fen, there were consistent decreases in pH as the groundwater in the coke mixed with the deepest peat layer (150 cm bgs) throughout the study period (Table 3 – 1). However, no notable trends were observed between the deepest, intermediate (90 cm bgs) and shallowest peat layers, in which the pH generally remained around neutral. The tailings sand beneath the fen experienced considerably higher pH than the upland tailings sand throughout 2013-2016.

Throughout 2013-2016, the surficial peat layer (50 cm bgs) had the highest overall mean groundwater temperature (~19°C), and generally experienced higher values than all construction materials (Table 3 – 1). Within the fen, mean groundwater temperature generally decreased with depth. The lowest values were typically observed in the coke and fen sand layers, in which the overall (i.e. 2013-2016) mean groundwater temperature of each was very similar (~14°C). Generally, statistical testing showed that temperature values in the petroleum coke and fen sand layers were significantly different between 2013-2014, and 2014-2015 (P <0.05; Table 3 – 1).

Table 3 – 1: Mean (± standard deviation) annual temperature and pH for Nikanotee fen-upland system. Fen data are collected from piezometers. Only wells were used in the upland. Note: October data not included, as there was inconsistency in sampling during the month. Z50, z90, z150 represent piezometers installed at 50, 90 and 150 cm below ground surface in the peat layer. Sample size is denoted by *n*.

Material		Temperature (°C)				pH			
		2013	2014	2015	2016	2013	2014	2015	2016
Coke	Mean	14.8±2.1	12.2±3.1*	14.4±3.1*	13.1±5.2	7.5±0.2	8.0±0.7	7.5±0.3*	7.5±0.1
	n	16	15	24	10	16	15	24	10
Upland Sand	Mean	19.8±2.7	18.3±3.2	16.4±2.2	15.2±5.2	5.9±0.8	6.6±0.5*	7.0±1.2	6.4±0.5
	n	8	14	20	7	8	14	20	7
Fen Sand	Mean	14.8±2.7	11.8±3.0*	15.7±2.1*	12.9±6.0	7.3±0.3	7.7±0.6*	7.4±0.3	7.5±0.1
	n	12	13	14	7	12	13	14	7
Peat (z50)	Mean	18.7±1.9	18.8±4.1	18.1±1.5	18.7±5.9	7.0±0.2	7.6±0.5*	6.9±0.3*	7.0±0.3
	n	12	16	14	11	12	16	14	11
Peat (z90)	Mean	16.0±2.0	15.7±4.5	17.7±1.5	17.7±6.6	7.0±0.2	7.6±0.5*	7.0±0.1*	7.0±0.3
	n	12	18	14	12	11	18	14	12
Peat (z150)	Mean	15.4±3.5	13.5±3.7	16.5±1.9*	15.6±4.9	7.1±0.2	7.7±0.6*	7.1±0.2*	7.1±0.2
	n	10	16	20	8	10	16	20	8

* Indicates statistically significant differences (P < 0.05) in pH or temperature values from previous year for a construction material (MWW)

3.4.2 Spatiotemporal distribution trends of pore water sulfate concentrations

Sulfate concentrations over the study period were typically different between the eastern and western regions of the system. In 2013, the first year following construction, the eastern region of the upland tailings sand aquifer experienced the highest SO_4^{2-} concentrations within the fen-upland system and consistently exceeded 2000 mg L^{-1} (Figure 3 – 2e). Throughout the season, SO_4^{2-} concentrations in both the east and west decreased but remained higher in the east than in the west (P <0.05, Table 3 – 2). The fen tailings sand experienced slightly higher SO_4^{2-} concentrations in the west than in the east, with no apparent time trends. The coke underdrain in both regions of the fen experienced much lower concentrations than the upland aquifer, where the east experienced higher concentrations than the west (P <0.05). In contrast, peat on the east side of the fen experienced significantly lower SO_4^{2-} concentrations than peat on the west (P <0.05, Table 3 – 2), ranging between ~500-600 mg L^{-1} in the east and exceeding 1000 mg L^{-1} in the west. However, peat on both regions of the fen experienced consistent decreases in concentrations throughout the season, with more pronounced trends on the west (Figure 3 – 2a; Figure 3 – 2e).

In 2014, SO_4^{2-} concentrations in both regions of the upland significantly decreased from values observed in 2013 (P <0.05; Table 3 – 2), with the west initially experiencing higher concentrations than the east. In the fen, the tailings sand experienced higher initial SO_4^{2-} concentrations in the west than in the east, after which concentrations remained similar (~450-600 mg L^{-1}). At the beginning of the season, the petroleum coke underdrain in the west had ~2 times SO_4^{2-} concentrations than those in the peat layer. However, concentrations tended to be similar after DOY 171 (Figure 3 – 2b). In the east, SO_4^{2-} concentrations in the petroleum coke underdrain were initially lower than the west and increased over the season from ~750 to 900 mg L^{-1}, while peat concentrations remained lower and continuously decreased throughout the season to <600 mg L^{-1} (Figure 3 – 2f).

In 2015, the driest year, the aquifer experienced significantly higher SO_4^{2-} concentrations than in 2014 (P <0.05, Figure 3 – 2c, g) on both regions of the upland. Here, concentrations increased to ~1000 mg L^{-1} in both eastern and western regions of the upland (not significantly different from each other; P >0.05). However, the west experienced roughly half the concentrations of the east at the beginning of the season. Higher SO_4^{2-} concentrations were observed in the fen tailings sand on the west than the east, with no apparent changes throughout the season in either region. Similarly, there were no notable trends in the petroleum coke underdrain on both sides of the fen, and concentrations remained similar (P >0.05), where both exceeded 1000 mg L^{-1}. Sulfate concentrations in the peat layer on both regions of the fen continued to be considerably lower than the coke underdrain and did not vary significantly (Table 3 – 2).

In 2016, the eastern region of the upland aquifer experienced higher dissolved SO_4^{2-} concentrations than the west. In the fen, peat had the lowest SO_4^{2-} concentrations throughout the season in both regions, ranging from ~500 to ~900 mg L^{-1} (Figure 3 – 2d, h). The coke and tailings sand were similar in SO_4^{2-} concentrations but tended to be higher in the west than in the east.

Significant differences were detected between pore water SO_4^{2-} concentrations in the eastern and western regions of the tailings sand layer beneath the fen ($P < 0.05$, Table 3 – 2). Similarly, the peat layer showed significant differences in pore water SO_4^{2-} concentrations between regions, where the west was again higher than the east ($P < 0.05$, Table 3 – 2). Here, concentrations were initially lower than the coke underdrain in both regions but approached similar values at the end of the season.

Table 3 – 2: Mean (± standard deviation) annual SO_4^{2-} and Ca^{2+} porewater concentrations of all construction materials within the East and West regions of the Nikanotee fen-upland system. Peat is an average of all 3 depths (z50, z90, z150). All values are mg L^{-1}. Sample size is denoted by *n.*

Material		Porewater SO_4^{2-} concentration (mg L^{-1})				Porewater Ca^{2+} concentration (mg L^{-1})			
		2013	2014	2015	2016	2013	2014	2015	2016
East Coke	Mean	768±111$^{\mathbf{a}}$	779±220$^{\mathbf{A}}$	1008±126$^{\mathbf{A}}$	775±69$^{\mathbf{A}}$	159±39$^{\mathbf{A}}$	85±23$^{\mathbf{A}}$	208±33$^{\mathbf{Aa}}$	138±32$^{\mathbf{A}}$
	n	12	9	13	8	12	9	13	8
West Coke	Mean	472±164$^{\mathbf{a}}$	680±328$^{\mathbf{A}}$	1190±283$^{\mathbf{A}}$	992±281	128±35$^{\mathbf{A}}$	77±35$^{\mathbf{A}}$	251±47$^{\mathbf{Aa}}$	160±67$^{\mathbf{A}}$
	n	10	9	11	6	10	9	11	6
East Upland	Mean	2453±564$^{\mathbf{Bb}}$	563±158$^{\mathbf{B}}$	1299±516$^{\mathbf{B}}$	1209±429	414±97$^{\mathbf{B}}$	82±22$^{\mathbf{B}}$	335±134$^{\mathbf{B}}$	283±126
	n	5	10	9	4	5	10	9	4
West Upland	Mean	1231±573$^{\mathbf{Bb}}$	644±250$^{\mathbf{B}}$	1005±180$^{\mathbf{B}}$	860±126	248±96$^{\mathbf{B}}$	83±38$^{\mathbf{B}}$	252±43$^{\mathbf{B}}$	357±125
	n	4	7	10	3	4	7	10	3
East Fen Sand	Mean	672±153	586±192$^{\mathbf{C}}$	1068±152$^{\mathbf{C}}$	685±117$^{\mathbf{Cc}}$	140±38$^{\mathbf{C}}$	67±24$^{\mathbf{C}}$	209±31$^{\mathbf{C}}$	157±6$^{\mathbf{C}}$
	n	6	6	8	5	6	6	8	5
West Fen Sand	Mean	850±406	619±288$^{\mathbf{C}}$	1277±206$^{\mathbf{C}}$	1130±204$^{\mathbf{c}}$	172±98$^{\mathbf{C}}$	80±30$^{\mathbf{C}}$	246±45$^{\mathbf{C}}$	182±44$^{\mathbf{C}}$
	n	10	9	12	6	10	9	12	6
East Peat	Mean	644±391$^{\mathbf{d}}$	524±310$^{\mathbf{D}}$	745±356$^{\mathbf{D}}$	552±313$^{\mathbf{Dd}}$	229±121$^{\mathbf{Dd}}$	102±48$^{\mathbf{D}}$	252±82$^{\mathbf{Dd}}$	121±76$^{\mathbf{Dd}}$
	n	27	23	33	19	27	23	33	19
West Peat	Mean	1040±453$^{\mathbf{Dd}}$	657±234$^{\mathbf{D}}$	890±366$^{\mathbf{D}}$	879±463$^{\mathbf{d}}$	424±110$^{\mathbf{Dd}}$	133±56$^{\mathbf{D}}$	331±108$^{\mathbf{Dd}}$	223±121$^{\mathbf{Dd}}$
	n	21	34	31	20	21	34	31	20

Shared upper case letters: Indicates statistically significant differences ($P < 0.05$) in concentrations from a previous year for a construction material in the same region (MWW).
Shared lower case letters: Indicates statistically significant differences ($P < 0.05$) in concentrations in a single year between east and west regions of a construction material (MWW).

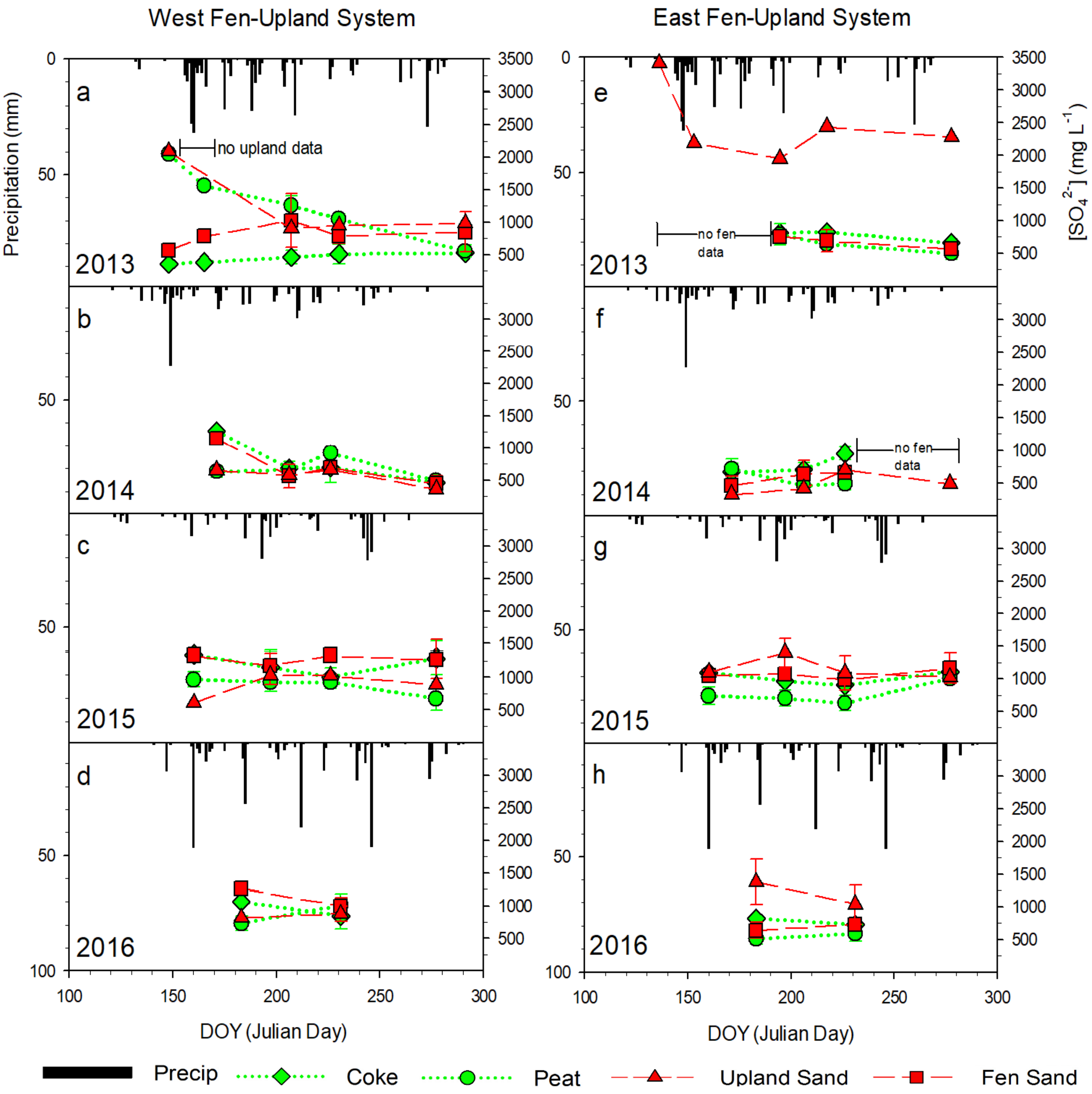

Figure 3 – 2: Spatiotemporal distribution of pore water SO$_4^{2-}$ concentrations for each construction material across the fen upland system. Each symbol is an average SO$_4^{2-}$ concentration of a sampling event. Each peat value is an average of z50, z90 and z150 data. Whiskers on symbols represent standard error. Panels a-d represent years 2013-2016 for the west fen-upland region while panels e-h represent years 2013-2016 for the east.

3.4.3 Surface runoff from reclaimed slopes

Data on SO_4^{2-} concentrations in pore water and runoff were not available consistently in each location/year; nevertheless, some distinct contrasts are notable. Average pore water SO_4^{2-} concentrations in the west, east and south-east reclaimed slopes show concentrations exceeding 500 mg L^{-1} (Figure 3 – 3a). In 2013, the west slope had the highest SO_4^{2-} concentrations (mean = ~2200 mg L^{-1}), while the east and south-east slopes had lower concentrations, but still exceeded or reached ~600 mg L^{-1}, respectively. Similarly, in June of 2014, the west slope continued to experience higher SO_4^{2-} concentrations than the east slope, although porewater concentrations in both were lower than in 2013. In August of 2014, porewater SO_4^{2-} concentrations were highest in the east slope, while concentrations in the west and south-east did not vary considerably.

Sulfate concentrations of surface runoff water from all slopes that eventually enters the fen-upland system have considerably lower concentrations than *in-situ* pore water of the slopes (Figure 3 – 3b). During snowmelt runoff in April of 2013, runoff from the east slope had the highest SO_4^{2-} concentrations (mean = ~1000 mg L^{-1}) in comparison to the west and south-east slopes, both of which experienced average SO_4^{2-} concentrations lower than 500 mg L^{-1} (Figure 3 – 3b).

In 2016, SO_4^{2-} concentrations in runoff from the slopes following heavy rainfall events also showed low concentrations of SO_4^{2-}, an order of magnitude lower than the porewater of the slopes measured in 2013 and 2014, and the snowmelt runoff in 2013 (Figure 3 – 3b). In July, the west slope had a mean concentration of ~120 mg L^{-1}, the highest in comparison to the east and south-east slopes. However, this pattern was reversed in August as runoff on the east and south-east slopes had SO_4^{2-} concentrations higher than that on the west, which averaged ~30 mg L^{-1} (Figure 3 – 3b).

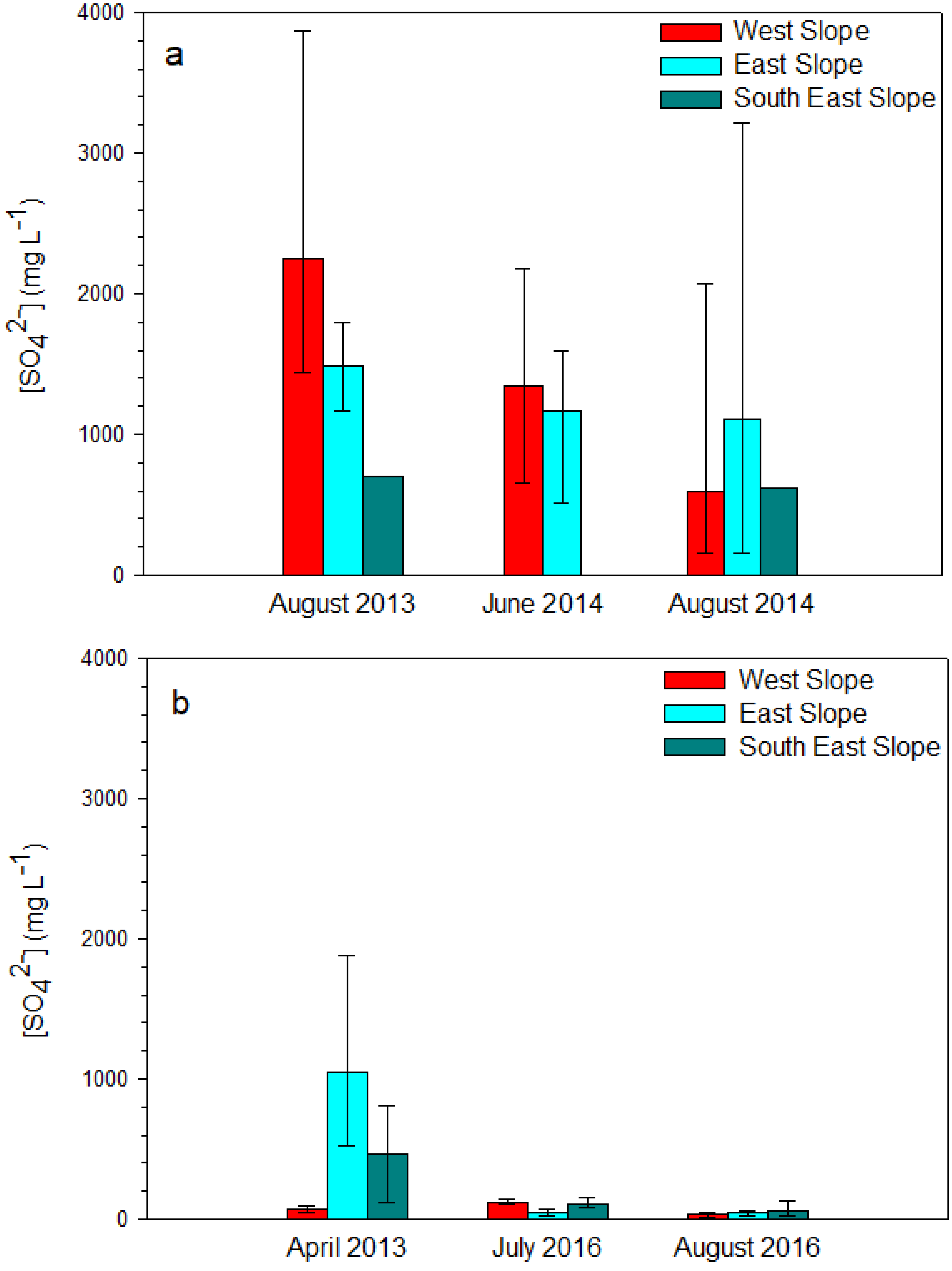

Figure 3 – 3: *In-situ* pore water SO_4^{2-} concentrations (a) in 2013 and 2014. Note *n* for south east slope was 1 in 2013 and 2014, data was not available in June 2014. Sulfate concentrations of runoff water measured after considerable precipitation events are shown in (b). Note April 2013 represents snow melt run-off. Bars represent maximum and minimum observed values.

3.4.4 Fen-upland spatiotemporal pore water distribution of calcium and sulfate

3.4.4.1 Upland Sand and Coke

In the upland tailings sand aquifer, all data deviate from the 1:1 Ca:SO_4 stoichiometric line in both regions (Figure 3 – 4a, b), and often had Ca:SO_4 molar ratios < 0.5 (Figure 3 – 5a, b). In the east, some upland samples from all years except 2014 were spread farther to the right side of the 1:1 line, resulting in enriched SO_4^{2-} concentrations (15 – 35 mmol L^{-1}) relative to the west (Figure 3 – 4b). In the west, such distinct deviation was not as pronounced. Here, nearly all upland samples plotted just below the 1:1 line and generally experienced lower SO_4^{2-} concentrations than in the east (Figure 3 – 4a). While pH for the western region of the upland aquifer tended to be clustered around ~6.5 (Figure 3 – 5a), this was not seen in the east as there was wider spread, with 2013 values experiencing pH values less than 6 (Figure 3 – 5b).

