Chemical characterization of construction materials and solute transport in peat from the Nikanotee Fen watershed at the Athabasca oil sands region, Alberta, Canada

by

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Examining Committee Membership

The following served on the Examining Committee for this thesis. The decision of the Examining Committee is by majority vote.

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis.

This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

This thesis has been structured in accordance with the manuscript option. Chapter two has been submitted and is under review in a peer-review journal while chapters three and four are under preparation for submission. Accordingly, these chapters will be subjected to the requests of reviewers and may differ from the respective chapters presented here.

Dr. J. Price was the advisor for this thesis. Accordingly, his contribution was critical in the presented research. Dr. Price contributed important ideas, suggestions and insight with respect to experimental setup, data analyses and interpretation. R. Simhayov was the first author on all of the chapters within this thesis. Accordingly, R. Simhayov did the majority of the writing. As the thesis advisor, all of the chapters within this thesis were reviewed by Dr. Price who provided comments and suggestions where needed. Dr. Price's comments often helped to strengthen experimental designs, goals and interpretation. Dr. Price also provided editorial revisions where appropriate.

Chapter two is submitted as:

Simhayov, R.B., Price, J. S., Smeaton, C. M., Parsons, C., Rezanezhad, F. & Van Cappellen, P. (In review). Solute pools in the Nikanotee Fen watershed at the Athabasca Oil Sands Region. Journal of Environmental Pollution. Ref: ENVPOL_2016_1072.

R. Simhayov did the data gathering, analysis and wrote this paper and provided the original conceptual ideas, which were subsequently advanced and adapted through contributions from the co-authors. Co-authors also provided experimental design, interpretation and editorial suggestions, which were incorporated into the chapter. Dr. Parsons and Dr. Smeaton provided the method subsections on the XRF and SEM respectively.

Chapter three is prepared (but not yet submitted) as:

Simhayov, R.B., Price, J.S., Smeaton, C.M., Parsons, C., Rezanezhad, F. and Van Cappellen, P. Assessment of metals leaching from petroleum coke incorporated in the Nikanotee Fen watershed.

R. Simhayov completed the data gathering, analysis and writing for this manuscript. Co-authors provided important comments and suggestions with respect to experimental design, data analyses and interpretation, as well as typically minor editorial revisions.

Chapter four is prepared (but not yet submitted) as:

Simhayov, R.B., Weber, T.K.D. and Price, J.S. Transport properties of peat from the Nikanotee Fen watershed at the Athabasca Oil Sands Region, Alberta.

The majority of data gathering, analysis, modeling and writing of this manuscript was completed by R. Simhayov. As second writer, T. Weber gathered the retention and conductivity data and provided the soil hydraulic parameters. Additionally, T. Weber provided valuable advice and assistance in improving the HYDRUS model. As advisor and third author, Dr. Price provided important comments and suggestions with respect to data analyses and interpretation, as well as typically minor editorial revisions, as outlined above.

Abstract

Overburden and tailings materials from oil sands production were used as construction materials as part of a novel attempt to create a self-sustaining, peat accumulating fen-upland ecosystem. To evaluate the potential for elemental release from the construction materials, total elemental concentrations in the tailings sand, petroleum coke and peat used to construct a fen ecosystem were determined using microwave-assisted acid digestions and compared to a leaching experiment conducted under environmentally-relevant conditions. A comparison of solid phase to aqueous Na, Ca, S and Mg concentrations showed they were highly leachable in the materials. Given that the concentrations of these elements can affect plant community structure, it is important to understand their leachability and mobility as they migrate between materials used to construct the system. To that end, a mass balance of aqueous Na, Ca, S and Mg was conducted based on leaching experiments and materials analysis coupled with existing data from the constructed system. The data indicate that there is a large pool of leachable Na, Ca, S and Mg in the system, estimated at 27 t of Na, 13.5 t of Ca, 37.3 t of S and 8.8 t of Mg. Since recharge mainly drives the fen-upland system water regime, and discharge in the fen, evapo-accumulation of these solutes on the surface may occur.