In the coke layer, some samples from only 2013 fell on the 1:1 line in the western region of the fen. Most of the coke samples in both regions clustered below the 1:1 line and did not exceed ~13 mmol L^{-1} in SO_4^{2-}. Throughout the study, pH in the coke underdrain was near circumneutral in both regions and did not show distinct spread.

3.4.4.2 Peat

As groundwater from the coke underdrain entered the peat layer in the eastern region of the fen, several peat samples from all years plotted on the 1:1 line but experienced lower SO_4^{2-} concentrations than that of the coke. In the west, only 2015 samples were found to lie on the 1:1 line, which experienced similar SO_4^{2-} concentrations to the coke. However, 2013 peat samples in the western region that experienced considerably higher SO_4^{2-} concentrations (>10 mmol L^{-1}; Table 3 – 2) than the coke underdrain fell near the 1:1 line, averaging a Ca:SO_4 molar ratio of ~0.8 (Figure 3 – 4c, Figure 3 – 5c). Unlike upland and coke samples, some peat samples fell to the left side of the 1:1 line (Figure 3 – 4c, d), resulting in higher pore water concentrations of Ca^{2+} than SO_4^{2-} and Ca:SO_4 molar ratios > 1 (Figure 3 – 5c, d). However, this was not observed in 2016. Throughout the study period, pH tended to be slightly higher in the underdrain in comparison with the peat and did not vary spatially.

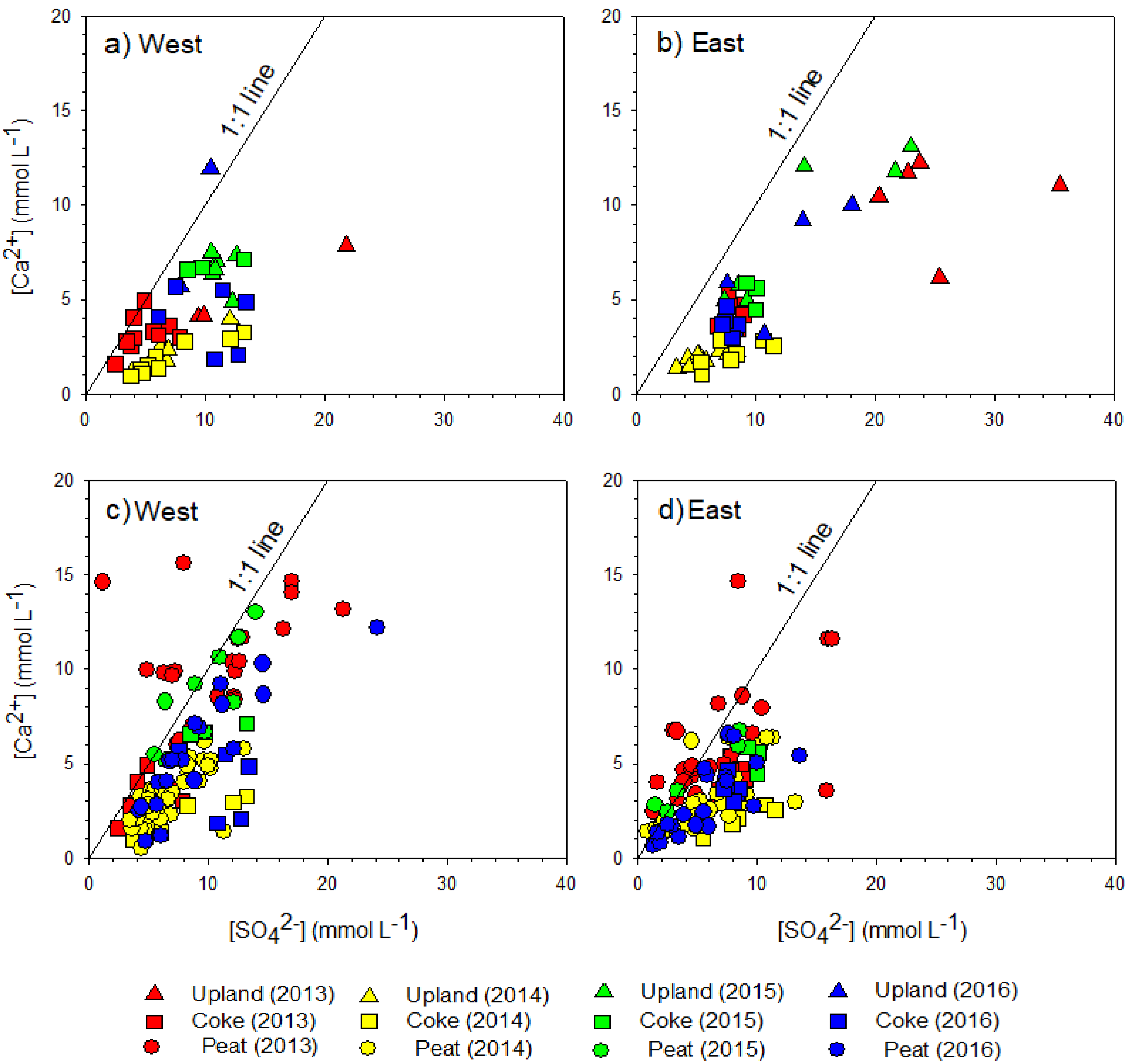

Figure 3 – 4: Scatter plots of Ca^{2+} and SO_4^{2-} from 2013-2016 across the fen-upland system. Panels a and b represent the west and east upland-coke regions, receptively, while panels c and d represent the west and east coke-peat regions, respectively. Data (2013-2016) are organized to follow the direction of groundwater flow and water mixing within the system's layers (i.e. Upland → Coke, Coke → Peat). Data falling on the 1:1 line is indicative gypsum dissolution. Data falling to the right (or below) suggests additional source of SO_4^{2-} and/or sink for Ca^{2+}. Data falling to the left (or above) suggests a sink for SO_4^{2-} and/or additional source of Ca^{2+}.

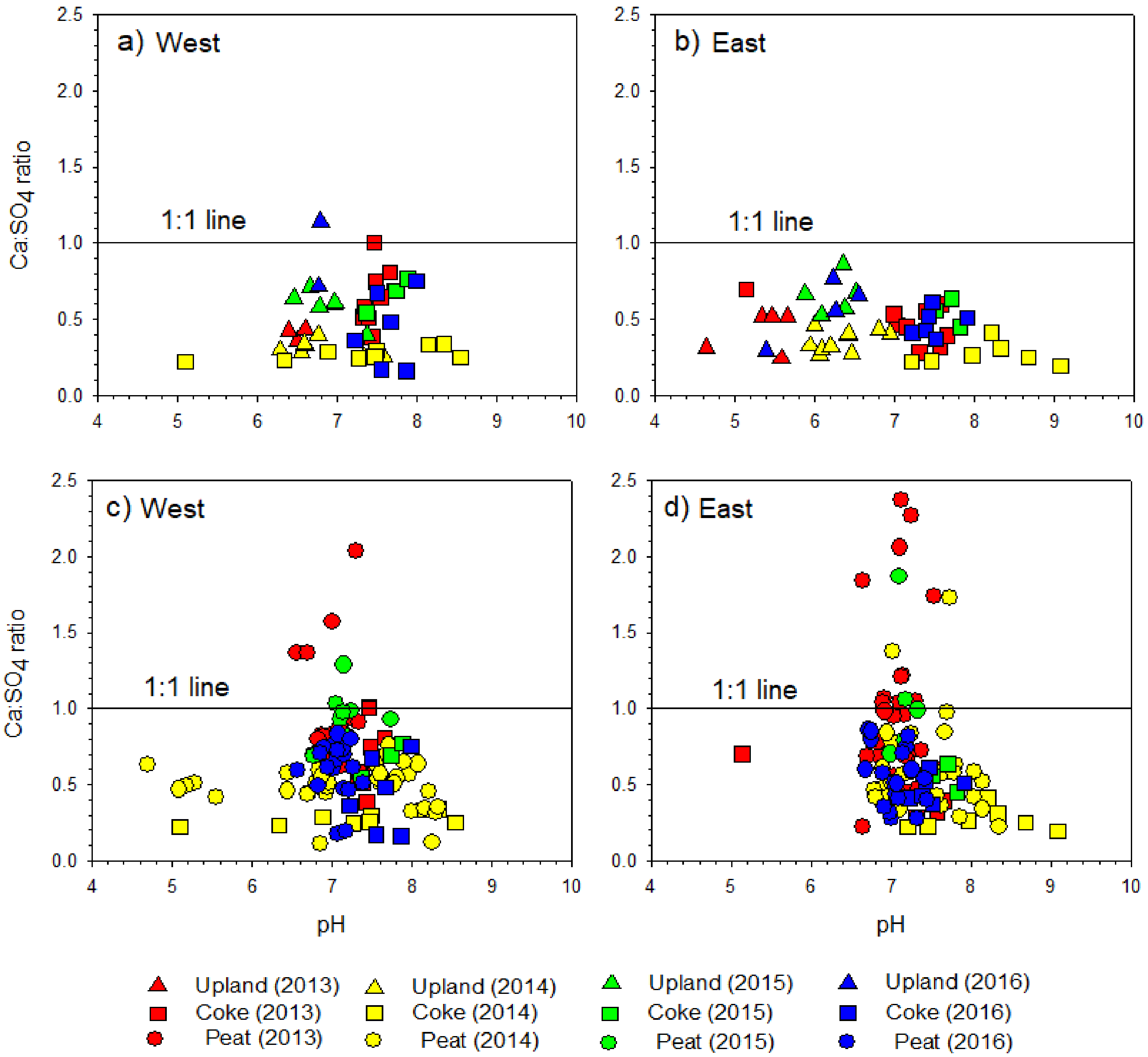

Figure 3 – 5: Scatter plots of Ca:SO_4 molar ratios of groundwater in relation to pH across the fen-upland system throughout 2013-2016. Panels a and b represent the west and east upland-coke regions while panels c and d represent the west and east coke-peat regions. Data (2013-2016) are organized to follow the direction of groundwater flow and water mixing within the system's layers (i.e. Upland → Coke, Coke → Peat). Data falling on the 1:1 line is indicative of gypsum dissolution. Data falling above suggests additional source of Ca^{2+} and/or sink for SO_4^{2-}. Data falling below suggests a sink for Ca^{2+} and/or additional source of SO_4^{2-}.

3.5 Discussion

3.5.1 Surface runoff from reclaimed slopes

Nikanotee Fen is surrounded by reclaimed hillslopes overlying Clearwater overburden substrates of marine origin. Therefore, the pore water has elevated concentrations of SO_4^{2-} (Figure 3 – 3a) and other salt constituents including Ca^{2+}, and Na^+ (see Table A-20, Appendix A). Ketcheson and Price (2016b) observed high run-off ratios from these slopes in spring of 2013. Additionally, meltwater also transported sediment, that was observed on the surface of the fen (Ketcheson and Price, 2016b). Run-off that entered the fen ponded, then percolated into the deeper peat layer to saturate it (Ketcheson and Price, 2016b). It was found that the isotopic composition ($\delta^{18}O$ and δ^2H) of ponded water on the fen surface was similar to that in the run-off collectors on the slopes, whereas the groundwater in the fen showed an isotopic signature that was representative of the upland aquifer water and run-off water from the slopes (Ketcheson and Price, 2016b). Given that salts can accumulate on the surface of the slopes via evapo-concentration (Fullerton and Pawluk, 1987; Kelln *et al.*, 2008), solutes elevated in concentration could be transported downslope during the spring freshet and heavy rainfall events. However, data from the surface-run off collectors following snowmelt and large rainfall events in 2013 and 2016, respectively (Figure 3 – 3b), show a clear dilution effect. For example, in 2013, average concentrations of SO_4^{2-} in snowmelt runoff from the west slope were measured to be 76 mg L^{-1} (Figure 3 – 3b), compared to an average concentration of 1040 mg L^{-1} in the peat pore water on the western region of the fen (Table 3 – 2). Low concentrations of SO_4^{2-} in surface runoff were again observed in the summer season of 2016, where SO_4^{2-} concentrations in run-off during the season did not exceed ~150 mg L^{-1} from any slope (Figure 3 – 3b). Ultimately, these landscape features play a relatively minor role in providing elevated concentrations of SO_4^{2-} to the lower lying fen and upland. Similarly, Kessel *et al.* (2018) found that the reclaimed slopes provided “freshwater” recharge inputs to the upland aquifer, that were retained by the recharge basins in the upland, and subsequently diluted Na^+ concentrations in the pore water of the tailings sand aquifer. In this study, however, it is worth noting that it was not possible to calculate mass fluxes of SO_4^{2-} generated from the slopes. Therefore, the total inputs of SO_4^{2-} from each could be different due to variable runoff volumes (Ketcheson and Price 2016b, c).

3.5.2 Controls on the pore water distribution and availability of sulfate

3.5.2.1 Upland Sand and Coke

Groundwater transport from the upland tailings sand aquifer, through the petroleum coke underdrain, is the primary source of solutes to the fen, as illustrated by Na^+ concentrations in groundwater flow in the system (Kessel *et al.*, 2018). Similar trends were expected for SO_4^{2-}, given that the tailings sand upland aquifer contains the largest reservoir of S (Simhayov *et al.*, 2017). Indeed, throughout 2013-2016, the increasing pore water SO_4^{2-} concentrations in the petroleum coke underdrain reflected an origin from the adjacent tailings sand aquifer. This was especially evident between 2013 and 2014, during which the tailings sand aquifer in the western and eastern regions of the upland initially (i.e. in 2013) experienced the highest porewater SO_4^{2-} concentrations within the fen-upland system (Figure 3 – 2a, e). However, the elevated concentrations did not reflect in the petroleum coke underdrain beneath the fen peat until 2014 (Figure 3 – 2b). A similar pattern of solute distribution was also seen for Na^+ (Kessel *et al.*, 2018). The instantaneous lower pore water SO_4^{2-} concentrations in the upland aquifer than the coke underdrain in 2014 can be attributed to dilution, due to freshwater recharge following tillage of the LFH soil cap layer of the upland in autumn of 2013, in addition to the integration of recharge basins which derived surface run-off from the surrounding reclaimed slopes (Kessel, 2016). Together, these management strategies promoted detention and infiltration of surface water in the upland (Kessel *et al.*, 2018; Irvine, 2018). Aside from significantly lower SO_4^{2-} concentrations in 2014 than in 2013 ($P < 0.05$; Table 3 – 2), this dilution effect was supported by substantially lower concentrations of Ca^{2+} ($P < 0.05$; Table 3 – 2), and other dissolved ions (see Appendix A). Furthermore, this influence of dilution seemed to be more pronounced in the eastern region of the upland aquifer (Table 3 – 2, $P > 0.05$), likely due to more effective freshwater recharge there (Kessel *et al.*, 2018). Kessel *et al.* (2018) proposed that during dry seasons, as in 2015, Na^+ concentrations increased in the upland as an artefact of sampling wells capturing the deeper and less diluted saturated zones of the aquifer, instead of additional mass inputs from geochemical processes. The high SO_4^{2-} concentrations in this region were reflected in the petroleum coke underdrain in the fen (Figure 3 – 2c, g), which demonstrates that during dry years SO_4^{2-} distribution in the coke underdrain is representative of SO_4^{2-} concentrations from the deeper zones of the aquifer (Kessel *et al.*, 2018), that are not significantly influenced by dilution. Although the differences were usually insignificant, the higher SO_4^{2-} concentrations of the tailings sand aquifer in the east than in the west is probably due to the heterogeneity of the sand that was placed during construction of the system.

Groundwater transport, influenced by freshwater recharge, are likely the dominant processes that control SO_4^{2-} distribution and dissolved pool in the tailing sand aquifer and coke underdrain. While previous studies have shown that SO_4^{2-} reduction could occur in SO_4^{2-} rich systems that contain oil sand tailings (Ramos-Padron *et al.,* 2011; Stasik *et al.,* 2014, Reid and Warren, 2016), the magnitude of this effect is not likely to be large in Nikanotee Fen, due to the lack of labile C compounds in tailings sand as well as the petroleum coke. Khadka *et al.* (2015) investigated DOC production in construction materials of Nikanotee Fen. They found that the petroleum coke and tailings sand produced very little DOC per unit mass, and it was aromatic in nature. However, this DOC source was consumed in their bioavailability study in which the substrates were amended with saline water. Their findings suggest that microbial activity in the tailings sand and petroleum coke might be very low. This is further supported by Reid and Warren (2016), who suggested that high sulfide ($\sum H_2S_{(aq)}$) production (>500 µM) in the sand cap (i.e. tailings sand) of Sand Hill Fen was due to SRB preferentially utilizing readily labile C derived from the overlying peat deposit, instead of more recalcitrant petroleum derived C sources in the tailings sand (Slater *et al.,* 2005; Penner and Foght, 2010). In this study, sulfide was never measured. Although monitoring SO_4^{2-} concentrations are not always indicators of SO_4^{2-} reduction (Mia *et al.,* 2012), in this case due to obscurity by constant flushing of SO_4^{2-} from the tailings sand in the upland, considerable changes in SO_4^{2-} concentrations independent of Ca^{2+} might lend support for microbially mediated processes like SO_4^{2-} reduction (Markel *et al.,* 1998). Specifically, this would be observed if Ca^{2+} molar concentrations are in excess over SO_4^{2-}. Based on ratios of $Ca:SO_4$, most of the data fell to the right of the 1:1 gypsum dissolution line (Figure 3 – 4a, b), suggesting an excess of SO_4^{2-} over Ca^{2+} (Appelo and Postma, 2005). This is especially prominent in the eastern region of the upland aquifer, wherein SO_4^{2-} concentrations were ~10 mM in excess over Ca^{2+} (Figure 3 – 4b). In addition to SO_4^{2-} inherent of legacy gypsum from oil sands process affected water (J. Martin, personal communication, 2017), an external source of SO_4^{2-} that could explain the low molar Ca:SO_4 ratios (<0.5; Figure 3 – 5a, b) in the porewater of upland aquifer could be from the sand's marine origin. Previous studies have shown that pyritic overburden shale sediments exist in oil sands deposits in the AOSR (Wall, 2005; Haug *et al.,* 2014), which upon oxidation can generate significant amounts of SO_4^{2-} (Purdy *et al.,* 2005; Huang *et al.,* 2015; Appels *et al.,* 2017).

3.5.2.2 Peat

Given that groundwater flow is persistently upwards in the fen, from the coke underdrain to the peat, (Figure 3 – 1), it is expected that porewater in the peat layer would experience an elevated standing pool of SO_4^{2-} over time. Interestingly, in 2013, the western peat deposit experienced average concentrations of SO_4^{2-}, and Ca^{2+}, that were roughly ~2 and ~3 times higher than those in the coke layer, respectively (Table 3 – 2). This variability was not only experienced in the surficial layer (i.e. where evapo-concentration might have caused this increase), but also in the deepest zone of the peat profile (i.e. 150 cm bgs; Appendix A Tables A-11, A-17). Additionally, the western region of the peat deposit experienced significantly higher porewater SO_4^{2-} and Ca^{2+} ($P < 0.05$; Table 3 – 2) concentrations than peat in the eastern region of the fen, which had pore water SO_4^{2-} concentrations comparable to the underlying coke underdrain. These findings suggest that groundwater transport alone was not the sole source of SO_4^{2-} in the peat layer, most strongly evident in 2013. A possible explanation for the excess SO_4^{2-} in the peat layer in the initial year could be at least in part due to the prolonged drainage of the donor rich fen from which the peat was extracted. Furthermore, although uncertain, the variability in SO_4^{2-} concentrations in the peat layer between the east and west regions may be due to the random placement of the peat during construction of the fen, supplemented by changes in SO_4^{2-} concentrations in the coke underdrain during transport over time; the former of which probably only of importance in the first year (Table 3 – 2). Simhayov *et al.* (2017) found that the drained donor peat had ~40,000 mg kg^{-1} total Ca and ~17,000 mg kg^{-1} total S. In comparison, Vitt and Chee (1990) found surficial peat in Alberta's extreme rich fens had ~49,000 mg kg^{-1} total Ca and ~9,400 mg kg^{-1} total S. The release of elements from peat, such as Ca and S, upon enhanced oxidation has previously been reported (Bayley *et al.,* 1986; Heathwaite 1990,1991, Warren *et al.,* 2001). With respect to Ca in Nikanotee Fen, however, *in-situ* cation exchange cannot be excluded as a process that releases Ca^{2+} into solution. Particularly, reverse ion exchange likely removes Na^{+} from solution, which comprises a large portion of total cations in the pore waters of the system (Appendix A), and replaces Ca^{2+} and Mg^{2+} at favorable exchange sites in the peat resulting in their release to the pore water of the peat deposit. This mechanism is an additional explanation for why pore water concentrations of Ca^{2+} (Table 3 – 2), and Mg^{2+} (see appendix A), are almost always higher in the peat layer than in the petroleum coke underdrain on both regions of the fen. Reverse ion exchange is known to occur in soils with adequate cation exchange capacity (Dance and Reardon, 1983; Rajmohan and Elango, 2004; Zaidi *et al.,* 2015).With respect to the excess SO_4^{2-} in the peat layer, it is known that enhanced mineralization of organic S from aerobic decomposition and/or oxidation of reduced S compounds (e.g. FeS and FeS_2) in the peat matrix contributes to elevated SO_4^{2-} concentrations (Eimers *et al.*, 2003; Knorr and Blodau, 2009; Reiche *et al.*, 2009; Estop-Aragonés *et al.,* 2013) and upon re-saturation of the peat this SO_4^{2-} would be mobilized (Zak and Gelbrecht 2007; Bougon *et al.*, 2011, Maassen *et al.,* 2015). Thus, it is conceivable that the management of the donor peat prior to placement on the constructed fen likely contributed to the elevated SO_4^{2-} pool found in Nikanotee Fen peat deposit in 2013.