Petroleum coke and tailing sands contain metals which raises concern about leaching to the water. A quantification of metals in the 3 main materials used to construct the fen and their potential of leaching was measured using a leaching experiment and solid digestion. The leaching experiment results indicated that only Manganese (Mn) was readily leachable in the petroleum coke. To contrast the findings with the field setting, samples were collected from the Nikanotee Fen watershed, analyzed and compared to water quality guidelines. The comparison

indicated that only Mn was present in the leached solution in concentrations above the 825 μg/l guideline with 3743±651 μg/l in coke and 1110±253 μg/l in peat. Based on SEM and sulfur (S) aqueous data from leaching experiments and field sampling it was concluded that under the slight alkaline pH (8.22±0.06) and anaerobic conditions and the clogged structure of the coke, the leaching is low for analyzed metals (Ti, V, Ni, Pb, Mn, Cu, Zn, U and Cd) except for Mn. Furthermore, high aqueous S concentration would act as a control for leached metal ions. Therefore, under the slight alkaline, anaerobic conditions present in the Nikanotee Fen watershed, there is a low risk of metals contamination resulting from the incorporation of coke in the constructed system.

Finally, the leachable solutes found are mainly located in the upland and are expected to be transported to the base of the fen, given the design and existing hydraulic gradients. For a better understanding and prediction of the transport rates and solute accumulation in the rooting zone of the fen, numerical models are needed. To determine the underlying transport processes in peat from the Nikanotee Fen watershed, soil hydraulic properties were measured and saturated and unsaturated solute breakthrough experiments were performed using Na^+ and Cl^- as reactive and non-reactive solutes, respectively. Inverse modeling and robust statistical evaluation indicated that the soil hydraulic properties and saturated solute breakthrough show that the unimodal van Genuchten-Mualem model (unimodal) described the results well using the Convection Dispersion Equation alone. Parameterization using a mobile-immobile physical non-equilibrium model (MIM) resulted in saturated hydraulic conductivity (454 cm/d) much higher than the measured value (100 cm/d); the unimodal approach produced a value of 106 cm/d. Furthermore, the MIM inverse fit required two additional parameters, one

with high uncertainty. The very high Damkohler number (→infinity) indicating instantaneous equilibration between mobile and immobile phases underscores the redundancy of the MIM approach for this particular peat, which is degraded sufficiently that cell-walls have disintegrated. Thus, while physical non-equilibrium of the MIM approach was unnecessary, chemical non-equilibrium for Na^+ breakthrough occurred, and could be modeled with the one site adsorption model. The parameters were used to predict the Cl^- and Na^+ rise in a lab based unsaturated steady state evaporation experiment using HYDRUS-1D. The simulation showed a good fit to observations, confirming the suitability of the parameters for use in a slightly unsaturated transport simulation. The findings improve the understanding of solute redistribution in the Nikanotee Fen watershed.

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1 Introduction

Surface mining operations in the Athabasca oil sands region (AOSR) in Alberta, Canada are potentially viable on approximately 4800 km^2 of the Western Boreal Plain (Government of Alberta, 2016). By 2014 ~17% of this area was disturbed by open-pit mining (Government of Alberta, 2016). Surface mining requires removal of different overburden layers to expose the oil sands layer (Bott, 2010).

The oil sands layer is composed of mixed bitumen and sand; the first step in production is called extraction and is designed to separate the two (Squires, 2005; Bott, 2010). During this stage, hot water is added to the oil sands, sometimes along with sodium hydroxide (NaOH) to change the viscosity of the bitumen and facilitate separation of bitumen from sand particles (Richard et al., 2002; Squires, 2005; Bott, 2010). The separated bitumen, called "froth" is passed on to the upgrading stage while the sand by-product and excess water is pumped to tailings ponds where the fine particles settle and water is reused for extraction (Squires, 2005; Bott, 2010). In some tailings ponds, $CaSO_4$ was added to facilitate faster settling of fine particles by increasing flocculation (Richard et al., 2002). However, this practice ceased in 2007 although water enriched with $CaSO_4$ is still reused for extraction. Tailings ponds are known to contain high concentrations of organic and inorganic solutes including metals and naphthenic acids (Leung et al., 2001; MacKinnon et al., 2001; Frank, 2008; Whitby, 2010; Holden et al., 2011).

The aforementioned froth is pumped to an upgrader where impurities and excess carbon are removed from the bitumen using high temperatures (~500 ^{0}C) to break down large carbon chains (Squires, 2005; Bott, 2010). This process is designed to produce crude oil and petroleum coke (coke) as a by-product, which contains unwanted elements such as metals and organic molecules that would potentially reduce the quality of the crude oil (Squires, 2005; Chmelar, 2006; El Din et al., 2011). Part of the coke is sold for commercial use and some is used to generate power to the oil sands operations but the demand is low compared to the production and excess coke is stockpiled (Squires, 2005; Puttaswamy and Liber, 2012). Baker et al. (2012) estimated that by 2008 about 60 million tons of coke was stockpiled in the AOSR. Although the coke was stockpiled in large concrete basins and monitored, concerns were raised over possible leaching of contaminants (metals and organic molecules) due to increased weathering (Fedorak and Coy, 2006; Jautzy et al., 2015). Acknowledging this potential leaching, oil sands companies were called to find a safe way to incorporate coke into landscape reclamation operations and have started to explore this option (ERCB, 2009; Luna-Wolter, 2012).

Mine closure regulations require the companies to reclaim a site to "a similar functionality" (Government of Alberta, 2016). Since ~50% of the area of AOSR are wetlands, and ~90% of those are fens, mining operations strips these landforms as part of their procedure (Vitt et al., 1996; Bott, 2010; Daly et al., 2012). Moreover, wetlands have an important role in sequestering and long term storage of carbon (Vitt et al., 2000; Blodau, 2002). Additionally, peatlands buffer the effects of periodic droughts as they supply water to upland areas via clonal aspen root systems (Petrone et al., 2011). However, reclaiming back to a peatland landform was impractical since it was considered to take thousands of years to form naturally (Clymo, 1983). A new conceptual approach by Price et al. (2010) proposed hydrological principles that guide construction of fen-upland systems in the AOSR. They used a numerical model that tested the optimal geometry and material hydraulic properties required to sustain a level of wetness assumed to adequately sustain peat formation processes (Price et al., 2010), based on historical climate records. Given that elevated levels of Naphthenic acids (NAs), sodium (Na) and other metals are commonly present in reclamation materials (Daly et al., 2012), the design called for 2 m of peat to attenuate their flux into the rooting zone (Price et al, 2011; Daly et al., 2012).

In the constructed system, planting focused on mosses and sedges that are characteristic of fens in the oil sands region (Daly et al., 2012) and halophytes (Price et al, 2011). This was done to achieve an understanding of the establishment of different plants in response to the water and solute fluxes from the constructed system (Price et al, 2011; Daly et al., 2012). The goal of the project was to design and build a watershed that supported a self-sustaining, peat-accumulating fen ecosystem (Price et al, 2011; Daly et al., 2012). Ideally this would support a vegetation community representative of local peatlands, which range from poor fens dominated by *Sphagnum* mosses to rich treed fens, both of which include brown moss species (Price et al, 2011; Daly et al., 2012). Mosses are often considered important to the peat formation process (Graf and Rochefort, 2009; Vitt, 2014), but are known to be sensitive to contamination by oil sands process-affected water (OSPW) (Rezanezhad et al., 2012b).