Unlike the upland aquifer and coke underdrain, Ca:SO_4 ratios in both regions of the peat deposit occasionally exceeded 1 (Figures 3 – 5c, d), especially in the first year. This was reflected in decreasing pore water SO_4^{2-} concentrations in the peat deposit throughout the season (Figure 3 – 2a, b), with more pronounced effects in the western region of the fen. Here, pore water SO_4^{2-} concentrations averaged 510 mg L^{-1} at the end of the season (DOY 291), whereas in the preceding sampling events SO_4^{2-} concentrations averaged 1234 mg L^{-1} (Figure 3 – 2a). However, average pore water Ca^{2+} concentrations did not show decreases over time, exceeding 400 mg L^{-1} at the end of the season and in the previous sampling events (Figure 3 – 4c, d; Appendix A Tables A-11, A-17). Additionally, the peat layer on both regions of the fen had lower mean annual pore water SO_4^{2-} concentrations than the underlying coke throughout the study period, except in 2013 (Table 3 – 2). This observation was more prominent in the eastern region of the fen, wherein average SO_4^{2-} concentrations were >200 mg L^{-1} lower in the peat layer than in the petroleum coke underdrain between 2014-2016 (Table 3 – 2). Furthermore, average $HCO3^-$ concentrations in 2016 were consistently higher in the peat layer than in the petroleum coke underdrain on both regions of the fen (Appendix A), suggesting that enhanced microbially mediated processes may have contributed to increased alkalinity there (Weiner, 2008; Cirkel *et al.,* 2014). Together, the aforementioned observations allude to SO_4^{2-} reduction as being an important anaerobic C mineralization process in the fen peat deposit, an outcome that was expected (Pester *et al.,* 2012). The likely recovery of SO_4^{2-} reduction in the peat layer over the 2013 season was due to the establishment of the vegetation on the fen, which provided fresh litter inputs and root exudates that were easily degradable by SRB. Hahn-Schofl *et al*. (2011) found that porewater SO_4^{2-} concentrations in degraded surficial peat from a re-wetted fen decreased throughout the duration of an incubation experiment. In contrast, incubated peat from the middle and lower portions of the fen peat profile did not experience substantial decreases in porewater SO_4^{2-} over time, and in some instances increased. The authors attributed this finding to the abundance of fresh and readily labile organic matter in the surficial peat (i.e. from rhizodeposition following establishment of plants), in comparison to the humified nature of the deeper peat. In peatlands, it is well known that prolonged drainage results in the depletion of labile C, leaving behind only recalcitrant residues, resulting in an overall poor organic matter quality of the peat substrate (Urbanova *et al.,* 2018). Khadka *et al.* (2015) found that peat from Nikanotee Fen produced very little DOC in comparison with *Juncus balticus* and *Carex aquatilis*, the latter of which are vascular plant species present in the constructed fen. They proposed that the lower DOC production from the peat may have been due its decreased lability, owing to prolonged drainage prior to placement. Additionally, they found that the produced DOC from the peat was more aromatic, and had lower molecular size, than of DOC produced from plants. This has led Nwaishi *et al.* (2016a) to suggest that re-vegetation practices in newly constructed fens would supply microbes with labile C inputs via rhizodeposition, thus stimulating belowground microbially mediated processes.

Although gypsum ($CaSO_4{\cdot}2H_2O$) precipitation is presumably never found to be of importance in undisturbed peatlands, due to low pore water concentrations of SO_4^{2-} and Ca^{2+}, it is worth discussing the potential influence of the process on SO_4^{2-} availability here, given the nature of the construction materials. Geochemical modeling was deemed inappropriate due to lack of alkalinity data in most years, thus potentially effecting saturation indices calculations (i.e. uncertainty in computation of activity coefficients). Nonetheless, we believe that dilution of Ca^{2+} and SO_4^{2-} in the upland aquifer and petroleum coke underdrain, in addition to SO_4^{2-} reduction in the peat deposit, would cause the solution to be undersaturated with respect to $CaSO_4{\cdot}2H_2O$ ($K_{sp} = 10^{-4.58}$) (Cirkel *et al.*, 2014). Thus, precipitation of the mineral cannot occur (Deutsch, 1997). It is conceivable, however, that $CaSO_4{\cdot}2H_2O$ may have been present in the tailings sand prior to placement, as it was in contact with process affected water (J. Martin, personal communication, 2017), and is marine in origin. Specifically, given that the sand was taken from a tailings pond in dry conditions, accumulation of solutes at the surface could have caused $CaSO_4{\cdot}2H_2O$ to precipitate (Fullerton and Pawluk, 1987), as suggested by Simhayov *et al.* (2017). After the addition of 5000 m^3 of water to aid in the compaction of the tailings sand aquifer, $CaSO_4{\cdot}2H_2O$ would have progressively dissolved and released Ca^{2+} and SO_4^{2-} into the porewater.

3.5.3 Influence of external sources

It is worth exploring the extent to which atmospheric deposition may contribute to the elevated pore water concentrations of SO_4^{2-} in Nikanotee Fen, since the constructed fen is the vicinity of oil sands mining activities. Also, the donor fen from which the peat was extracted to construct Nikanotee Fen was located 12 km southeast from a bitumen upgrading plant (Simhayov *et al.*, 2017). Although not directly measured in this study, studies that quantified rates of SO_4^{2-}-S atmospheric deposition in peat bogs can be explored, as bogs are solely fed by nutrients from precipitation inputs.

Wieder *et al*. (2010) found deposition rates in bogs within the AOSR averaged 1.14 kg SO_4^{2-}-S ha^{-1} yr^{-1} between 2005 and 2008. These sites were located 26-150 km away from Syncrude mine site facilities. More recently, Wieder *et al.* (2016b) found average bulk deposition rates (2009-2014) of SO_4^{2-}-S, Ca^{2+} and Mg^{2+} to be ~15, ~13 and ~5 kg ha^{-1} yr^{-1} for a bog 12 km away from oil sands operations, and ~2, ~7 and ~2 kg ha^{-1} yr^{-1} for a bog that was 250 km farther out. Despite the aforementioned deposition rates of SO_4^{2-}-S being elevated in proximity to industrial operations, they cannot be ascribed as an important *in-situ* contributor to the elevated pore water SO_4^{2-} concentrations (>500 mg L^{-1}) observed in Nikanotee Fen. Wieder *et al.* (2016a) reported porewater SO_4^{2-}-S concentrations in peat bogs within 6-43 km of industrial activity north of Fort McMurray, receiving average SO_4^{2-}-S deposition rates that are within the range of the above, peaked at ~3 mg L^{-1} in SO_4^{2-}-S.

Albeit SO_4^{2-}-S deposition rates are not available directly from the donor fen, Syncrude's Sand Hill Fen had an average deposition rate of ~12 kg SO_4^{2-}-S ha^{-1} yr^{-1} (Wieder *et al.,* 2016a). Studies have shown that between 60-75% of atmospherically deposited SO_4^{2-}-S can be accumulated in peat (Moore *et al.,* 2004; Wieder *et al.,* 2016b), via DSR (Vile *et al.,* 2003b). Moreover, it has been previously proposed that the S pool of wetlands receiving higher SO_4^{2}-S deposition rates becomes augmented, in comparison to wetlands that are rather "pristine" systems (Eimers *et al.,* 2007). Thus, it is likely that more S would have accumulated in the donor fen peat, than peat in systems that received lower rates of SO_4^{2-}-S deposition. This may have had an influence on the amount of SO_4^{2-} released following drainage of the donor fen peatland. In partial support of this reasoning, following drying in an experimental peatland, Coleman-Wasik *et al.* (2015) observed higher SO_4^{2-} release from peat that was formerly amended with SO_4^{2-}, to simulate elevated SO_4^{2-}-S deposition rates, than peat that was not manipulated. The authors suggested that recently elevated SO_4^{2-} loading led to an accumulation of labile organic S compounds in the peat, that were more readily oxidized after drying periods, and consequently resulted in higher SO_4^{2-} release to the porewater. Given the donor fen's proximity to industrial activity, and its prolonged drainage, it is speculated that a similar process occurred there.

3.5.4 Implications for constructed fens in the AOSR

The work shown here provides an initial assessment of the pore water SO_4^{2-} distribution in constructed fen landscapes in the AOSR. Given that fen construction in the region is at the pilot stage, the findings of this work can be used to assess the current trajectory of Nikanotee Fen with respect to overall S biogeochemistry, in addition to building a solid baseline as to how the availability of SO_4^{2-} in future landscapes, that may mimic the design of Nikanotee Fen, might change over time.

Ultimately, the goal of fen creation is to mimic the functions (e.g. peat accumulation) of natural, undisturbed, peatlands. Usually, standing pools of dissolved SO_4^{2-} in such systems are low, and in turn appreciable rates of SO_4^{2-} reduction are sustained by the replenishment of SO_4^{2-} through various hydrological and biogeochemical mechanisms, which to this day are still being investigated owing to a rather cryptic S cycle in peatland systems (Pester *et al.,* 2012). Albeit the work here did not precisely focus on estimating rates of SO_4^{2-} reduction, it is likely that the incorporation of mine waste materials that are inherently rich in SO_4^{2-} would allow DSR to be a prominent anaerobic C mineralization process. Additionally, the incorporation of donor fen peat provides a confounding source of SO_4^{2-}, although impacts of the employed management practices on SO_4^{2-} availability in fen peat must be further examined. Evidence of SO_4^{2-} reduction being an important process in the constructed fen has already emerged; CH_4 emissions are low in Nikanotee Fen (Murray *et al.,* 2017), owing to a suppression effect by high SO_4^{2-} concentrations that are driving SRB to outcompete methanogens for substrates (Nwaishi *et al.*, 2016b). Suppressed CH_4 emissions from constructed fen landscapes might seem advantageous for the oil sands industry, but peat accumulation process may become degraded as long as SO_4^{2-} reduction dominates the anaerobic C mineralization pool (Wieder *et al.,* 1990), which may not be a targeted reclamation goal.

Although the results of this study showed that dilution was likely the main mechanism in decreasing the dissolved concentrations of SO_4^{2-} in the upland aquifer, and in turn in the porewaters of the fen, it is likely that SO_4^{2-} reduction would still be a prominent C mineralization process, specifically in the peat deposit of the fen where labile C substrates are available, given that SO_4^{2-} would still be most dominant electron acceptor in the pore water. Therefore, it is the progressive flushing of the finite amounts of SO_4^{2-} inherent of the tailings sand (Simhayov *et al.*, 2017), that may ultimately determine when SO_4^{2-} reduction rates might be comparable to those typical of natural peatlands. In the long-term, after the solutes have been flushed from the tailings sand, the replenishing of SO_4^{2-} would largely be mediated by recycling within the peat deposit, which would likely have enhanced pools of reduced inorganic S compounds, that are known to turnover rapidly (Wieder and Lang, 1988; Chapman and Davidson, 2001).

3.6 Conclusion

The work presented here is the first step towards better understanding the sources of SO_4^{2-}, and hydrogeochemical controls on its dissolved pool in Nikanotee Fen. An origin of the elevated SO_4^{2-} concentrations in the pore waters of the upland is, in part, from legacy $CaSO_4 \cdot 2H_2O$ constituents in process affected water that was in contact with the tailings sand prior to placement on constructed system. However, low Ca:SO_4 ratios in the porewater of the upland aquifer manifested in an excess of SO_4^{2-} over Ca^{2+}, owing to the marine origin of the sand.

The large pool of SO_4^{2-} in the upland aquifer migrated to the fen via the petroleum coke underdrain, most clearly observed between 2013 and 2014 on both regions of the system. Dilution as a result of precipitation inputs, and due to freshwater recharge from the reclaimed slopes, was likely the main mechanism controlling the dissolved SO_4^{2-} pool in the upland aquifer, and in the petroleum coke underdrain. This pool of SO_4^{2-} entered the peat deposit, due to persistent upward groundwater flow in the fen. However, in 2013, substantially higher SO_4^{2-} concentrations in the peat deposit than in the coke underdrain indicated that the donor peat initially had an elevated SO_4^{2-} pool, perhaps from the drainage of the donor fen, although must be confirmed. Nonetheless, at the end of the 2013 season and in subsequent years, lower SO_4^{2-} and higher HCO_3^- concentrations in the peat deposit than in the petroleum coke underdrain, and Ca:SO_4 ratios > 1, indicated that DSR was likely occurring in the peat layer of the fen. Throughout the study, differences in SO_4^{2-} distribution between the eastern and western regions of the system were due to the heterogeneity of the sand in the upland, and perhaps in part, to the random placement of the peat.

The findings of this research provide insight into the initial distribution of SO_4^{2-} in newly constructed fen landscapes in the AOSR, from which a solid baseline can be established for future reclamation projects.

4. The effects of aeration and inundation on sulfate availability in fen peat

4.1 Context

Open pit mining activities have disturbed a large area of the boreal forest in the Athabasca Oil Sands Region (AOSR), wherein large deposits of recoverable bitumen are found beneath the surface (Government of Alberta, 2017). In this ecozone, climatic and hydrological conditions have favored the development of fen peatlands, which are abundant in the region (Vitt *et al.*, 1996). Due to the large-scale disturbance of these peatlands during surface mining operations, they are removed from the landscape (Rooney *et al.,* 2012). Given that Alberta's oil sands industries are required to reclaim their post mined sites to land capability equivalent to that in pre-disturbed conditions (OSWWG, 2000), fen reclamation is being tested (Price *et al.,* 2010). To date, Sandhill Fen and Nikanotee Fen are the two pioneering projects testing the feasibility of fen creation (Ketcheson *et al.,* 2016a). The latter, which is this the focus of this research, receives groundwater inputs to maintain saturated conditions from a constructed tailings sand upland aquifer that is supplied with recharge runoff water from reclaimed hillslopes (Ketcheson *et al.,* 2017). Oil sands process affected water containing legacy salt constituents, from gypsum ($CaSO_4 \cdot 2H_2O$) and caustic ($NaOH$), was in contact with the tailings sand prior to placement on the constructed system (Simhayov *et al*., 2017). Therefore, the pore water of the upland aquifer has elevated soluble concentrations of calcium (Ca^{2+}), sulfate (SO_4^{2-}) and sodium (Na^+) (Simhayov *et al.*, 2017). At high concentrations, the mobilization of these constituents will increase the salinity of the fen pore water and can have significant impacts on the establishment of vegetation species (Renault *et al.*, 1998; Purdy *et al.,* 2005; Trites and Bayley, 2009).

In the fen, pore water SO_4^{2-} concentrations in the peat profile are 1 to 2 orders of magnitude higher than in surrounding peatlands (Chapter 1). In the initial year post-construction, it was found that pore water SO_4^{2-} concentrations in the peat layer significantly exceeded those in the underlying petroleum coke underdrain (Chapter 3). Therefore, aside from the transport processes from the tailings sand aquifer, additional sources of SO_4^{2-} are present in the fen peat. It is well established that abundant SO_4^{2-} pools can stimulate dissimilatory SO_4^{2-} reduction (DSR). As a product of DSR, sulfide may be toxic to wetland vegetation species (Geurts *et al.*, 2009; Lamers *et al.*, 2013). However, sulfide is also known to control heavy metal mobility through the formation of metal sulfides (Koretsky *et al.*, 2007; Smieja-Krol *et al.*, 2010). Additionally, enhanced DSR is known to suppress methanogenesis (Dise and Verry, 2001, Gauci *et al.*, 2002, Goldhammer and Blodau, 2008), but at the expense of potentially degrading peat accumulation if DSR is a dominant anaerobic carbon (C) mineralization pathway (Wieder *et al.*, 1990). Thus, it is necessary to investigate why this large soluble sulfur (S) pool exists in the peat.

The peat used in the construction of Nikanotee Fen was highly disturbed prior to placement due to prolonged drainage of the donor fen peatland, which is known to alter peat physicochemical properties (Nwaishi *et al.*, 2015). Nwaishi *et al.* (2015) found that the lower organic matter content resulted in higher concentrations of extractable nutrients, such as phosphorus (P) and nitrogen (N) in the donor peat. This was attributed to drainage and re-wetting causing changes in redox conditions, and increased mineralization in the peat profile due to enhanced decomposition (Nwaishi *et al.*, 2015). However, the influence of the donor peat's management practices on soluble SO_4^{2-} availability has not been examined. Given that peatland reclamation is a newly tested concept, such a knowledge gap must be investigated. Some studies have examined drought-induced SO_4^{2-} production in wetland catchments following water table decline, which experienced strong pulses of SO_4^{2-} release to drainage streams, due to the oxidation of reduced inorganic S (RIS) and organic S compounds in surficial soil layers (Devito and Hill, 1999a; Devito *et al.*, 1999b; Eimers *et al.*, 2007). Other studies have found elevated pore water SO_4^{2-} concentrations following re-wetting of drained fens, attributed to mobilization of SO_4^{2-} that was produced by the oxidation of RIS within the peat matrix (Zak and Gelbrecht, 2007; Zak *et al.*, 2009). Furthermore, laboratory studies have simulated drying and re-wetting of peat, where release of SO_4^{2-} was evident (Eimers *et al.*, 2003; Whitfield *et al.*, 2010; Brouns *et al.*, 2014). However, none of the aforementioned laboratory studies have included a combination of different extended temperature and saturation treatments that simulate drainage of the peat, and subsequent re-inundation after placement on a constructed landscape. Since the donor fen was in the dry sub-humid climate of the Western Boreal Plain (WBP), strong temperature gradients and prolonged drought periods can occur, which can result in enhanced decomposition of the peat (Kong *et al.*, 1980). Furthermore, a better understanding is needed of the effects of re-inundating the disturbed donor peat after placement on the soluble SO_4^{2-} pool.

Therefore, this study aims to simulate the donor peat drainage and subsequent management practices used in the construction of Nikanotee Fen, to better understand attendant impacts on SO_4^{2-} availability in the peat. Specifically, the objectives are to: 1) evaluate the effects of incubating dried and re-wet fen peat on soluble SO_4^{2-} availability under aerobic and inundated conditions; and 2) determine the role of temperature on SO_4^{2-} release and retention. It is hypothesized that; 1) higher soluble SO_4^{2-} concentrations will be observed under aerobic conditions; and 2) peat incubated at warmer temperature will result in higher retention and release of SO_4^{2-} due to enhanced microbial activity.

4.2 Study Site

Peat cores were collected from a ~0.7 km^2 moderate-rich fen ("Poplar Fen" 56°56.330'N 111°32.934'W) located northwest of Fort McMurray, Alberta, in August of 2016. At Poplar Fen, the vegetation structure is similar to that of the donor fen from which the peat was extracted in constructing Nikanotee Fen. Vegetation communities include *Larix laricina, Betula glandulosa, Equisetum fluvatile, Smilacina trifoliata, Carex prairea, C. diandra, Stellaria longipe,* and moss species including *Tomenthypnum nitens, Campyllium stellatum and Hylocommium splendens* (Nwaishi *et al*., 2015; Daté, 2016). The system has peat depths ranging from ~1.2-3.0 m, thinning to less than 0.5 m along the margins between the fen and the upland (Elmes *et al.,* 2018). Underlying the peat are layers of fluvial sand and gravel overlying the Clearwater and McMurray formations (Elmes *et al.,* 2018).

4.3 Methods

4.3.1 Collection and preparation of samples

To extract the soil cores, a sharp knife was used to cut blocks of surficial peat to a depth of ~20 cm. A total of 20 blocks were cut out approximately 10 m apart. The cores were collected at the interface of hummocks and hollows. After extraction, cores were wrapped in plastic and immediately put in a freezer to maintain field integrity. Frozen cores were then transported to the laboratory where they were kept in the freezer (-15°C) until beginning of the experiment, which occurred 25 days after sample collection. Before the beginning of the experiment, three selected peat cores were removed from the freezer and thawed for a period of 24 hours. Sub-samples from each core were then taken to measure background moisture content (MC), organic matter content (OMC), pH and SO_4^{2-} concentrations.

4.3.2 Experimental design

4.3.2.1 Pre-incubation

One peat core, the "Moist-control" sample, was used to represent the undrained condition; it was sorted and kept field moist in an incubator at 4°C during the pre-incubation period. The remaining two peat cores, the "Dry-rewet" samples, were used to represent conditions associated with peatland drainage and re-wetting; they were sorted (i.e. visible roots were removed) and homogenized by hand as much as possible into two separate large pans and were left at ambient room temperature (~22°C) to dry (approximately 1 week) until noticeably dehydrated (Eimers *et al.,* 2003), which happened to occur at ~65% MC (gravimetric). The "Dry-rewet" samples were then re-wet over a period of 4 hours to ~80% MC using Milli-Q water. This MC value is optimal for mineralization at 25°C for stockpiled peat in the AOSR (Kong *et al.*, 1980). The homogenized "Moist-control" and "Dry-rewet" samples were then moved into four separate 2 L rectangular plastic containers (two for "Moist-control" and two for "Dry-rewet"), each with five 2-mm diameter openings to allow for some gas exchange and treated as described below. Prior to the drying and re-wetting procedure, the initial mass of peat used was roughly ~300 g from each of the "Dry-rewet" cores. Approximately ~400 g of peat (200 g for each treatment) from the "Moist-control" core was used.

4.3.2.2 Incubation period: Temperature and saturation treatments

To represent natural wetland conditions, the "Moist-control" containers were inundated (peat was completely submerged) and incubated at 15°C and 25°C in the dark (two separate incubators) for a period of 56 days; hereafter referred to as "Moist control @ 15°C" and "Moist control @ 25°C" (Figure 4 – 1). To monitor how temperature affects the soluble SO_4^{2-} pool under aerobic (i.e. drained) conditions, the "Dry-rewet" containers were incubated for 28 days (day 8 – 36), in the dark, at 15°C and 25°C ("Aeration treatment", Table 4 – 1); hereafter referred to as "Dry-rewet @ 15°C" and "Dry-rewet @ 25°C". To examine the effects of inundating the drained peat on SO_4^{2-} availability, the same "Dry-rewet @ 15°C" and "Dry-rewet @ 25°C" containers were completely submerged in Milli-Q water and again incubated for 28 days (day 36 – 64), in the dark, at 15°C and 25°C (“Inundation treatment”, Table 4 – 1). Throughout the incubation, all containers were wrapped in aluminum foil to prevent light exposure.

4.3.3 Analyses

In total, there were 6 sampling events completed to monitor changes in SO_4^{2-} concentrations and pH (Table 4 - 1). Sampling for SO_4^{2-} determination was done in triplicates. On day 50 and 64 of the inundation treatment, there was only enough peat remaining (by mass) in the “Dry-rewet @ 15°C” container for duplicate sampling to measure SO_4^{2-} concentrations. Prior to sampling, peat was not oven dried to avoid further drying and possible changes in SO_4^{2-} release. Sulfate was determined from saturated paste extracts, whereby 25 mL of 0.01 M NH_4Cl extractant solution was added to 5 g of peat to make a 1:5 soil to solution ratio in a soil specimen container (Eimers *et al.*, 2003; Kane *et al.*, 2013). Samples were then placed on a mechanical shaker (MaxQ 3000) for 2 hours, after which they were left in suspension for 30 minutes. Extracts were then paper filtered (Whatman No. 42) and further syringe filtered to 0.22 μm prior to decanting into 1.5 mL polypropylene vials. Vials were then frozen until further analyses for SO_4^{2-} concentrations with a capillary ion chromatograph (IC) system Dionex ICS-5000 (Thermo Scientific™) at the Ecohydrology Laboratory at University of Waterloo, Canada. The detection limit of the IC method was 0.02 mg L^{-1}. Every extraction event also included a blank for quality assurance, which contained the NH_4Cl extractant solution only. Throughout sampling, syringes used were triple rinsed with Milli-Q water in between soil extractions. Results were converted from mg L^{-1} and reported in mg kg^{-1} of dry soil, accounting for dilution (Robertson *et al.*, 1999). Net release of S-SO_4^{2-} throughout the incubation experiment is the difference of S-SO_4^{2-} between each extraction event and the previous in a single treatment. All re-usable glassware and equipment were acid washed with 10% HCl and triple-rinsed with Milli-Q water after sampling.

Measurement of pH prior to and during the incubation was done in duplicates and occurred on the same days as sampling for determination of SO_4^{2-}. All pH measurements were done by adding 25 mL of Milli-Q water to 5 g of soil, which was taken directly from the containers without additional drying, to make a 1:5 soil-solution paste. The pH of the paste was then measured using an Orion™ Versa Star™ Benchtop Meter (Thermo Scientific™ A300 series) and three-point calibration was always completed prior to taking measurements.

Moisture content was determined gravimetrically by selecting 3 subsamples of recorded mass from each container for the different treatments and oven drying in dry aluminum pans (12 pans in total per event) at 85°C for 24 hours. Values are expressed on a wet weight basis (equation 4.1),

$$MC(\%) = \left(\frac{W_w - W_d}{W_w}\right) * 100 \qquad [4.1]$$

where *MC (%)* is the gravimetric moisture content, W_w is the weight (g) of the wet sample and W_d is the weight (g) of the sample after oven drying. This procedure was done during the pre-incubation and incubation periods. Throughout the experiment's duration, to ensure desired MC was maintained, water losses in each container were recorded every other day. If needed, Milli-Q water was added to restore the original weight. During day 8 – 22, the laboratory was inaccessible. Thus, the MC in both "Dry-rewet" containers decreased substantially (55% for "Dry-rewet @ 15°C" and 63% for "Dry-rewet @ 25°C"). The lost weight was restored as per procedure above, prior to sampling on day 22.

To assess the degree of decomposition in all samples, OMC was determined using loss on ignition (LOI) following Rowell (1995), where a known portion of oven dried samples were finely ground, placed in dry crucibles and burned in a muffle furnace at a temperature of 550°C for 4 hours to determine ash content mass. This procedure was done in triplicates for "Dry-rewet" and "Moist-control" samples and occurred once at the beginning of the experiment and once at the end.

Table 4 – 1: Sampling events of the "Moist-control" and "Dry-rewet" samples throughout the experiment. OMC stands for Organic Matter Content, MC stands for Moisture Content. [SO_4^{2-}] stands for SO_4^{2-} concentration. Sample size (*n*) for pH was 2 for all treatments, while *n* for OMC and MC measurements was 3. Sample size for measurement of [SO_4^{2-}] was 3 for all treatments, except on day 50 and 64 where *n* was 2 for "Dry-rewet @ 15°C" samples.

Condition	Day of sampling in experiment	Parameter measured
Initial	0	pH, [SO_4^{2-}], OMC, MC
(pre-incubation) Drying only	7	MC
(pre-incubation) 24h after re-wetting	8	pH, [SO_4^{2-}], MC
Aeration treatment	22,36	pH, [SO_4^{2-}], MC
Inundation treatment	50,64	pH, [SO_4^{2-}], OMC, MC

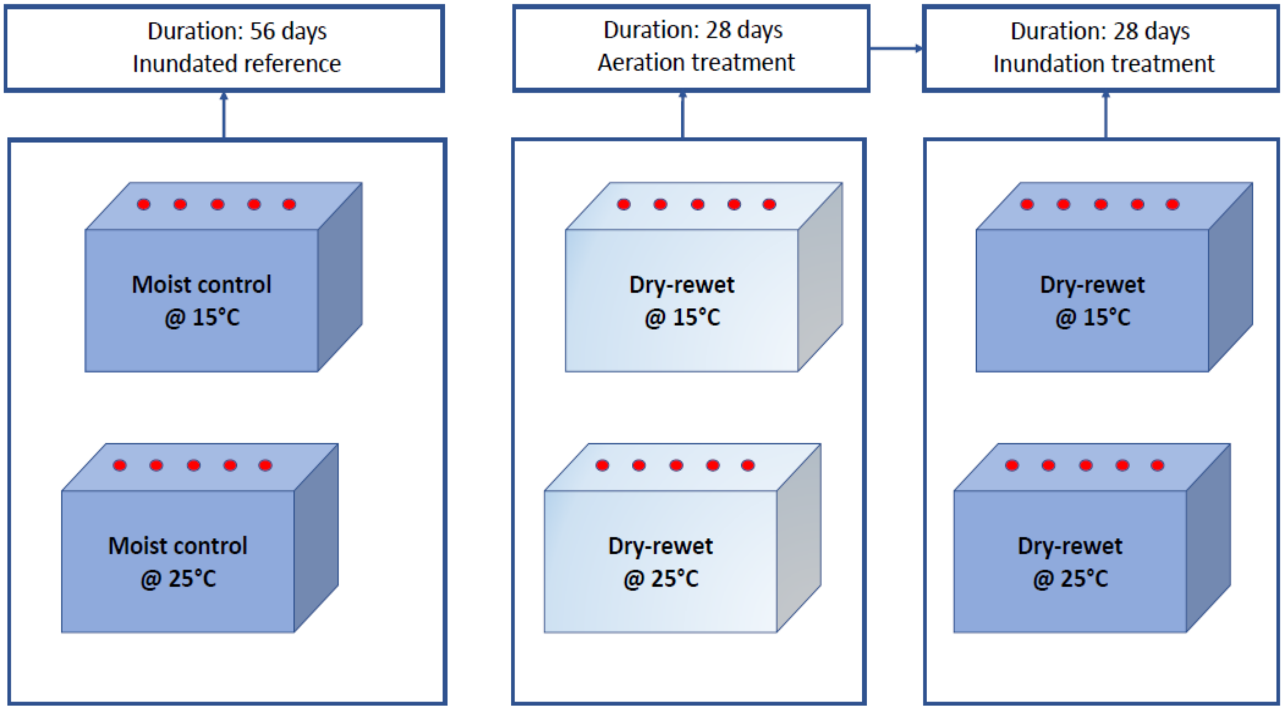

Figure 4 – 1: Experimental set-up of the peat drying and re-wetting incubation experiment.

4.4 Results

4.4.1 Effects of drying and re-wetting peat on pH

4.4.1.1 Pre-incubation

Background pH of peat cores used for “Moist control” and “Dry-rewet” samples were initially neutral and did not vary considerably (Figure 4 – 2a). At the end of the pre-incubation period (i.e. day 8), the “Moist control” samples showed a slight increase in pH. This effect was not seen after drying and re-wetting of the “Dry-rewet” peat cores. Here, the pH of both decreased considerably to reach ~6.4 on day 8, with a more apparent decrease (~0.6 units) in the “Dry-rewet @ 25°C” sample (Figure 4 – 2a).

4.4.1.2 Aeration and Inundation

At the end of the aeration treatment (i.e. day 36), the reference “Moist control @ 15°C” and “Moist control @ 25°C” samples did not experience any notable changes in pH, remaining near neutral for both. In contrast, persistent decreases in pH were observed in the “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” samples, both of which experienced the lowest pH values (pH < 6.4) throughout the entire duration of the experiment (day 22 and 36; Figure 4 – 2a).

The pH of both “Moist control” samples decreased over time throughout the inundation treatment, nearly reaching background pH (day 0) for “Moist control @ 25°C” at the end of the experiment, but not for “Moist-control @ 15°C”, which was ~0.2 units lower than background values. Increases in pH were seen for both “Dry-rewet” samples following inundation (Figure 4 – 2a), though more pronounced increase (~0.5 units) was observed for “Dry-rewet @ 15°C” on day 50. At the end of the experiment, “Dry-rewet @ 15°C” increased to higher pH than initial levels. This was not reflected in “Dry-rewet @ 25°C, where pH (6.6) was ~0.5 units lower than initial.

4.4.2 Effects of drying and re-wetting peat on sulfate availability

4.4.2.1 Pre-incubation

Background S-SO_4^{2-} concentrations for all peat cores did not vary substantially (Figure 4 – 2b). The “Moist control @ 15°C” and “Moist control @ 25°C” samples experienced a net retention of 17 and 44 mg kg^{-1} S-SO_4^{2-} at the end of the pre-incubation period on day 8, respectively. In contrast, the “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” samples had a net release of 16 and 57 mg kg^{-1} S-SO_4^{2-}, respectively (Figure 4 – 2b).

4.4.2.2 Aeration and Inundation

Throughout the aeration and inundation treatments, S-SO_4^{2-} concentrations in both of the “Dry-rewet” samples responded markedly to the different temperature and saturation conditions. In contrast, the reference “Moist-control” samples showed minor changes in concentrations, as there was no pronounced net retention/release of S-SO_4^{2-} from day 22-63 (Figure 4 – 2b).

Continuous aeration of both “Dry-rewet” samples showed distinct signatures of S-SO_4^{2-} release throughout the aeration treatment (i.e. day 8 – 36). At the end of the first half of the aeration treatment (i.e. on day 22), net release of S-SO_4^{2-} was 76 and 258 mg kg^{-1} in the “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” samples, respectively (Figure 4 – 2b). At the end of the aeration treatment (i.e. on day 36), net release of S-SO_4^{2-} was not shown as markedly as on day 22. Here, the “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” experienced a net release of 23 and 42 mg kg^{-1} S-SO_4^{2-}, respectively (Figure 4 – 2b).

Following inundation of the “Dry-rewet” samples, both experienced substantial net retention of S-SO_4^{2-} during the first half of the inundation treatment (i.e. day 50). Here, 126 and 319 mg kg^{-1} soluble S-SO_4^{2-} was removed from the peat in the “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” samples, respectively (Figure 4 – 2b). At the end of the experiment (i.e. day 64), both samples had near background S-SO_4^{2-} concentrations. However, unlike the first half of the inundation treatment, net retention of S-SO_4^{2-} was substantially lower in both “Dry-rewet @ 15°C” and “Dry-Rewet @ 25°C” samples, which experienced a decrease of only 0.5 and 31 mg kg^{-1} S-SO_4^{2-}, respectively (Figure 4 – 2b).

Organic matter content measured at the start of the pre-incubation and end of the incubation periods did not change notably (± 2%) in the “Moist-control” or in the “Dry-rewet” samples and remained roughly near ~90%.

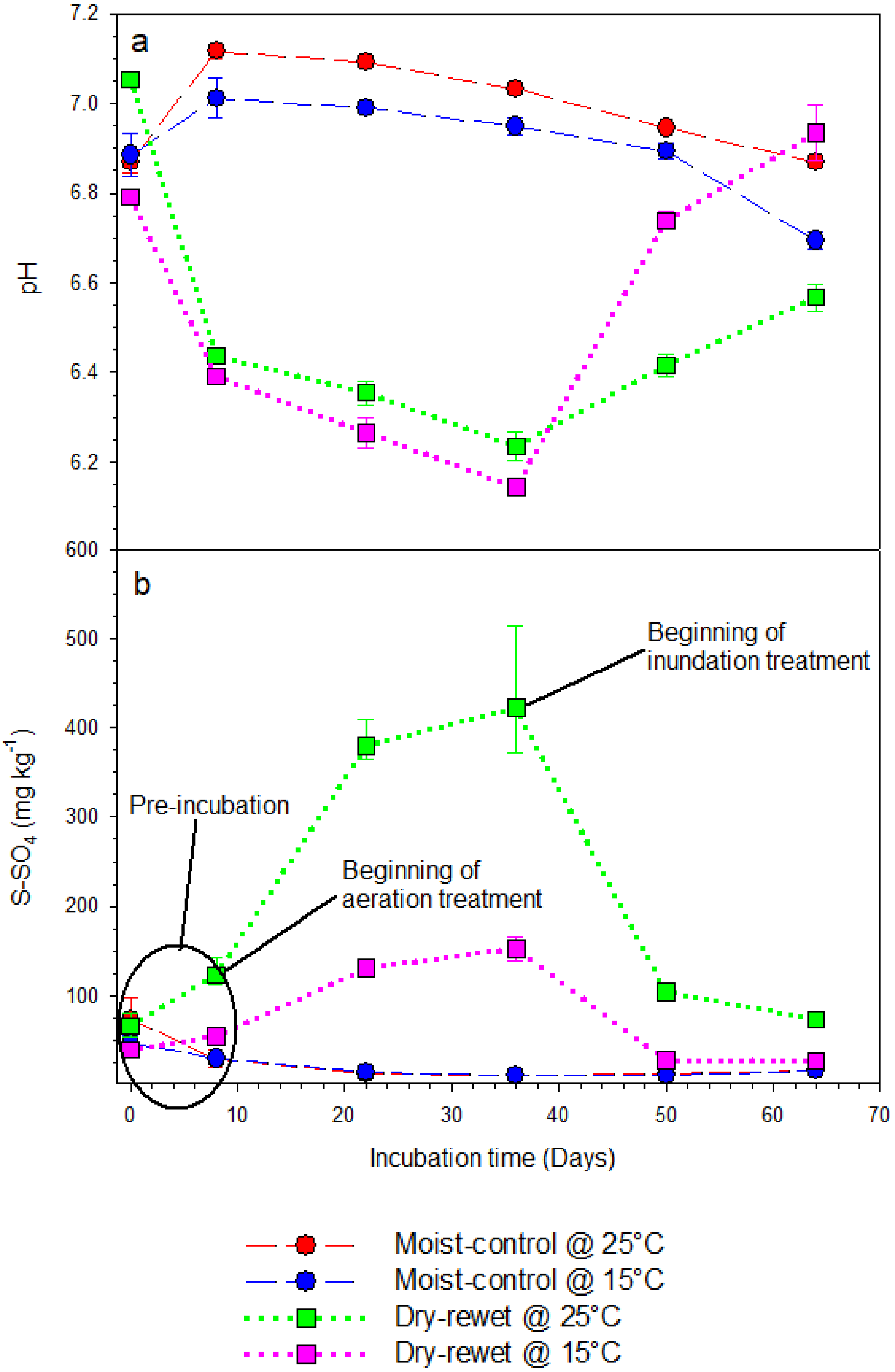

Figure 4 – 2: pH (a) and sulfate concentrations (b) of peat extracts for each treatment throughout the incubation experiment. Values were converted from mg L^{-1} to mg kg^{-1} to compare sulfate release/retention between sampling events. Whiskers on symbols represent max and min values.

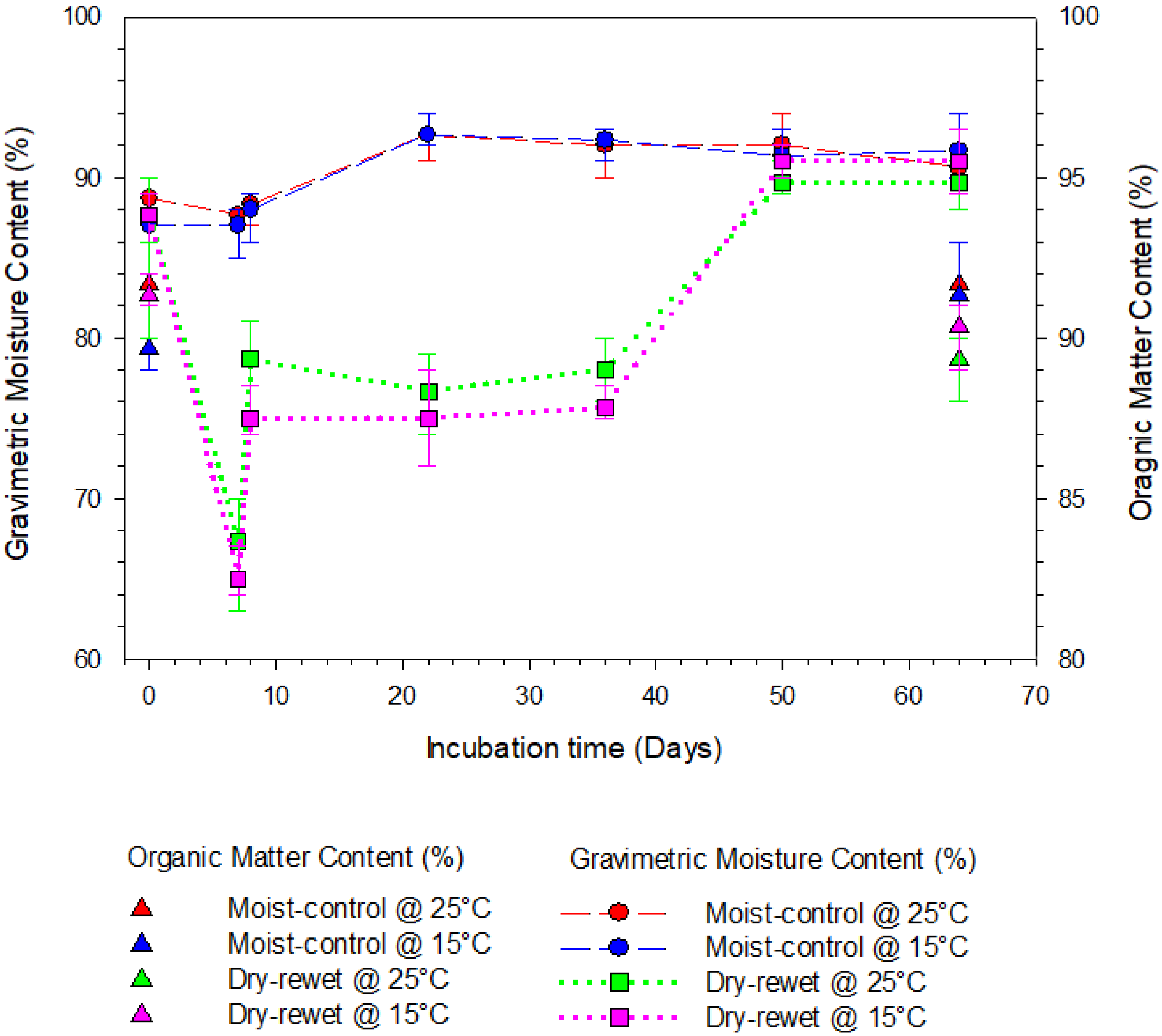

Figure 4 – 3: Gravimetric Moisture Content and Organic Matter Content of peat on each sampling event for all treatments. Day 0 – 8 represents the "pre-incubation" period. Day 8 – 36 represents the aeration treatment. Day 36-64 represents the inundation treatment. Note: secondary y-axis (right) is for organic matter content (triangle shapes). Whiskers on symbols represent maximum and minimum observed values.