The final design of the constructed system was modified from the original conceptualization by Price et al. (2010) to include a more permeable underdrain that extends from beneath the fen part-way into the constructed upland, for the purpose of more evenly distributing hydraulic pressures (thus water and solute flows) beneath the fen (Daly et al., 2012). The building materials used in the project are peat for the fen, tailings sand (sand) for the upland and petroleum coke (coke) as the connecting layer of the underdrain, all lying over a geosynthetic barrier to prevent deep recharge. These earth materials are all locally available and are either excavated or derived as part of the mining and oil production process (Price et al, 2011; Daly et al., 2012). Peat (and other overburden materials) is being stripped from new mine sites to expose the oil sands; sand and coke are by-products of the oil sands upgrading process (Bott, 2007). Since these by-products contain elevated concentrations of inorganic ions and other metals, and organic constituents such as naphthenic acids (Bott, 2007; Price et al, 2011), a better understanding is needed on the leachability and mobility of these constituents. This work handles inorganic contaminants alone.

The rationale of this research is to understand which of the elements comprising the construction materials are leachable and mobile, and the transport processes and properties that govern their migration through fen peat. To this end, a series of experiments including incubation experiments, saturated breakthrough and unsaturated breakthrough experiments along with analyses such as solid material composition, scanning electron microscope imaging, X-ray diffraction and soil hydraulic properties were conducted.

1.1 Objectives

The overall goal of the presented research is to understand what mobile contaminants are present in the earth materials used to construct the Nikanotee Fen watershed, and the transport properties of the peat used. The specific objectives that address each aspect of the overall goal are outlined below and these include:

1) Identify and quantify the major ions that are readily leachable in the construction materials. Combine this knowledge with the known placement and dimensions of the materials in the Nikanotee Fen watershed to understand the size and location of the solute pools;

2) Identify and quantify metals leaching introduced through incorporation of petroleum coke in the design of the Nikanotee Fen watershed. Comparison of the lab and field based values to strict fresh water guidelines to provide a risk assessment of incorporating petroleum coke in oil sands reclamation;

3) Examine the transport properties of a reactive and non-reactive solute in peat under saturated and unsaturated conditions.

1.2 Organization of thesis

This thesis consists of five chapters that have been structured in accordance with the manuscript option at the University of Waterloo. The introduction presented in chapter one provides the context to the thesis topic and outlines the overall goal and specific objectives of the research. Each of the following three chapters, which will be submitted as research articles, addresses one of the specific objectives outlined in the first chapter.

Chapters two to four are based on empirical data collected for this thesis. Chapter two identifies and quantifies which are the major ions that are leachable and their pools in respect to the design. Chapter three addresses the second objective of this thesis by identifying metals leached from petroleum coke and comparing them along with field based samples to fresh water guidelines. Chapter four provides insight on the transport properties of the peat used in the Nikanotee Fen watershed, thus addressing the third objective.

Chapter five provides a summary of the conclusions from each of the presented manuscripts. This chapter highlights the main contributions of the thesis and provides a synthesis of the recommendations and considerations for future research and peatland reclamation projects.

Appendixes located at the end of the thesis, contain supplementary data, incubation solution preparation scheme, pictures from the various experiments, explanations and equations regarding soil hydrological properties and measured experimental conditions during the unsaturated column experiment.

2 Solute pools in Nikanotee Fen watershed in the Athabasca Oil Sands Region.

2.1 Introduction

Fen construction is a new concept in landscape reclamation that is being tested in the Athabasca oil sands region (AOSR) of Alberta. Previously, recreating a peatland was considered infeasible because it takes thousands of years to form naturally (Clymo, 1983) and thus wetland reclamation focused mainly on marshes (Harris, 2007). Peatlands in the AOSR comprise >50% of the landscape (Vitt et al., 1996) and have an important role in sequestration and long-term carbon storage (Vitt et al., 2000; Blodau, 2002). Additionally, peatlands buffer the effects of periodic droughts as they supply water to upland areas via clonal aspen root systems (Petrone et al., 2011).