4.5 Discussion

4.5.1 Elevated sulfate concentrations in donor peat

Simhayov *et al.* (2017) found elevated SO_4^{2-} concentrations, as high as ~200 mg L^{-1} ($n = 15$) when the donor fen peat was incubated under anaerobic conditions for 56 days. Although bacterial SO_4^{2-} reduction was expected in such conditions, there were no sharp decreases in SO_4^{2-} throughout their incubation experiment. This could have been due to their low incubation temperature (3°C) limiting the activity of SO_4^{2-} reducing bacteria (SRB; Spratt and Morgan, 1987; Wieder and Lang, 1988; Nedwell and Watson, 1995), and/or the availability of labile organic C compounds was low (Vile *et al.,* 2003b, Whitmire and Hamilton, 2005; Zak *et al.,* 2009; Schofl *et al.,* 2011). In our case, during time of collection of the peat cores in 2016, SO_4^{2-} concentrations were less than 10 mg L^{-1} in the pore water of surficial peat layers at Poplar Fen (M.Elmes, personal communication, 2017). Furthermore, background SO_4^{2-} concentrations of the peat cores used in this incubation study were comparable to pore water field values (Figure 4 – 2b).

4.5.2 The effects of drying and inundation of peat on pH and sulfate availability

4.5.2.1 Changes in pH

The decreases in pH following drying of the peat (Figure 4 – 2a) is likely due to the release of organic acids following enhanced decomposition (Glaser *et al.,* 2004; Dasgupta *et al.,* 2015), as well as oxidation of RIS compounds, such as FeS and/or FeS_2 (Lamers *et al.,* 1998b; Appleyard *et al.,* 2004; Sommer, 2006). After inundation of the peat, pH gradually increased in both "Dry-rewet" treatments (Figure 4 – 2a). The recovery of the pH may be attributed to the buffering capacity of the peat (Kida *et al.,* 2005). Organic matter is known to have acid neutralizing capacity, specifically carboxylic functional groups that bind H^+ following acidification (Magdoff and Bartlett, 1985; Krull *et al.,* 2004). Given that the OMC of the peat is ~90% (Figure 4 – 3), it seems a plausible scenario for the increase in pH (Sommer, 2006). Additionally, the recovery of anaerobic respiration processes, such as DSR (Wieder, 1985; Koretsky *et al.,* 2007), would have consumed H^+ ions and generated alkalinity (McLaughlin and Webster, 2010), resulting in higher pH (Sommer, 2006; Yuan *et al.,* 2015).

4.5.2.2 Changes in sulfate concentrations: Control treatment

Prior to inundation of the "Moist-control" samples, when they were stored at 4°C during the pre-incubation period, both experienced decreases in S-SO_4^{2-} concentrations on day 8 (Figure 4 – 2b). Although a more pronounced trend was observed in the peat that was used for the "Moist-control @ 25°C" treatment, both decreased to roughly ~30 mg kg^{-1} S-SO_4^{2-} on day 8. This finding suggests that some microbial immobilization occurred (Brown, 1986; Eimers *et al.,* 2003). On day 22, the subsequent decrease of S-SO_4^{2-} to ~15 mg kg^{-1} in both treatments is indicative of SO_4^{2-} reduction, as inundation of the peat would have introduced redox conditions required for SO_4^{2-} reducing bacteria to become active (Brown, 1985; Knorr and Blodau, 2009; Knorr *et al.,* 2009). The negligible changes in S-SO_4^{2-} concentrations of the peat thereafter indicates that there was neither net release or retention of SO_4^{2-} (Figure 4 – 2b). Similarly, Eimers *et al.* (2003) found that S-SO_4^{2-} concentrations in incubated field moist peat were comparable to background concentrations after a period of 30 days. This finding is not surprising given that inundation of the "Moist-control" samples was meant to simulate pristine peatland conditions (i.e. water table at the surface). In peatlands, SO_4^{2-} is retained under saturated and anaerobic conditions due to DSR (Bayley *et al.,* 1986; Urban *et al.,* 1989, Moore *et al.,* 2004), thereby decreasing the concentrations of dissolved SO_4^{2-} until the activity of SRB is diminished due to the absence of required SO_4^{2-} pools or lack of labile substrates (Vile *et al.,* 2003a, b).

4.5.2.3 Changes in sulfate concentrations: Aeration treatment

It was hypothesized that drying and re-wetting of peat would increase SO_4^{2-} concentrations under aerobic conditions. Indeed, this was clear throughout the aeration treatment of the incubation experiment. For example, on day 36, measured average S-SO_4^{2-} concentrations of peat in "Dry-rewet @ 25°C" and "Dry-rewet @ 15°C" samples were approximately 420 and 150 mg kg^{-1}, respectively, in comparison with ~20 mg kg^{-1} in both "Moist-control" samples (Figure 4 – 2b), indicating that aeration of the peat resulted in a release of SO_4^{2-}. The increases are attributed to oxidation of RIS compounds (such as FeS and FeS_2) and/or mineralization of organic S (Bayley *et al.,* 1986; Devito and Hill, 1999; Eimers *et al.,* 2003; Zak and Gelbrecht, 2007; Maassen *et al.,* 2015; Vermaat *et al.,* 2016). The experiment does not distinguish the extent to which the two processes serve as sources of SO_4^{2-} in the peat; RIS fractions, organic S fractions, and Fe species were not measured throughout the experiment. Additionally, the concentrations of dissolved Fe at Poplar Fen are unknown. Other studies have found oxidation of both RIS and/or organic S fractions in peat contributed to SO_4^{2-} release following drying and re-wetting cycles. For example, Estop-Aragonés *et al.* (2013) found that SO_4^{2-} release following drying and re-wetting of minetrophic fen peat was influenced by RIS content, part of which was FeS. In contrast, Coleman-Wasik *et al.* (2015) ascribed SO_4^{2-} release to mineralization of carbon bound S (CBS) instead of oxidation of RIS, following drying and re-wetting in an experimental peatland. Carbon bonded S is known to be the main pool of total S in peat soils, comprising >80% (Wieder and Lang, 1988, Novak and Wieder, 1992). The ester-SO_4^{2-} fraction comprises much less of the total S pool and is known to be an important contributor of SO_4^{2-} only under SO_4^{2-} limiting conditions in peatlands (Jarvis *et al.,* 1987); its hydrolysis becomes inhibited under an abundant supply of SO_4^{2-} (Wieder *et al.,* 1987). Therefore, ester SO_4^{2-} mineralization (if any) was probably only of importance during the pre-incubation period, when SO_4^{2-} concentrations were lowest before the aeration treatment (Figure 4 – 2b). Regardless of the source, the release of SO_4^{2-} following drying and re-wetting of peat agrees with other studies (Eimers *et al.,* 2003; Sommer, 2006; Goldhammer and Blodau, 2008; Reiche *et al.,* 2009; Whitfield *et al.,* 2010).

Average S-SO_4^{2-} concentration of peat on day 22 was nearly 2.4 and 3 times higher than that on day 8, for “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” samples, respectively. This pronounced increase occurred due to the additional, and more intensive drying during this period, which resulted in MC dropping below desired value (see section 4.3.3). This finding suggests that alternate drying and re-wetting cycles can manifest in increased SO_4^{2-} concentrations (Germida *et al.,* 1992), and that drying intensity may have a control on the generation of SO_4^{2-}, in agreement the findings of Estop-Aragonés *et al.* (2013). Additionally, given that the net release of S-SO_4^{2-} in “Dry-rewet @ 25°C” treatment was substantially higher than in “Dry-rewet @ 15°C”, temperature may have had a control on SO_4^{2-} release during this period (Figure 4 – 2b). However, on day 36, although higher net S-SO_4^{2-} release was again observed in the warmer treatment, only 23 and 42 mg kg^{-1} S-SO_4 was released from peat in “Dry-rewet @ 15°C” and “Dry-rewet @ 25°C” (Figure

4 – 2b), respectively. This suggests that the readily oxidizable pool of S may have already diminished during the first half of the aeration treatment, where most intensive drying oxidized labile organic S as well as RIS compounds, and that more recalcitrant S remained which takes longer to break down by microbial activity (Coleman-Wasik *et al.,* 2015). Alternatively, if there was a more apparent temperature sensitivity from day 22-36, it may have been obscured by the microbial assimilation of SO_4^{2-} to form organic S (Brown, 1986). Eimers *et al.* (2003) reported a release of SO_4^{2-} following 24 hours of re-wetting peat that was previously dried for a week, and observed slightly larger increases thereafter when the peat was aerobically incubated at 25°C, in comparison with peat at incubated at 18°C. However, their study had multiple sampling events throughout the aerobic incubation, which was not the case in this study. As such, they observed more apparent temperature dependent SO_4^{2-} release. Ultimately, however, they determined that drying of peat was quantitatively the main mechanism in the production of SO_4^{2-} (Eimers *et al.,* 2003). Similarly, this study's findings are consistent with their conclusion. Finally, it is worth noting that the limited temperature range (10°C) tested here may not have been large enough to clearly elucidate temperature induced release. This means that, perhaps, temperature sensitivity would have been more pronounced if more extreme temperatures were chosen (e.g. 5°C and 30°C). Generally, increased temperature is known to stimulate aerobic decomposition of soil organic matter (Davidson and Janssens, 2006). Devito and Hill (1999a) did not find a significant relationship between surface peat temperature and net SO_4^{2-} production in a southern Ontario swamp. However, their study was conducted in the field, where water table fluctuations occurred. The authors proposed that both mineralization of organic S and DSR were possibly stimulated by temperature. Ultimately, they determined that water table elevation controlled which process was dominant. In their case, when the water table was stable at the surface; DSR would retain SO_4^{2-} that was previously produced from the peat during drought periods, resulting in an overall net immobilization of SO_4^{2-} (Devito and Hill, 1999a). Given that our study was in a controlled environment, the peat was not submerged during the aeration treatment at any point. Thus, mineralization of organic S would have been a more dominant process than DSR, since the latter would not be favored to occur in oxic conditions.

Aside from Eimers *et al.* (2003), we are not aware of any studies that tested the aerobic mineralization of organic S from peat soils under different temperatures, specifically at "extreme" ranges. Nonetheless, given that mineralization of CBS to inorganic S is controlled by microbially driven decomposition of the peat, presumably increased mineralization rates of organic S would be expected under warmer temperatures (Reddy and DeLaune, 2008).

4.5.2.4 Changes in sulfate concentrations: Inundation treatment

The decreases in S-SO_4^{2-} concentrations during the inundation treatment are indicative of DSR, a C mineralization process known to occur in anaerobic soils (Reddy and DeLaune, 2008), and numerous studies have provided evidence of its occurrence in peat incubation experiments (Vile *et al.*, 2003a; Blodau *et al.*, 2007; Goldhammer and Blodau, 2008; Knorr and Blodau, 2009). The steep declines observed during the first half of the inundation treatment (i.e. day 36-50) were not surprising, given that an abundant supply of formerly generated SO_4^{2-} was available for SRB to utilize. Vile *et al.* (2003a) found that rates of SO_4^{2-} reduction in an Alberta bog peatland were lower in comparison to 2 bogs in Czech Republic, owing to the latter receiving much higher atmospheric deposition of S. Similarly, in an incubation study, Goldhammer and Blodau (2008) found that upon drying and re-wetting of bog peat, rates of SO_4^{2-} reduction immediately increased and suppressed methanogenesis due to re-generation of SO_4^{2-}. Although we did not measure SO_4^{2-} reduction rates in our experiment, S-SO_4^{2-} concentrations in peat for both “Dry-rewet” samples were substantially higher than that in peat for the “Moist-control” samples on day 36, which experienced negligible changes in S-SO_4^{2-} concentrations on day 50, in comparison with the rapid consumption observed for “Dry-rewet” (Figure 4 – 2b). This suggests that the production of SO_4^{2-} in the peat likely stimulated SO_4^{2-} reduction in both “Dry-rewet” samples. Thus, our findings are consistent with previous research, in that reintroducing saturated conditions to previously aerated peat results in redox conditions that stimulate the activity of SRB, and subsequent recovery of DSR (Knorr *et al.*, 2009).

Although net S-SO_4^{2-} retention was again observed in both “Dry-rewet” samples at the end of the experiment, only a decrease of 0.5 mg kg^{-1} of S-SO_4^{2-} was observed in “Dry-rewet @ 15°C”, compared to 31 mg kg^{-1} in “Dry-rewet @ 25°C” (Figure 4 – 2b). This suggests that a threshold to the SO_4^{2-} reduction reaction was reached, and the process may have been limited by some factor(s), especially in the “Dry-rewet @ 15°C” treatment. While previous studies have proposed that low

SO_4^{2-} availability limits SO_4^{2-} reduction rates in peat (e.g. Duddleston *et al.,* 2002; Vile *et al.*, 2003b), that may not be the scenario in this study, specifically in the "Dry-rewet" treatments. For example, in the "Moist-control" treatments, S-SO_4^{2-} concentrations in peat decreased (day 22) after inundation of the samples (Figure 4 – 2b), presumably due to SO_4^{2-} reduction. Prior to inundation of the "Moist-control" samples, average S-SO_4^{2-} concentration in peat from each was ~30 mg kg^{-1}. This concentration is roughly the same as that in peat from "Dry-rewet @ 15°C" on day 50, yet virtually no decrease in S-SO_4^{2-} from peat in "Dry-rewet @ 15°C" was seen on day 64 (Figure 4 – 2b). This indicates that peat in the "Dry-rewet" samples became limited by a factor other than SO_4^{2-} availability.

Dissimilatory SO_4^{2-} reduction is known to be a temperature sensitive process, provided that SO_4^{2-} availability and labile C compounds are not limiting factors (Wieder *et al.,* 1990). Due to the resolution of this experiment, however, it is not possible to confirm if temperature stimulated SO_4^{2-} reduction during the inundation treatment. This is because at the beginning of the treatment, initial S-SO_4^{2-} concentrations in peat in "Dry-rewet @ 25°C" were roughly 3 times higher than that in "Dry-rewet @ 15°C" (Figure 4 – 2b), and S-SO_4^{2-} concentrations were only measured twice throughout the inundation treatment of the "Dry-rewet" samples. Additionally, it is likely that that the temperatures tested here could have contributed to what appeared to be a lack of response of SO_4^{2-} reduction to changes in temperature. Wieder and Lang (1988) showed that incubated surficial peat at 26°C experienced significantly higher SO_4^{2-} reduction rates than at 4°C, and this response of SO_4^{2-} reduction to temperature extremes has also been elsewhere in peatlands (e.g. Spratt and Morgan, 1990; Nedwell and Watson, 1995). Groscheova *et al.* (2000) tested SO_4^{2-} reduction in peat at 15°C in a 44-day incubation experiment. They found that porewater SO_4^{2-} concentrations decreased rapidly after 8 days, but the declines slightly plateaued for the remainder of their experiment's duration. Two key scenarios can be noted from their observations. First, 15°C was an adequate temperature for SRB. Second, SO_4^{2-} reduction became limited by a factor other than temperature, possibly labile C substrates and/or SO_4^{2-} availability. In our case, given that SO_4^{2-} availability was unlikely to be limiting in the 15°C "Dry-rewet" samples (as previously alluded), and that the 15°C treatment should have been sufficient for SO_4^{2-} reducing bacteria (Groscheova *et al.*, 2000), labile C may have a had a control on DSR, and to a lesser extent on the 25°C treatment. Although peat is organic C, the pool of labile C is comparatively smaller (Updegraff *et al.*, 1995; Bridgham *et al.*, 1998), which progressively diminishes in respiratory reactions carried out by various microbial communities. To that end, several studies that have examined S cycling in peatlands have shown that an abundance of SO_4^{2-} did not necessarily stimulate SO_4^{2-} reduction. Vile *et al.* (2003b) conducted a study in which bog peat was amended with SO_4^{2-} to resemble elevated atmospheric deposition, and found that relative to control treatments, the SO_4^{2-} pool increased yet SO_4^{2-} reduction rates did not, partially due to a short supply of labile C substrates. Mitchell *et al.* (2008b) studied the effect of stimulating SO_4^{2-} availability on methylmercury (MeHg) concentrations in a peat bog using an in-situ mesocosm approach; MeHg production is known to be evidence of SO_4^{2-} reduction (Branfireun *et al.*, 1999, Mitchell *et al.*, 2008a). They showed that addition of two separate SO_4^{2-} treatments (4 times and 10 times the annual atmospheric deposition of SO_4^{2-}) increased MeHg production, however the difference in MeHg production between treatments did not appear to be statistically significant. Additionally, they found that the addition of SO_4^{2-} alone resulted in considerably less MeHg production than the addition of SO_4^{2-} accompanied with labile organic C. Based on these observations, they proposed that if there is abundant SO_4^{2-} in the porewater, such that SRB are not limited by its availability, it is the quality and quantity of labile C that may regulate the reduction of SO_4^{2-}, and in turn the production of MeHg. Caution, however, must be taken when comparing the results of our experiment to the aforementioned studies, as the local geochemical conditions were not the same. Such case is worth mentioning since the peat in this study was dried for a period of 28 days prior to inundation. As such, it is conceivable that during this period, aerobic respiration oxidized labile C and depleted its pool in the process (Keller and Bridgham, 2007). After inundation, the resultant limited and readily degradable substrates for SO_4^{2-} reducing bacteria were quickly consumed during the first half of the inundation treatment (day 36-50). Notwithstanding, the results of this experiment are consistent with those in other studies; SO_4^{2-} reduction eventually becomes limited by labile C, even when SRB are not limited by SO_4^{2-} availability.

4.5.3 Implications for constructed fens in the AOSR

The aim of this study was to simulate the management practices of the donor peat used in constructing Nikanotee Fen and evaluate attendant impacts on SO_4^{2-} availability. The results provide contribution into better understanding how S biogeochemistry may be altered following the prolonged drainage of a donor fen, extraction of the peat, and subsequent random placement and inundation on a newly constructed fen landscape. However, the findings of this study must be further contextualized at the field scale, especially since biogeochemical and hydrological conditions are not necessarily the same as those in a controlled environment.

In a drained peatland setting, the portion of the peat profile that is constrained to oxic conditions results in enhanced mineralization of organic S, as well as oxidation of RIS compounds in the peat. Thus, SO_4^{2-} is progressively released from the peat. However, water inputs (i.e. from precipitation and/or run-off) would cause downward leaching of the produced SO_4^{2-}, such that elevated SO_4^{2-} concentrations would be present in the bottom portion of the peat profile. This flushing phenomenon was also described by Zak and Gelbrecht (2007). They found evidence of elevated SO_4^{2-} concentrations in incubated slightly decomposed fen peat that had experienced little to no drainage activity but was overlain by a highly decomposed layer of peat that was consistently oxidized due to drainage. Later on, when peat from a donor fen is extracted and placed on a constructed landscape, the random placement of the peat may contribute to spatially variable pore water concentrations of SO_4^{2-}. However, depending on the availability of labile C, this pool of SO_4^{2-} in the peat may be short-lived due to the recovery of SO_4^{2-} reduction. If labile C supply is abundant, unless there are groundwater inputs rich in SO_4^{2-} from adjacent upland features as is the case in Nikanotee Fen, or frequent water table drawdowns that oxidize RIS in the peat, then pore water SO_4^{2-} concentrations will likely progressively decrease in constructed fens. In natural peatlands, labile organic C is found near the surface of the peat profile, whereby deeper and older peat is of more recalcitrant C (Hogg *et al.*, 1992). For this reason, SO_4^{2-} reduction is typically highest near the surface, and declines with depth (Wieder and Lang, 1988; Novák and Wieder, 1992, Bergman *et al.*, 2012). In the case of constructed fen landscapes, however, prolonged drainage of a donor fen would stimulate aerobic decomposition of the exposed donor peat and leave behind recalcitrant residues and attendant poor organic matter quality of peat (Nwaishi *et* *al.,* 2015 & 2016a; Kononen *et al.,* 2016; Urbanova *et al.,* 2018), which may not be favorable to immediately resume anaerobic respiration processes such as DSR (Zak *et al.,* 2009, Hahn-Schofl *et al.,* 2011). Following inundation of reclaimed fen landscapes and the establishment of vegetation (Glatzel *et al.,* 2004), inputs of fresh labile C from root exudates and litter (Strack *et al.,* 2015; Jauhiainen *et al.,* 2016), would reactivate microbially mediated processes (Nwaishi *et al.,* 2016a), such as SO_4^{2-} reduction (Hahn-Schofl *et al.,* 2011). Ultimately, depending on the rate of SO_4^{2-} reduction, methane emissions would be suppressed (Dise and Verry, 2001; Gauci *et al.,* 2002), but at the expense of potentially degrading peat accumulation in constructed fens (Wieder *et al.,* 1990), which may not be a targeted goal.

4.6 Conclusion

Incubated dried and re-wet peat under aerobic and inundated conditions resulted in marked responses of S-SO_4^{2-} availability. Sulfate release was evident immediately after drying and re-wetting of peat, and further enhanced when peat was incubated under aerobic conditions at 15°C and 25°C incubation temperatures. Drying was the main mechanism controlling S-SO_4^{2-} release due to oxidation of RIS as well as mineralization of organic S, as sensitivity of S-SO_4^{2-} release to the tested temperatures was not comparatively pronounced. Inundation of the dried and re-wet peat caused an initial substantial decrease in S-SO_4^{2-} concentrations due to SO_4^{2-} reduction occurring in both treatments, but this was less pronounced thereafter, possibly due to limitation by labile C compounds. Sulfate reduction sensitivity to the tested temperatures was not apparent.

This study provided insight into how S biogeochemistry may be altered following current donor peat management practices used in the construction of fen landscapes in the AOSR. Following drainage of donor peatlands, the aerated peat becomes a source of SO_4^{2-}. After extraction of the donor peat, placement on a constructed fen landscape and re-introduction of anaerobic conditions, elevated pore water SO_4^{2-} concentrations inherent of the peat would gradually decline as long as labile C is not limiting. However, if reclamation construction material contaminated with legacy salt constituents are incorporated into fen designs, then SO_4^{2-} will no longer be limiting, and DSR may be a dominant anaerobic C mineralization process dependent on the residence time of SO_4^{2-} in the pore water and the supply of labile substrates. Further research should focus on determining the roles of RIS and organic S pools in contributing to SO_4^{2-} release in AOSR fen peat following drying. Additionally, incubation experiments attempting to investigate the sensitivity of organic S mineralization and SO_4^{2-} reduction to temperature should be tested at a higher range of temperatures (e.g. 5°C and 30°C).

5. Thesis summary

5.1 Summary and recommendations

This research provided an assessment of the sources of SO_4^{2-} and hydrogeochemical controls on its dissolved pool in Nikanotee Fen. Specifically, the findings of this study provided an understanding as to how the use of accessible reclamation material may influence pore water SO_4^{2-} availability and distribution in constructed fen landscapes. These findings are helpful in providing a general baseline for future fen reclamation projects that may mimic the design of Nikanotee Fen, and more generally, for the use of peat as a reclamation material.

Chapter 3 investigated the sources of SO_4^{2-} within Nikanotee Fen Watershed and explored hydrogeochemical controls on its dissolved pool within the system. The reclaimed hillslopes experienced elevated pore water SO_4^{2-} concentrations, but generated surface runoff, which recharges the upland aquifer, was diluted along the flow path. In turn, this caused decreases in SO_4^{2-} concentrations in the pore water of the upland aquifer. It was unlikely that SO_4^{2-} reduction, in appreciable magnitude, was occurring in the upland aquifer or the petroleum coke underdrain as they were previously shown to be very poor sources of labile C (Khadka *et al.,* 2015). This was supported by $Ca:SO_4$ ratios that were virtually always below 1, with an excess of SO_4^{2-} over Ca^{2+} especially in the eastern region of the upland aquifer. Aside from SO_4^{2-} derived from legacy gypsum in oil sand process affected water, that was in contact with the sand prior to its placement on the constructed system, this finding rather reflected the marine origin of the sand, which likely contributed to the excess SO_4^{2-} in the upland aquifer. In the fen, SO_4^{2-} concentrations in the peat deposit were unexpectedly substantially higher than in the underlying coke underdrain in 2013. In addition to SO_4^{2-} originating via transport from the upland aquifer, it was proposed that the drainage of the donor fen peatland may have led to this confounding source of SO_4^{2-}. In the subsequent years, geochemical evidence showed that a sink for SO_4^{2-}, likely SO_4^{2-} reduction, existed in the peat deposit. It is recommended that future research is required to better understand SO_4^{2-} reduction in Nikanotee fen. Specifically, analyses of S isotopes, measurement of RIS pools, *in-situ* mineral phase analyses, and measurement of dissolved sulfide (with standard preservation techniques) can help address the uncertainties gathered from this research. Additionally, it is important to understand the dynamics of SO_4^{2-} reduction. For example, what is the rate of SO_4^{2-} reduction? What is the fate of the produced sulfide? Are metals leached from the petroleum coke being sequestered as sulfides in the peat layer? Addressing such questions would help assess the trajectory of the overall biogeochemical functioning of Nikanotee Fen, with respect to anaerobic C mineralization pathways and attendant impacts on C cycling.

Chapter 4 simulated the donor peat management practices, as it was hypothesized in Chapter 3 they likely have contributed to the elevated soluble S pool within the peat layer of Nikanotee Fen in the initial year. Results in this chapter showed that $S\text{-}SO_4^{2-}$ was immediately released following drying and re-wetting of peat. This release was more pronounced during subsequent aerobic incubation of the dried peat at 15 and 25°C, owing to more extensive drying rather than temperature sensitivity (due to the limited range in temperature tested). The $S\text{-}SO_4^{2-}$ likely originated from a combination of both "true" mineralization of organic S, and oxidation of RIS pools (Eimers *et al.,* 2003, Maassen *et al.,* 2015; Vermaat *et al.,* 2016). Inundation of the dried and re-wet peat caused an initial substantial decrease in $S\text{-}SO_4^{2-}$ concentrations at both incubation temperatures, and again temperature sensitivity was not apparent. This decrease was most likely due to SO_4^{2-} reduction occurring. However, a threshold was reached at the end of the experiment; SO_4^{2-} reduction possibly became limited by labile C, despite the apparent abundance of SO_4^{2-} for SRB. This study showed that the aeration of formerly anoxic peat results in a release of $SO_4^{2-}$and subsequent inundation of the peat would result in a retention of SO_4^{2-}. It is important to note that the duration of the experiment conducted in this study was short, in comparison to prolonged drainage of donor fens as a current practice for constructing fen landscapes. After the depletion of RIS pools during initial drainage phase, microbial activity begins to break down the more recalcitrant organic S compounds, which require longer periods of time to mineralize to SO_4^{2-}. This effect was likely present in the incubation experiment, in which during the first 2 weeks of the aerobic incubation a maximum of ~260 mg kg^{-1} of $S\text{-}SO_4^{2-}$ was released, comparatively higher than during the latter half of the incubation period, in which only a maximum of ~40 mg kg^{-1} of $S\text{-}SO_4^{2-}$ was released. Additionally, with respect to SO_4^{2-} retention via SO_4^{2-} reduction, it is worth noting that prolonged drainage of a donor fen would degrade labile C in the peat, and predominantly leave behind recalcitrant residues (Urbanova *et al.*, 2018). Following stripping and extracting of such peat, SO_4^{2-} reduction is unlikely to recover until vegetation is re-established to provide fresh C inputs that SRB can use (Hahn-Schofl *et al.*, 2011). This was partly observed in this experiment, as net SO_4^{2-} retention was observed to be negligible at the end of the experiment despite SO_4^{2-} seemingly being abundant for the activity of SRB. It is recommended that future reclamation projects consider reducing the time frame between drainage, extraction and harvesting of the peat, potentially limiting elevated SO_4^{2-} concentrations that may be mobilized from the peat upon placement on a new landscape. Additional research is required to expand onto the findings of this study. For example, it is important to distinguish between oxidation of RIS and mineralization of organic S in contributing to the overall soluble S pool of the peat under aerobic conditions, and to explore the fate of the produced sulfide after inundation of AOSR fen peat.

5.2 Project limitations

5.2.1 Water sampling

There are some possible sources of error that should be recognized with respect to water sampling in the field. Firstly, there is some concern that sulfide, in aqueous form, may have oxidized to SO_4^{2-} during *in-situ* sampling of water drawn from the anaerobic regions of the system, and during storage/analysis thereafter. Thus, this would yield inaccurate results. Although sulfide was not measured since no preservation of water samples was done, the magnitude of this effect is unlikely to be substantial to influence results and interpretations, at least in this particular study. A more in-depth discussion in this regard is included in Appendix B.

The collection of water samples from the Nikanotee fen-upland system followed standard water quality monitoring procedures. However, it is recognized that a larger potential error is associated with a monitoring network that may have underrepresented the true distribution of SO_4^{2-} in the system's layers, specifically in the upland tailings sand. Samples there were collected from fully slotted wells, which means that repeated samples were not necessarily drawn from the same layer, since it depends on the saturated thickness, which varies in time (Kessel *et al.*, 2018).

5.2.2 Incubation experiment

In the laboratory simulation study, one of the incubators used showed ±2°C fluctuation in temperature readings, which may have affected the production of SO_4^{2-}. This problem was probably due to the incubator being an older machine, but it is unlikely that it would have significantly altered results of the experiment. The analytical accuracy was satisfactory. Perhaps the biggest source of error that must be addressed is the heterogeneity in sampling of the peat during the aeration and inundation treatments. For instance, some of the peat at the top of the container that was analyzed throughout the aeration treatment may have oxidized more than peat at the bottom of the container, thus potentially leading to variability in SO_4^{2-} concentrations. However, this was the intent of homogenization of the samples prior to sampling. Moreover, the triplicate sampling procedure, for the most part, showed that analyzed SO_4^{2-} concentrations for each treatment during all sampling events did not have large variations.

As previously stated, the calculated MC values are based on sub-samples in each container. Therefore, it is likely that the measured MC for peat during a sampling event was slightly different than the peat that was actually analyzed for SO_4^{2-}, which would cause error in conversions of IC data to mg kg^{-1}, although it is unlikely that this effect was large.

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Appendix A: Chemical composition of Nikanotee fen-upland system (2013-2016)

Table A-1: Pore water concentrations of major cations and anions within the western region of the upland. Upper wells are located furthest south in the upland, while lower wells are closest to the transition zone (Figure 3 – 1). All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4$$^{2-}$	HCO$_3$$^-$
28-May-13	**West_Upper**	6.5	3488	17.8	681	17.2	104	314	102	2090	N/A
14-Jun-13	**West_Upper**	6.56	3324	16.1	590	20.4	26.2	308	150	80	N/A
26-Jul-13	**West_Upper**	6.6	2816	18	223	12.4	30	164	106	906	N/A
18-Aug-13	**West_Upper**	6.39	2753	20.3	264	14.2	34.1	166	80.4	947	N/A
18-Oct-13	**West_Upper**	2.22	3623	9.8	380	27.3	81.7	346	69.2	981	N/A
10-Jun-14	**West_Upper**	6.55	2722	14.6	202	34.3	7.74	57.4	42.8	493	N/A
20-Jun-14	**West_Upper**	7.59	2740	15.1	238	36.5	10.1	68.8	38.1	654	N/A
5-Jul-14	**West_Upper**	6.6	2600	16.3	589	31.3	124	158	83	1160	N/A
25-Jul-14	**West_Upper**	7.33	2785	17.8	234	14	43.3	58.6	25.5	574	N/A
8-Aug-14	**West_Upper**	6.76	3015	20.3	108	14.6	28.4	98.5	35.3	598	N/A
14-Aug-14	**West_Upper**	6.59	2998	23.4	188	20	46	94.6	32.1	664	N/A
9-Jun-15	**West_Upper**	N/A	2652	17.7	137	10.7	40.73	168.4	10.87	604.2	N/A
30-Jun-15	**West_Upper**	7.37	2677	15.2	274	22.8	82.35	195.3	17.96	1178	N/A
30-Jun-15	**West_Lower**	6.96	2604	17.5	231	18.2	74.03	254.7	32.56	1018	N/A
16-Jul-15	**West_Upper**	N/A	2643	21.1	240	22	82.97	280.8	17.3	1174	N/A
16-Jul-15	**West_Lower**	N/A	2246	21.4	197	16.9	65.65	239.1	29.1	887.1	N/A
31-Jul-15	**West_Upper**	6.78	2752	18.2	235	24.9	85.63	294.5	20.31	1208	N/A
31-Jul-15	**West_Lower**	6.46	2645	19.4	248	17.9	76.5	280.5	36.29	1050	N/A
14-Aug-15	**West_Upper**	6.97	2543	20.7	203	21.4	72.74	264.9	19.85	1036	N/A
14-Aug-15	**West_Lower**	6.66	2678	17.8	221	16.9	80.14	300.2	31.54	1012	N/A
4-Oct-15	**West_Upper**	N/A	2357	8.7	205	17.6	61.85	244.5	14.12	884.8	N/A
1-Jul-16	**West_Upper**	N/A	N/A	N/A	79.3	22.9	106.1	366.2	5.617	817.5	216
17-Aug-16	**West_Upper**	6.79	4262	10.6	27.9	1.64	57.37	477.7	2.673	1001	176
17-Aug-16	**West_Lower**	6.77	3124	11.7	146	16.5	67.43	227.5	19.19	760	343

Table A-2: Pore water concentrations of major cations and anions within the eastern region of the upland. Upper wells are located furthest south in the upland, while lower wells are closest to the transition zone (Figure 3 – 1). All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
28-May-13	**East_Upper**	4.64	3344	24.6	310	3.5	109	444	47.2	3410	N/A
14-Jun-13	**East_Upper**	5.66	3241	21.4	429	15.1	41.2	469	50.2	2186	N/A
26-Jul-13	**East_Upper**	5.34	4182	18.8	218	11.8	83	419	56	1950	N/A
18-Aug-13	**East_Upper**	5.58	4088	21.1	176	10.3	61.9	246	47.4	2440	N/A
18-Oct-13	**East_Upper**	5.47	4095	8.9	279	20	99	490	55.8	2280	N/A
10-Jun-14	**East_Upper**	6.06	2729	14.4	125	64.1	10.7	90.2	34.7	808	N/A
20-Jun-14	**East_Upper**	6.95	2502	13.9	24.7	8.86	0.57	54.6	3.79	325	N/A
5-Jul-14	**East_Upper**	6	1842	17.7	60.6	6.1	31.1	134	8.25	700	N/A
25-Jul-14	**East_Upper**	6.8	2314	17.9	77.5	7.5	23.4	74.9	17.1	413	N/A
8-Aug-14	**East_Upper**	6.42	3006	20.4	57.7	11.1	26	83.4	19.6	507	N/A
8-Aug-14	**East_Lower**	6.42	2762	19.7	93.6	9.86	21	83.4	21.4	495	N/A
14-Aug-14	**East_Upper**	5.94	2209	22.9	65.2	11.5	27.2	91	22	671	N/A
14-Aug-14	**East_Lower**	6.46	2858	22.4	200	19.1	37.32	83.6	15.2	733	N/A
4-Oct-14	**East_Upper**	6.09	2767	9.1	127	8.8	25.5	69.6	42.2	556	N/A
4-Oct-14	**East_Lower**	6.2	3200	9.4	95.5	8.37	24.3	56.2	22.2	423	N/A
9-Jun-15	**East_Upper**	N/A	2265	16.3	193	19.2	55.52	252.1	18	1097	N/A
30-Jun-15	**East_Upper**	6.52	2264	14.3	140	12.4	65.73	198.8	13.8	708.5	N/A
30-Jun-15	**East_Lower**	7.45	3739	14.2	257	21.5	144.7	471.8	48.2	2079	N/A
16-Jul-15	**East_Upper**	N/A	2332	18.6	199	21.9	54.46	265.6	31.5	1179	N/A
16-Jul-15	**East_Lower**	N/A	3067	17.3	205	19.5	120.2	404.7	36.8	1620	N/A
31-Jul-15	**East_Upper**	6.08	1824	16.5	132	26.4	41.86	197.4	24.8	894.3	N/A
31-Jul-15	**East_Lower**	6.38	3862	15.8	245	26.5	163	524.9	46.8	2206	N/A
14-Aug-15	**East_Upper**	5.88	1894	16.8	85.2	11.4	27.64	230.2	12.4	827.9	N/A
14-Aug-15	**East_Lower**	6.36	1398	16.2	56.9	6.37	24.38	482.8	9.39	1347	N/A
4-Oct-15	**East_Upper**	N/A	2576	3.2	133	18.2	50.24	235.8	25.5	1026	N/A
1-Jul-16	**East_Upper**	5.39	1864	19.8	51	6.16	28.15	126.5	14.8	1031	41
1-Jul-16	**East_Lower**	6.26	3401	21.4	200	24.8	108.2	400.2	41.7	1734	51
17-Aug-16	**East_Upper**	6.23	2194	11.3	96.4	11.1	48	235.5	11.9	731.8	35
17-Aug-16	**East_Lower**	6.55	4216	10.6	123	12.4	64.57	368.8	26.1	1340	49

Table A-3: Pore water concentrations of major cations and anions within the peat profile in the eastern marginal region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$
26-Jul-13	**z50**	7.09	2026	21.8	132	8.69	35.8	319	30.9	1000	N/A
26-Jul-13	**z90**	7.38	2670	14.5	128	8.03	42.7	464	19.4	1530	N/A
26-Jul-13	**z150**	7.34	4.1	23.7	132	5.47	17.8	137	38.3	694	N/A
18-Aug-13	**z50**	6.9	1932	17.4	93.5	5.71	26.1	135	23.9	469	N/A
18-Aug-13	**z90**	6.64	2647	17.6	134	8.55	50.6	141	25.3	1520	N/A
18-Aug-13	**z150**	7.09	1605	17.6	157	6.73	22.8	109	46.5	601	N/A
18-Oct-13	**z50**	6.92	2230	9.2	154	11.6	64.6	344	32.8	841	N/A
18-Oct-13	**z90**	7.54	2923	10.1	193	13.6	94	588	28.5	810	N/A
18-Oct-13	**z150**	6.83	2027	10	284	14.7	44.5	191	50.6	583	N/A
20-Jun-14	**z50**	8.15	2288	17.1	132	60.7	5.13	170	68	785	N/A
20-Jun-14	**z90**	8.04	3039	12.8	86.5	50.6	2.55	102	43.7	584	N/A
20-Jun-14	**z150**	8.35	3062	11.2	356	63.8	11.2	118	79.7	1270	N/A
25-Jul-14	**z50**	7.64	2521	20.6	185	9.96	70.1	241	64.4	996	N/A
25-Jul-14	**z90**	7.62	2886	17.4	164	9.95	66.4	133	71.2	883	N/A
25-Jul-14	**z150**	7.86	3091	17.8	194	10.7	29.7	88.6	33.6	737	N/A
14-Aug-14	**z50**	6.88	2988	23.5	130	9.26	79.6	189	70	961	N/A
14-Aug-14	**z90**	7.01	3034	20.5	97.7	5.58	38.7	137	39.5	642	N/A
14-Aug-14	**z150**	7.1	3125	16.7	192	13.6	43.2	116	51	824	N/A
9-Jun-15	**z50**	N/A	3153	12.1	413.6	6.6	71.2	250.6	58.2	1350	N/A
9-Jun-15	**z90**	N/A	3008	10.9	368	7.64	54.2	308.6	53.7	1217	N/A
9-Jun-15	**z150**	N/A	2749	10.7	330.1	14.6	60.7	273.5	49.4	1083	N/A
16-Jul-15	**z50**	N/A	3177	20.2	420.4	6.02	70	373.2	52.6	1181	N/A
16-Jul-15	**z90**	N/A	2886	17.3	272.6	6.08	41.8	237.2	35	849	N/A
16-Jul-15	**z150**	N/A	2621	17.6	190.5	8.51	32.6	191.6	27	692	N/A
14-Aug-15	**z50**	7.14	3244	17.9	375.5	6.42	63.6	256.8	48.1	1085	N/A
14-Aug-15	**z90**	7.25	2831	16.5	144.8	3.32	17.8	254.7	17.4	730	N/A
14-Aug-15	**z150**	7.25	2652	15.4	315.2	14	55.1	256.3	46.6	1043	N/A
4-Oct-15	**z50**	N/A	3400	6.2	383.6	5.04	68.2	322.4	53.5	1136	N/A
4-Oct-15	**z90**	N/A	3041	7.2	199.2	4.4	26.2	283.8	25.5	797	N/A
4-Oct-15	**z150**	N/A	2755	7.4	301.1	14.4	60.4	244.8	46.5	1043	N/A
1-Jul-16	**z50**	7	2901	18.7	348.6	3.03	57.6	108.7	40.2	940	393
1-Jul-16	**z90**	7.06	1773	16.8	185.7	3.76	34.2	96.88	23.1	531	320
1-Jul-16	**z150**	7.32	1686	14.4	96.24	4.17	21.6	66.08	24.2	570	204
18-Aug-16	**z50**	7.45	5324	6.1	480.2	3.27	86.8	217.2	62	1302	876
18-Aug-16	**z90**	7.19	3814	5.8	329.9	7.64	59.5	173.9	27.9	562	639
18-Aug-16	**z150**	7.42	3397	5.8	225.7	12.1	49.3	162.5	33.1	721	420

Table A-4: Pore water concentrations of major cations and anions within the coke layer in the eastern marginal region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$
26-Jul-13	**z225**	7.57	1757	17	162	8.69	26	101	58.5	770	N/A
18-Aug-13	**z225**	7.31	2042	16.7	212	11.6	28.2	90.9	66.5	774	N/A
18-Oct-13	**z225**	5.14	2629	9.6	367	22	60.7	217	51.9	744	N/A
20-Jun-14	**z225**	8.68	3231	9.9	204	38.3	6.63	83.6	37.1	804	N/A
25-Jul-14	**z225**	7.97	3028	15.2	312	18	64.2	113	49.8	1020	N/A
14-Aug-14	**z225**	7.21	2970	16.3	165.5	14.9	52.1	102	46.7	1104	N/A
9-Jun-15	**z225**	N/A	2479	7.7	275.5	17.3	68.4	227	51.2	1066	N/A
16-Jul-15	**z225**	N/A	2452	13.2	266.8	18.6	69.7	234	44.5	1044	N/A
14-Aug-15	**z225**	7.51	2362	14.2	252.4	15.4	68.1	225	40.8	968	N/A
1-Jul-16	**z225**	7.22	1989	19.4	183.4	15.7	61.1	137	29.4	792	198
18-Aug-16	**z225**	7.43	2614	4.8	153.3	13.6	52.9	155	23.3	713	226

Table A-5: Pore water concentrations of major cations and anions within the tailings sand layer in the eastern marginal region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$
26-Jul-13	**z275**	7.47	1641	18.6	194	10.3	28.8	123	49.2	676	N/A
18-Aug-13	**z275**	7.07	1657	14.4	156	10.7	21.3	73.4	41.7	524	N/A
18-Oct-13	**z275**	6.94	1841	10	270	19	43	143	55.7	626	N/A
20-Jun-14	**z275**	8.22	2471	11.3	87.7	13.1	2.09	34	16.4	325	N/A
25-Jul-14	**z275**	8	2558	13.4	271	14.9	45.2	100	44.1	843	N/A
14-Aug-14	**z275**	7.25	2912	16.1	102	11.2	26	62.6	41.7	564	N/A
9-Jun-15	**z275**	N/A	2407	9.3	272.9	17.2	66.4	166	46.4	1056	N/A
16-Jul-15	**z275**	N/A	2422	12.4	261.7	17	66.7	227	44.4	989	N/A
14-Aug-15	**z275**	7.41	2316	13.5	259.1	17.8	69	191	42.1	999	N/A
4-Oct-15	**z275**	N/A	2329	7.6	225.5	14.8	62.4	203	38.4	927	N/A
1-Jul-16	**z275**	7.27	2042	16	189.9	14.1	64.8	160	28.6	761	226
18-Aug-16	**z275**	7.59	2679	4.5	177.3	13.9	62.3	162	27.1	778	299

Table A-6: Pore water concentrations of major cations and anions within the peat profile in the eastern lower region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	SO$_4^{2-}$	HCO$_3^{-}$
26-Jul-13	**z50**	7.31	1270	17.6	75.6	4.97	26.1	148	14.4	337	N/A
26-Jul-13	**z90**	7.11	1741	14.2	62.6	7.01	35.4	188	14.1	432	N/A
26-Jul-13	**z150**	7.14	2430	13.6	65.7	7.44	55	465	26	1562	N/A
18-Aug-13	**z50**	7.04	1347	19.4	75.9	3.98	27.9	125	11.9	316	N/A
18-Aug-13	**z90**	6.9	1670	14.4	40.6	11.2	39.5	162	10.5	372	N/A
18-Aug-13	**z150**	6.69	2289	12.8	39.9	5.58	44.7	265	16.1	929	N/A
18-Oct-13	**z50**	6.65	1420	9.9	53.6	5.6	32.1	99	7.72	129	N/A
18-Oct-13	**z90**	7.11	1811	7.1	56.6	18.8	69	269	15.9	313	N/A
18-Oct-13	**z150**	7.12	1926	5.9	63	10.7	80.8	328	11.1	651	N/A
25-Jul-14	**z50**	7.69	1446	22.1	24.4	4.29	23.9	60.6	9	149	N/A
25-Jul-14	**z90**	7.67	1640	13.5	37.7	9.56	42.3	69.9	21	199	N/A
25-Jul-14	**z150**	7.57	1970	10.5	64.8	8.7	36.6	71.6	34.8	401	N/A
14-Aug-14	**z50**	7	1599	2	46.7	6	34	56	13.7	172	N/A
14-Aug-14	**z90**	6.94	1665	16.7	42.8	10.2	43.2	77.9	22	222	N/A
14-Aug-14	**z150**	6.81	2008	4.5	73.7	9.2	51.5	90.9	42.5	526	N/A
9-Jun-15	**z50**	N/A	1502	10.3	80.87	3.56	51.95	101.4	17.8	167.1	N/A
9-Jun-15	**z90**	N/A	1994	8.3	100.5	9.222	70.3	228.5	33	436.4	N/A
9-Jun-15	**z150**	N/A	2126	5.9	170.5	10.23	60.57	235.7	48.3	599.1	N/A
16-Jul-15	**z50**	N/A	1469	25	94.1	6.731	66.35	195.6	18.1	186.4	N/A
16-Jul-15	**z90**	N/A	1485	25	67.57	7.238	46.69	206.6	21.3	207.4	N/A
16-Jul-15	**z150**	N/A	2157	11.7	188.8	9.769	62.1	251.5	48.8	726.8	N/A
14-Aug-15	**z50**	7.1	1813	17.2	94.87	7.52	71.27	111.6	15.6	143.2	N/A
14-Aug-15	**z90**	7.33	1801	17.7	73.15	8.27	52.28	97.92	29	237.1	N/A
14-Aug-15	**z150**	6.99	2244	14.5	190.6	13.1	60.42	237.6	51.1	814.1	N/A
1-Jul-16	**z50**	7.04	1551	20	82.76	3.689	51.69	26.39	17.8	123.3	505
1-Jul-16	**z90**	7.09	1484	22.5	68.39	5.398	48.31	30.99	22.6	184	399
1-Jul-16	**z150**	6.91	1702	19.1	167.7	7.704	50.07	69.06	38.5	471.5	434
18-Aug-16	**z50**	7.22	2512	4	105	1.674	65.99	53.5	22.8	157.1	781
18-Aug-16	**z90**	7.15	2572	4.4	102.2	6.192	67.85	70.14	29.3	238	703
18-Aug-16	**z150**	7.26	2896	3.7	129.8	5.597	39.35	92.48	27	371.1	499

Table A-7: Pore water concentrations of major cations and anions within the coke layer in the eastern lower region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z225**	7.58	1423	13.6	120	6.33	22.3	188	19	752	N/A
26-Jul-13	**z255**	7.52	1680	19.6	141	7.83	23.7	208	22.8	909	N/A
18-Aug-13	**z225**	7.03	1515	12.1	131	7.78	33	168	23.5	866	N/A
18-Aug-13	**z255**	7.49	1711	15.4	135	6.65	29	171	20.4	843	N/A
18-Oct-13	**z225**	7.15	1811	5.9	195	15.1	45.6	143	57.3	763	N/A
18-Oct-13	**z255**	7.5	1900	5.1	260	13.5	46.1	151	33.2	487	N/A
25-Jul-14	**z225**	8.33	2834	8.4	104	8.83	26.6	67.7	5.16	520	N/A
25-Jul-14	**z255**	8.39	2872	8.3	105	8.71	24.6	85.3	29.6	601	N/A
14-Aug-14	**z225**	7.46	2735	13.8	109	12	37.3	72.5	32.8	763	N/A
14-Aug-14	**z255**	7.76	2785	11.2	128	15.5	51	83.3	45.8	1000	N/A
9-Jun-15	**z225**	N/A	2512	6	325.67	16.643	69.64	174.3	56.1	1118	N/A
9-Jun-15	**z255**	N/A	2535	5.1	323.95	17.49	68.66	159.6	26.6	1108	N/A
16-Jul-15	**z225**	N/A	2476	9.5	307.5	14.954	68.25	218.2	51	1030	N/A
16-Jul-15	**z255**	N/A	2478	8.8	217.37	11.632	49.95	164.1	35.2	820	N/A
14-Aug-15	**z225**	7.82	2230	12.4	245.03	12.62	57.6	179	41.9	959	N/A
14-Aug-15	**z255**	7.97	2373	9.9	163.22	9.26	36.11	179.2	25	792	N/A
1-Jul-16	**z225**	7.52	2001	11.4	205.28	11.874	55.13	119.2	35.4	775	222
1-Jul-16	**z255**	7.75	2269	13.3	117.59	6.4935	31.53	73.63	39.7	912	249
18-Aug-16	**z225**	7.91	2388	2.1	179.89	10.951	51.68	146.8	27.5	692	493
18-Aug-16	**z255**	7.97	2635	1.8	193.02	13.315	60.34	143.3	32.3	771	656

Table A-8: Pore water concentrations of major cations and anions within the peat profile in the eastern middle region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z50**	7.16	1488	16.9	62.4	4.89	32.4	172	12.8	432	N/A
26-Jul-13	**z90**	7.14	1366	18.4	53.8	5.11	32.5	188	12.4	370	N/A
26-Jul-13	**z150**	7.21	1777	12.3	81	4.24	36.1	217	78.1	750	N/A
18-Aug-13	**z50**	6.86	1428	19.2	55.4	4.05	31.9	135	9.7	469	N/A
18-Aug-13	**z90**	6.91	1666	14.2	38.3	3.04	32.1	196	27.5	439	N/A
18-Aug-13	**z150**	7.04	1670	12.4	85.2	3.23	33.5	161	24.5	699	N/A
18-Oct-13	**z50**	7.13	1300	7.7	62.7	8.3	54.7	161	6.65	163	N/A
18-Oct-13	**z90**	7.25	1773	7.5	62	8.4	63.7	271	37.1	286	N/A
18-Oct-13	**z150**	7.17	1682	6.5	133	7.3	52.7	198	41.9	693	N/A
20-Jun-14	**z90**	8.04	2144	11.9	54.2	66.3	2.4	121	58.1	499	N/A
20-Jun-14	**z150**	8.15	1879	12.5	91.7	32.9	1.3	63.5	33.3	452	N/A
25-Jul-14	**z50**	7.73	1495	19	36.9	4.22	26.8	56.2	8.63	78	N/A
25-Jul-14	**z90**	7.8	2044	14.5	64.1	4.66	55.2	116	37.9	443	N/A
25-Jul-14	**z150**	7.79	1998	13.1	67.8	3.41	19.7	60.4	23	253	N/A
14-Aug-14	**z50**	6.9	1713	22.2	32.5	4.73	32.6	48.1	15.2	190	N/A
14-Aug-14	**z90**	6.78	2023	19.9	44.8	4.54	51.3	88.8	42.8	462	N/A
14-Aug-14	**z150**	6.95	1913	16.3	61.6	4.34	34.8	70.2	36.2	404	N/A
9-Jun-15	**z50**	N/A	1820	12.7	74.9	5.91	70.75	254.7	32.4	369.1	N/A
9-Jun-15	**z90**	N/A	1893	9.8	137	6.29	68.47	272.8	45.5	586.4	N/A
9-Jun-15	**z150**	N/A	2208	7.7	212	7.05	63.2	250.9	57	809	N/A
16-Jul-15	**z50**	N/A	1915	16.9	88.2	6.24	74.94	174.5	36.3	430.9	N/A
16-Jul-15	**z90**	N/A	1894	14.6	306	16.8	76.08	262.4	52.4	1134	N/A
16-Jul-15	**z150**	N/A	2318	13.4	228	7.31	63.03	263.1	58.9	898	N/A
14-Aug-15	**z50**	7.02	1932	18.1	90.3	5.98	74.11	248.3	38.9	432.6	N/A
14-Aug-15	**z90**	7.18	1873	17.1	56.9	2.44	29.96	142.3	19.1	322.8	N/A
14-Aug-15	**z150**	7.16	2412	17.8	182	6.26	47.4	269.8	43.3	820.5	N/A
4-Oct-15	**z50**	N/A	2073	6.1	156	3.48	120.7	518.5	26.5	1187	N/A
4-Oct-15	**z90**	N/A	1985	6.4	135	8.72	105.8	348	17.6	837.6	N/A
4-Oct-15	**z150**	N/A	2679	6.8	122	9.29	110.4	384.9	20.1	1035	N/A
1-Jul-16	**z50**	6.72	2350	18.3	96.8	3.4	97.07	263	39.5	734.2	664
1-Jul-16	**z90**	6.98	1272	21.9	42.4	2.37	21.22	42.86	28.3	329.6	100
1-Jul-16	**z150**	6.9	2042	17.7	185	5.85	52.72	171	38.2	711.1	342
18-Aug-16	**z50**	6.75	2875	12.2	128	3.53	121	258.9	46.5	781.3	427
18-Aug-16	**z90**	6.75	2108	14	146	5.44	72.86	190.2	48	536.2	634
18-Aug-16	**z150**	7.07	2858	11	271	8.23	72.07	202.5	50.3	962.9	415

Table A-9: Pore water concentrations of major cations and anions of porewater within the coke layer in the eastern middle region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$
26-Jul-13	**z225**	7.4	1692	12.4	179	10	30	190	35.5	829	N/A
18-Aug-13	**z225**	7.66	1694	11.4	178	10	27.3	136	47.1	825	N/A
18-Oct-13	**z225**	6.99	1767	6.5	197	16	46.8	144	42.5	650	N/A
20-Jun-14	**z225**	9.08	2847	8.8	146	34.2	6.23	42.3	38	526	N/A
25-Jul-14	**z225**	8.21	2778	8.3	177	9.48	36.8	115	27.1	672	N/A
9-Jun-15	**z225**	N/A	2603	7	301	17.1	69	233	50.7	1084	N/A
14-Aug-15	**z225**	7.71	2550	13	202	10.7	48.8	235	33.5	888.9	N/A
4-Oct-15	**z225**	N/A	2511	6.2	339	14.9	79.3	263	80.1	1248	N/A
1-Jul-16	**z225**	7.39	2104	17.8	195	15.6	66.6	146	34.8	818.8	246
18-Aug-16	**z225**	7.47	2248	11.6	181	12.8	62.2	186	29.7	728.3	325

Table A-10: Pore water concentrations of major cations and anions within the tailings sand layer in the eastern middle region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$
26-Jul-13	**z275**	7.54	1760	11.8	136	6.93	26.1	169	25.8	843	N/A
18-Aug-13	**z275**	7.47	1679	10.9	162	8.5	31.3	160	32.3	860	N/A
18-Oct-13	**z275**	4.5	1825	6.1	173	11.9	46.8	174	19.4	504	N/A
20-Jun-14	**z275**	8.82	2901	7.2	164	31.6	5.41	53.1	35.6	602	N/A
25-Jul-14	**z275**	8.25	2834	7	133	6.21	17.5	67.2	2.26	433	N/A
14-Aug-14	**z275**	7.51	2724	11.1	114	8.38	32.9	86.4	31.5	750	N/A
9-Jun-15	**z275**	N/A	2610	5.6	290	16.6	67.2	240	49.1	1047	N/A
16-Jul-15	**z275**	N/A	2674	8.8	305	17	76.9	260	54	1157	N/A
14-Aug-15	**z275**	7.74	2486	14.8	235	13.2	58.7	184	41	966	N/A
4-Oct-15	**z275**	N/A	2517	6	401	18.2	89.8	204	88.5	1402	N/A
1-Jul-16	**z275**	7.4	2229	17.3	65.6	4.43	22.1	148	10.8	521.9	121
18-Aug-16	**z275**	7.67	2642	2.4	197	14.2	69.2	156	27.4	679.3	192

Table A-11: Pore water concentrations of major cations and anions within the peat profile in the western marginal region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z50**	7.2	2766	20	124	11.7	51.8	465	14.5	1200	N/A
26-Jul-13	**z90**	7.34	2630	17.6	99.2	8.06	43.9	468	13.4	1230	N/A
26-Jul-13	**z150**	7.13	2908	15.3	119	9.13	46.3	586	24.1	1630	N/A
18-Aug-13	**z50**	6.85	3037	21.2	104	8.7	54.3	343	14.6	1040	N/A
18-Aug-13	**z90**	7.02	2859	19.4	92.4	7.52	54.4	397	12.5	1180	N/A
18-Aug-13	**z150**	6.87	2968	16.2	65.6	5.27	39.5	417	11.6	1210	N/A
18-Oct-13	**z50**	6.5	3081	10	151	14	153	395	13.8	694	N/A
18-Oct-13	**z90**	7.3	2885	8.9	71.5	8.3	67.4	399	6.9	469	N/A
18-Oct-13	**z150**	5.85	3126	10	139	13.8	148	585	16.8	110	N/A
20-Jun-14	**z50**	7.97	2932	19.6	52	47.2	3.33	114	9.45	485	N/A
20-Jun-14	**z90**	8.08	3564	14.2	80	88.2	3.72	246	15.6	930	N/A
25-Jul-14	**z50**	7.71	3147	21	48.6	6.66	38.6	131	10.1	415	N/A
25-Jul-14	**z90**	7.65	3652	17.3	50.6	5.24	38.6	144	11.3	502	N/A
25-Jul-14	**z150**	7.61	3630	14.1	91.4	7.32	71.6	135	14.6	636	N/A
14-Aug-14	**z50**	6.86	3177	25.7	48.4	11	43.2	19	16	418	N/A
14-Aug-14	**z90**	6.9	3534	21.2	78.4	10.2	127	189	22.4	978	N/A
14-Aug-14	**z150**	6.93	3509	20.7	77.1	7.64	95.25	231	19.3	1245	N/A
4-Oct-14	**z50**	5.56	2972	7.8	53.9	5.39	40.3	60.7	11.6	348	N/A
4-Oct-14	**z90**	4.7	3400	7.6	22.8	3.12	21.4	125	4.68	476	N/A
4-Oct-14	**z150**	5.29	3500	8.3	35	3.26	36.2	83.5	7.09	391	N/A
9-Jun-15	**z50**	N/A	3541	18	159	10.68	135.3	312	38.6	1072	N/A
9-Jun-15	**z90**	N/A	3488	15.2	199	10.56	155.6	187.9	39.7	1120	N/A
9-Jun-15	**z150**	N/A	3453	12.6	157	9.52	149.6	283.5	25.2	1217	N/A
16-Jul-15	**z50**	N/A	3595	21.6	180	11.47	140.9	348.8	46.5	1024	N/A
16-Jul-15	**z90**	N/A	3437	19.7	28	2.485	20.41	178.6	5.71	368	N/A
16-Jul-15	**z150**	N/A	3540	17	142	9.055	139.8	442.4	21.4	1147	N/A
14-Aug-15	**z50**	7.2	3780	20.7	64.2	3.06	54.38	208.6	15.8	612	N/A
14-Aug-15	**z90**	7.15	3254	20	103	9.06	102.3	331.8	20	618	N/A
14-Aug-15	**z150**	7.09	3502	18.3	137	9.65	136	330.3	24.2	1160	N/A
1-Jul-16	**z50**	7.15	3440	23.5	216	6.095	122.3	231.7	52.9	1169	499
1-Jul-16	**z90**	7.07	2671	21	93.7	6.048	96.62	33.69	17.5	453	492
1-Jul-16	**z150**	7.02	2371	19	52.6	2.499	45.71	101.6	10.2	405	243
18-Aug-16	**z50**	7.39	6964	4.9	487	5.989	223.2	489.3	91.7	2320	915
18-Aug-16	**z90**	7.17	4730	6.1	138	8.209	134.3	47	28.2	586	1020
18-Aug-16	**z150**	7.22	4766	5.5	135	8.394	135.6	164.3	20.7	851	544

Table A-12 Pore water concentrations of major cations and anions within the coke layer in the western marginal region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z225**	7.32	1677	14.3	171	8.34	21.4	144	58.2	670	N/A
18-Aug-13	**z225**	7.44	1974	16.8	183	9.59	29.6	121	60.3	755	N/A
18-Oct-13	**z225**	3.46	2282	9.9	295	18.8	55.1	197	38.9	470	N/A
20-Jun-14	**z225**	8.54	3206	12.6	364	62.5	11.6	131	108	1269	N/A
25-Jul-14	**z225**	8.14	3369	13.7	269	14.3	50.7	111	71.8	794	N/A
14-Aug-14	**z225**	7.27	3372	18.1	261	21	70.5	118	32.4	1160	N/A
4-Oct-14	**z225**	6.34	3400	8.6	133	7.56	26.8	43.7	41.2	453	N/A
9-Jun-15	**z225**	N/A	3126	11.2	400	18	82.8	175	92.2	1297	N/A
16-Jul-15	**z225**	N/A	3148	17.6	148	7.21	33.8	193	37.5	679	N/A
14-Aug-15	**z225**	7.36	3123	17.1	359	17	84.2	286	84.8	1269	N/A
1-Jul-16	**z225**	7.22	3282	15.7	381	19.8	89.6	194	89.2	1288	332
18-Aug-16	**z225**	7.5	3927	4.7	222	11.2	61.3	163	38.5	583	450

Table A-13 Pore water concentrations of major cations and anions within the tailings sand layer in the western marginal region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z275**	7.26	2901	15.1	189	17.7	74.8	392	51.7	1830	N/A
18-Aug-13	**z275**	6.45	2537	13.6	128	12.7	48	142	39.6	1030	N/A
18-Oct-13	**z275**	7.36	2788	9.7	231	23.4	136	307	46.3	1160	N/A
20-Jun-14	**z275**	7.62	3266	11.8	238	81.1	13.1	105	78.1	1148	N/A
25-Jul-14	**z275**	7.71	3297	13.1	160	10.3	41.5	130	35.4	781	N/A
14-Aug-14	**z275**	6.76	3398	17.3	122	13	39.6	97.1	54.4	679	N/A
4-Oct-14	**z275**	6.86	3500	9.1	67	4.42	14.1	57.5	19.2	409	N/A
9-Jun-15	**z275**	N/A	3097	9.7	416	19.9	81	181	93.9	1345	N/A
16-Jul-15	**z275**	N/A	3178	14.4	241	16.7	75.6	291	54.9	1246	N/A
14-Aug-15	**z275**	7.45	3147	17.3	364	18.9	77.6	248	83	1306	N/A
1-Jul-16	**z275**	7.34	2921	16.5	370	17.7	80.4	216	76.3	1247	370
18-Aug-16	**z275**	7.55	3882	4.5	213	11.5	56	160	41.1	944	250

Table A-14 Pore water concentrations of major cations and anions within the peat profile in the western lower region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z50**	7.22	1691	15.9	72	4.94	34	241	19.9	712	N/A
18-Aug-13	**z50**	6.89	1820	18.3	64.8	3.99	37.8	248	16.3	727	N/A
18-Aug-13	**z90**	6.83	2265	14.9	95.5	6.91	43.9	280	14.5	838	N/A
20-Jun-14	**z50**	8.17	2375	11.4	302	51.1	10.9	82.7	13.4	577	N/A
20-Jun-14	**z90**	8.3	2463	9.3	235	37.9	8.49	59.1	8.8	453	N/A
20-Jun-14	**z150**	8.33	2927	8	101	22.2	2.39	61.6	8.57	422	N/A
25-Jul-14	**z50**	7.58	2481	17.6	85.6	8.4	82.9	208	29.4	922	N/A
25-Jul-14	**z90**	7.6	2635	17.9	52.3	6.07	54.5	141	14.4	593	N/A
25-Jul-14	**z150**	7.79	2881	13.4	59	7.02	66.5	160	15.4	761	N/A
14-Aug-14	**z50**	6.96	2993	15.3	71.5	5.98	43.7	132	28.9	618	N/A
14-Aug-14	**z90**	6.72	2892	25.8	67	8	84.3	164	19	887	N/A
14-Aug-14	**z150**	6.84	2561	18.2	54.3	6.26	63	197	14.7	794	N/A
4-Oct-14	**z50**	6.69	3100	7.5	78.7	4.87	48.6	93.4	7.2	517	N/A
4-Oct-14	**z90**	6.45	2730	7.8	34.8	3.32	28.6	80.3	2.11	333	N/A
4-Oct-14	**z150**	6.87	2899	7.2	46.9	4.39	40	111	10.8	483	N/A
9-Jun-15	**z50**	N/A	2921	11.8	131.8	4.086	66.87	200.7	6.098	360.7	N/A
9-Jun-15	**z90**	N/A	2815	11.8	145	8.662	107.8	405	21.43	893.5	N/A
9-Jun-15	**z150**	N/A	2818	10.4	122	7.592	105.2	362.9	24.91	997	N/A
16-Jul-15	**z50**	N/A	2735	17.2	36.43	1.803	20.61	208.9	6.594	483	N/A
16-Jul-15	**z90**	N/A	2777	16.9	84.7	5.254	60.88	309.5	11.85	544.4	N/A
16-Jul-15	**z150**	N/A	2971	15.4	131.6	8.236	116	420.3	22.6	1050	N/A
14-Aug-15	**z50**	6.77	2723	17.7	131.2	5.78	102.1	266.9	20.93	933.5	N/A
14-Aug-15	**z90**	7.06	2374	17.1	140.8	8.35	107.6	369.8	20.75	859.2	N/A
14-Aug-15	**z150**	7.14	2904	15.4	121.6	7.21	109.3	424.8	23	1048	N/A
4-Oct-15	**z50**	N/A	3294	6.3	56.51	1.74	76	237.3	39.9	255.8	N/A
4-Oct-15	**z90**	N/A	3049	7	120.8	5.99	76.56	261.9	73.86	537.4	N/A
4-Oct-15	**z150**	N/A	3243	7.2	372.3	12.14	79.57	335.6	88.8	1377	N/A
1-Jul-16	**z50**	6.57	3410	19.6	209	1.202	133.5	346.7	36.15	1403	600
1-Jul-16	**z90**	6.83	2181	19.7	95.35	4.806	77.59	113	14.03	552.2	383
1-Jul-16	**z150**	7.14	2329	18.6	85.78	5.712	82.31	206.5	14.27	669.7	516
18-Aug-16	**z50**	6.85	5741	4.1	269.4	0.299	145.7	412.5	43.29	1399	254
18-Aug-16	**z90**	6.94	1427	3.3	139.6	5.95	108.6	209.9	1.32	45.68	1137
18-Aug-16	**z150**	7.24	4580	3.3	137.1	7.876	124.7	284.8	20.72	853.3	937

Table A-15: Pore water concentrations of major cations and anions within the coke layer in the western lower region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z225**	7.66	800	16.5	63.9	3.63	16.3	111	13.1	329	N/A
18-Aug-13	**z225**	7.54	831	12.6	44.5	2.36	12	64	9.5	237	N/A
25-Jul-14	**z225**	8.34	2048	9.8	108	9.36	31.2	79.8	51.6	563	N/A
14-Aug-14	**z225**	6.88	2850	115.4	91.9	8.53	27.7	53.1	8.6	442	N/A
4-Oct-14	**z225**	7.47	2554	6.8	98.7	4.93	17.3	37.9	30	359	N/A
9-Jun-15	**z225**	N/A	2996	7.8	460	19.6	87.8	251	111	1450	N/A
16-Jul-15	**z225**	N/A	2978	13.4	394	16.3	79.4	257	91	1285	N/A
14-Aug-15	**z225**	7.88	3020	12	129	5.23	26.9	262.6	28.1	818	N/A
4-Oct-15	**z225**	N/A	3163	5.9	286	18.7	106	339.6	58.1	1534	N/A
18-Aug-16	**z225**	7.99	4353	14.4	343	13.8	86.9	227.2	52.5	723	444

Table A-16: Pore water concentrations of major cations and anions within the tailings sand layer in the western lower region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
26-Jul-13	**z275**	7.74	1146	15.3	100	8.16	19.8	134	35.5	475	N/A
18-Aug-13	**z275**	7.26	1078	14	77.1	7.03	15.3	113	25.5	671	N/A
25-Jul-14	**z275**	7.97	1440	11.6	23	5.89	9.7	51.2	12.6	209	N/A
4-Oct-14	**z275**	7.25	2642	6.8	61.7	3.2	11	35.7	23.9	266	N/A
9-Jun-15	**z275**	N/A	3008	13.8	382	17.2	74.7	271.6	91.2	1279	N/A
16-Jul-15	**z275**	N/A	3130	13.3	222	10.1	47.5	206.1	52.4	834	N/A
14-Aug-15	**z275**	7.71	3188	15.2	332	15.1	70.8	248.5	74.9	1269	N/A
4-Oct-15	**z275**	N/A	3444	5.5	287	18.9	108	331.5	58.1	1561	N/A
1-Jul-16	**z275**	7.7	3564	13.3	196	8.26	43.7	103.4	78.6	1342	N/A
18-Aug-16	**z275**	7.91	4471	1.4	375	16.3	84	217.1	78.7	1238	500

Table A-17: Pore water concentrations of major cations and anions within the peat profile in the western middle region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
28-May-13	**z150**	7.13	2970	17.9	236	4.7	126	528	31	2050	N/A
14-Jun-13	**z150**	7.08	2711	11.9	265	8.2	32	486	35	1566	N/A
26-Jul-13	**z50**	6.98	3137	16.4	113	9.5	49	563	19	1630	N/A
26-Jul-13	**z90**	7.09	2164	17.1	68	7.6	39	417	17	1150	N/A
18-Aug-13	**z50**	6.77	3071	20.2	98	9.4	54	341	16	1170	N/A
18-Aug-13	**z90**	6.91	2396	14.1	77	6.2	48	337	16	1180	N/A
18-Oct-13	**z90**	7.01	2653	5.9	92	11	85	394	7.7	601	N/A
18-Oct-13	**z150**	6.7	2687	6.3	162	9.1	79	387	11	678	N/A
20-Jun-14	**z50**	8	2863	14.5	46	42	1.5	91	8.2	666	N/A
20-Jun-14	**z90**	8.21	3056	10	48	44	1.4	86	9.9	459	N/A
20-Jun-14	**z150**	8.26	2883	9.9	69	32	4.7	55	17	1084	N/A
25-Jul-14	**z50**	7.55	3253	19.7	47	6.8	51	214	11	807	N/A
25-Jul-14	**z90**	7.9	3053	10.8	46	4.4	49	142	11	524	N/A
25-Jul-14	**z150**	7.81	3126	13.6	93	5.6	54	180	18	797	N/A
14-Aug-14	**z50**	6.8	3126	20.9	59	9.1	92	208	16	984	N/A
14-Aug-14	**z90**	6.94	2902	18	73	8.8	87	195	21	963	N/A
4-Oct-14	**z50**	6.45	3400	8.4	48	5.4	54	107	11	560	N/A
4-Oct-14	**z90**	5.18	3100	7.6	74	5.9	58	138	14	670	N/A
4-Oct-14	**z150**	5.09	3400	6.6	63	3.9	39	125	1.6	640	N/A
9-Jun-15	**z50**	N/A	2736	10	146	10	129	478	28	1496	N/A
9-Jun-15	**z90**	N/A	3303	9.8	29	2.5	21	209	5.5	498	N/A
9-Jun-15	**z150**	N/A	3185	5.9	85	3.8	46	380	12	1037	N/A
16-Jul-15	**z50**	N/A	3397	18.3	138	10	130	548	26	1441	N/A
16-Jul-15	**z150**	N/A	3256	12	181	7.4	108	510	31	1369	N/A
14-Aug-15	**z50**	7.74	3333	21	123	9.7	121	522	27	1343	N/A
14-Aug-15	**z90**	7.1	3147	19.4	137	11	118	468	25	1205	N/A
14-Aug-15	**z150**	7.24	3066	15.4	98	6	65	219	42	531	N/A
4-Oct-15	**z50**	N/A	3589	6.2	84	5.4	76	210	37	420	N/A
4-Oct-15	**z90**	N/A	3475	7.6	89	3.7	44	222	30	412	N/A
4-Oct-15	**z150**	N/A	3392	7.8	251	8	71	284	57	1050	N/A
1-Jul-16	**z50**	7.05	2570	23.4	88	7.3	79	207	25	750	423
1-Jul-16	**z90**	6.98	2647	22.4	103	5.9	78	206	22	657	583
1-Jul-16	**z150**	7.15	2307	19.3	71	2.8	42	161	25	556	265
18-Aug-16	**z50**	7.07	5087	4.7	144	3.6	130	326	25	1077	702
18-Aug-16	**z90**	7.08	5053	3.7	148	9.1	138	368	25	1062	773
18-Aug-16	**z150**	7.26	4500	3.6	105	6.2	74	108	34	424	583

Table A-18: Pore water concentrations of major cations and anions within the coke layer in the western middle region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	SO$_4^{2-}$	HCO$_3^{-}$
28-May-13	**z225**	7.71	855	14.9	93	2.1	20.8	103	11.5	359	N/A
14-Jun-13	**z225**	7.46	944	13.6	402	14.9	19.9	162	14.9	386	N/A
26-Jul-13	**z225**	7.48	971	14.3	71.7	4.74	15.3	119	13.2	382	N/A
18-Aug-13	**z225**	7.34	1247	14.8	93.8	5.33	22.9	132	18.6	542	N/A
18-Oct-13	**z225**	7.39	1212	5.2	107	9.5	35.7	125	27.5	585	N/A
14-Aug-14	**z225**	7.49	2455	11.9	107	7.74	25.2	61.1	8.9	496	N/A
4-Oct-14	**z225**	5.1	3100	3.8	161	9.26	39	54.1	47	582	N/A
9-Jun-15	**z225**	N/A	3189	8.2	348	15.09	69.008	220	81.39	1290	N/A
16-Jul-15	**z225**	N/A	3301	10.3	452	18.36	95.568	288	102.3	1492	N/A
14-Aug-15	**z225**	7.74	3333	13.1	181	9.83	49.29	267.6	33.58	929.4	N/A
4-Oct-15	**z225**	N/A	3535	6.5	247	15.1	66.15	219	43.38	1043	N/A
1-Jul-16	**z225**	7.55	3013	18.5	155	7.201	31.492	73.53	79.01	1034	243
18-Aug-16	**z225**	7.87	4424	2.4	160	6.814	36.023	83.1	86.5	1222	350

Table A-19: Pore water concentrations of major cations and anions within the tailings sand layer in the western middle region of the fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note red values resemble error and were not included in any results.

Date	Depth	pH	EC	Temp	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	SO$_4^{2-}$	HCO$_3^{-}$
28-May-13	**z275**	7.34	1991	18.4	395	9.2	52	158	38.2	563	N/A
14-Jun-13	**z275**	7.36	843	19.7	375	12.2	14.8	147	93.7	783	N/A
26-Jul-13	**z275**	7.28	1915	11.5	254	12.2	25.2	132	96.3	777	N/A
18-Aug-13	**z275**	7.28	1666	14.5	198	9.77	22.4	98.5	75.8	671	N/A
18-Oct-13	**z275**	7.3	1490	6.3	196	13.3	35.9	98.2	60.2	539	N/A
25-Jul-14	**z275**	8.02	2610	9.4	150	8.94	36	96.2	48.7	712	N/A
14-Aug-14	**z275**	7.47	2710	10.6	146	10.8	37.6	76.5	17	703	N/A
4-Oct-14	**z275**	6.6	3000	4.5	181	8.42	36.5	71.6	58.6	667	N/A
9-Jun-15	**z275**	N/A	3473	11.3	429	19.96	85.067	195.6	96.63	1357	N/A
16-Jul-15	**z275**	N/A	3348	13.3	447	19.36	95.869	239.5	100.3	1462	N/A
14-Aug-15	**z275**	7.67	3306	14.7	380	16.97	81.4	277.1	83.53	1402	N/A
4-Oct-15	**z275**	N/A	3566	6	242	14.54	64.76	218.2	40.33	981.9	N/A
1-Jul-16	**z275**	7.49	3094	18.5	393	16.37	81.584	192.7	85.08	1191	359
18-Aug-16	**z275**	7.7	4354	3	362.64	16.77	83.52	201.73	65.97	814.77	321

Table A-20: Pore water concentrations of major anions and cations in the slopes surrounding Nikanotee fen. All values for analytes are reported in mg L^{-1}. Electrical Conductivity (EC) and Temperature (T) are reported in uS/cm and °C, respectively. Note alkalinity was not measured.

Date	Slope	pH	EC	T	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
18-Aug-13	West	N/A	N/A	N/A	372	15.6	35.3	218	21.7	1440
18-Aug-13	West	N/A	N/A	N/A	1260	46.2	76.5	410	105.9	3870
18-Aug-13	West	N/A	N/A	N/A	424	14.9	38.8	251	50.9	1460
18-Aug-13	East	N/A	N/A	N/A	580	21.7	61.5	288	63.1	1800
18-Aug-13	East	N/A	N/A	N/A	93.9	15.3	54.6	338	14.6	1170
18-Aug-13	South-East	N/A	N/A	N/A	190	13.8	22.9	160	10.4	703
10-Jun-14	West	6.8	6182	17.9	778	55	8.88	167	63.7	2180
10-Jun-14	West	6.84	4223	19.1	285	59.5	8.07	123	19.2	1190
10-Jun-14	West	7.02	2973	17.3	114	30.9	1.53	91.6	4.72	658
10-Jun-14	East	6.55	5474	13.3	507	78.6	8.04	102	34.7	1590
10-Jun-14	East	6.96	2600	16	67.4	26.3	3.3	76.2	7.1	516
10-Jun-14	East	6.94	3018	14.5	140	82.5	11.3	199	16.1	1390
2-Aug-14	West	6.49	1521	28	89.2	6.36	14.5	55.1	8.13	309
2-Aug-14	West	6.65	2026	24.7	207	18	45.2	105	18.1	680
2-Aug-14	West	6.7	1828	23.9	161	10.5	21.1	67.3	12.8	443
2-Aug-14	West	6.7	4802	23.5	803	23.1	86.2	98.6	43	2074
2-Aug-14	West	6.67	1751	24.1	104	13.8	15.3	81.4	4.57	334
2-Aug-14	West	6.59	1993	23.6	52.8	3.39	14.1	56.6	6.12	209
2-Aug-14	West	6.1	1348	24.8	94.6	6.97	11.8	39.5	14.5	158
2-Aug-14	West	6.76	3833	24	159	6.46	18.7	93.1	9.18	535
2-Aug-14	East	6.5	9485	21.9	1230	21.9	162	80.9	65.3	2570
2-Aug-14	East	6.92	850	22.8	57.9	7.85	12.4	39.2	6.81	150
2-Aug-14	East	6.74	1212	20.6	79.8	12.3	28.3	62.9	9.08	261
2-Aug-14	East	6.77	6918	23.4	1720	39.4	149	117	8.66	3215
2-Aug-14	East	6.71	2395	22.7	208	23.7	107.2	213	17.4	974
2-Aug-14	East	6.85	967	22.3	62	32.5	32.5	80.7	14	313
2-Aug-14	East	6.92	1603	20.9	66.4	11.2	26.3	63.4	11.6	235
2-Aug-14	South-East	6.75	2377	24.1	232	12.5	47.7	83.7	11.5	621

Appendix B: Pore water sulfate analysis accuracy

First, it is important to acknowledge that SO_4^{2-} reduction in Nikanotee Fen would be carried out only through biotic pathways (i.e. catalysis of the reaction by SRB), as abiotic SO_4^{2-} reduction would be extremely slow at the groundwater temperatures measured here (Appelo and Postma, 2005, Rickard and Luther, 2007). Throughout 2015-2016, Irvine (2018) found average *in-situ* DOC concentrations in the peat and petroleum coke layers ranged from 30-60 mg L^{-1}, and 30-40 mg L^{-1}, respectively. During the same period, average SO_4^{2-} concentrations in the peat and petroleum coke layers were 816 mg L^{-1} and 1001 mg L^{-1}, respectively. Based on the SO_4^{2-} reduction reaction in equation A1 (Reddy and DeLaune, 2008), and assuming all DOC is in the form of labile CH_2O (Reid and Warren, 2016), the maximum proportional amount of HS^- that could be formed according to stoichiometric calculations, in consideration of CH_2O as limiting reactant, is 1 mM (33 mg L^{-1}) in the peat layer and 0.67 mM (22 mg L^{-1}) in the petroleum coke layer.

$$SO_4^{2-} + 2CH_2O \rightarrow HS^- + 2HCO_3^- + H^+ \qquad [A1]$$

First, it must be noted that a supply of DOC from either the tailings sand in the upland or the petroleum coke could theoretically provide constant fluxes of C within the system. However, in a DOC production study by Khadka *et al.* (2015), virtually no DOC was produced from the construction materials of Nikanotee Fen (tailings sand and petroleum coke), and the nature of the DOC available (even from the peat) was aromatic (i.e. harder to mineralize by microbes). This indicates that SO_4^{2-} reduction in Nikanotee Fen, and therefore sulfide production, as previously stated in section 3.5.2, was likely C limited. Elsewhere, in SO_4^{2-} rich systems like Nikanotee Fen (e.g. in systems comprising oil sand tailings), it is not rare to see SO_4^{2-} being the dominant aqueous species despite being theoretically unstable in anoxic conditions (e.g. Salloum *et al.*, 2002, Warren *et al.*, 2016). Additionally, an assumption was made in the calculation above that all of CH_2O was in the form of labile C, which is likely invalid, as was demonstrated by Reid and Warren (2016). They found that the measured amount of HS^- produced was highest in the sand cap (8m bgs) of Sand Hill Fen. There, only 46% (549.2 µM) of the maximum theoretical yield (1.2 mM) was observed. Instantaneous porewater SO_4^{2-} concentrations were around 2 mM in this region.

Additionally, they found that in the upper wetland-sand interface (1-2m bgs), where dissolved oxygen (DO) saturation was 0%, the maximum SO_4^{2-} concentration was around ~7 mM and instantaneous HS^- concentration was ~15 µM. They suggested that the DOC pool was recalcitrant, so bacteria could not efficiently use this substrate source in SO_4^{2-} reduction.

It has been very well established that the accumulation of dissolved sulfide in peatland systems is almost negligible; standing pools of aqueous sulfide are lower than SO_4^{2-} even when SO_4^{2-} reduction rates are higher than those found in coastal marine sediments (Wieder and Lang, 1988) This is due to the fact that sulfide reacts with dissolved metals to form insoluble precipitates (Koretsky *et al.,* 2007; Smieja-Krol *et al.,* 2014). The petroleum coke used in the construction of the underdrain in Nikanotee Fen is known to have heavy metals, some of which have the potential to leach (Simhayov, 2017) and therefore are anticipated to precipitate out as sulfides. Alternatively, sulfide may also react with organic matter to form relatively stable CBS. It has been previously shown that CBS can be the main sink of sulfide produced by DSR in peatlands with low aqueous concentrations of metals such as iron (e.g. Vile *et al.,* 2003b).