One novel approach to constructing a peatland for landscape reclamation was based on a conceptual model developed by Price et al. (2010), who used a numerical model to simulate the optimal geometry and hydraulic properties that sustain a level of wetness assumed to support peatland processes. Given that elevated levels of naphthenic acids (NAs), sodium (Na) and other metals are commonly present in the reclamation materials (Leung et al., 2001; MacKinnon et al., 2001; Scott, 2007; Frank, 2008; Whitby, 2010; Holden et al., 2011; Daly et al., 2012), the fen design called for a 2 m deep layer of peat to attenuate their flux into the rooting zone (Price et al., 2011; Daly et al., 2012). In the constructed (Nikanotee) fen, revegetation focused on mosses and sedges that are characteristic of fens in the AOSR (Daly et al., 2012) and halophytes (Price et al., 2011). This scheme was done to achieve an understanding of the establishment of different plants in response to water and solute fluxes from the constructed system (Price et al., 2011; Daly et al., 2012). The goal of the project was to design and build a watershed that supported a self-sustaining, peat-accumulating fen ecosystem (Price et al., 2011; Daly et al., 2012). Ideally, this would support a vegetation community representative of local peatlands, which range from nutrient poor fens dominated by *Sphagnum* mosses to nutrient rich treed fens, both of which include brown moss species (Trites and Bayley, 2009; Daly et al., 2012). Mosses are often considered to be important to the peat formation process (Graf and Rochefort, 2009; Vitt, 2015), but are also known to be sensitive to contamination by oil sands process-affected water (OSPW) (Rezanezhad et al., 2012b).

The design of the Nikanotee Fen watershed includes a permeable underdrain that extends from beneath the fen part-way into the constructed upland, for the purpose of more evenly distributing the hydraulic pressures (thus water and solute flows) beneath the fen (Daly et al., 2012) (Fig. 2.1). The construction materials used in the project are peat for the fen, tailings sand (sand) for the upland and petroleum coke (coke) as the connecting layer of the underdrain, all lying over a geosynthetic barrier that prevents deep recharge (Fig. 2.1). These materials are all locally available and are either excavated or derived as part of the mining and oil production process (Price et al., 2011; Daly et al., 2012). Peat (and other overburden materials) is being stripped from new mine sites to expose the oil sands; sand and coke are by-products from different stages of crude oil production from the oil sands deposits (Bott, 2010). Sand contains elevated concentrations of inorganic ions such as sodium (Na), and organic constituents such as NAs whereas coke contains elevated concentrations of metals (e.g., V) (Leung et al., 2001; MacKinnon et al., 2001; Scott, 2007; Frank, 2008; Whitby, 2010; Holden et al., 2011). This paper only focuses on the major inorganic ions found in the materials (B, Na, Mg, Al, K, S, Ca and Fe) in an attempt to understand which of them are leachable and might transport to the root zone.

Sodium has been highlighted specifically as a potential risk to plants in the Nikanotee Fen watershed (Price et al., 2011; Daly et al., 2012). It is an abundant element, which exists naturally in almost all soils and plants (Matthuis, 2014). Na is not considered an essential nutrient, although it does have functions in plants such as maintaining turgor pressure (Subbarao et al., 2003). In high concentrations, Na causes stress to plants in two ways (Blumwald et al., 2000) by changing 1) the water potential in the root zone causing a water deficit to the plant that may lead to wilting, and 2) the potassium (K)/Na ratio inside the plant which disrupts cellular enzymatic processes. Na in the sand and coke has two sources; the main source is overburden material of marine origin (Purdy et al., 2005), and the second source is from recycled processed water, which contains legacy NaOH. NaOH was used until 2007 to facilitates the separation of the bitumen from the sand during the extraction process. After separation, the sand and process affected water are sent to tailing ponds where the fines settle and the water is pumped back into the extraction process, while the bitumen is upgraded to crude oil, at which point coke is produced as a byproduct (Bott, 2010).

A quantification of potentially leachable ions is required to evaluate and understand the possible ecological implications of incorporating process-based materials into the Nikanotee Fen watershed. The main objectives of this paper are: A) to determine the solid phase concentrations of the major elements of interest in the construction materials used to build the system; B) to identify which major elements leach under the geochemical conditions expected in the fen in order to assess their leachability relative to their overall reserve; and C) to integrate the results with known dimensions of the constructed upland-fen system to assess the size of leachable major ion pools in the different layers.

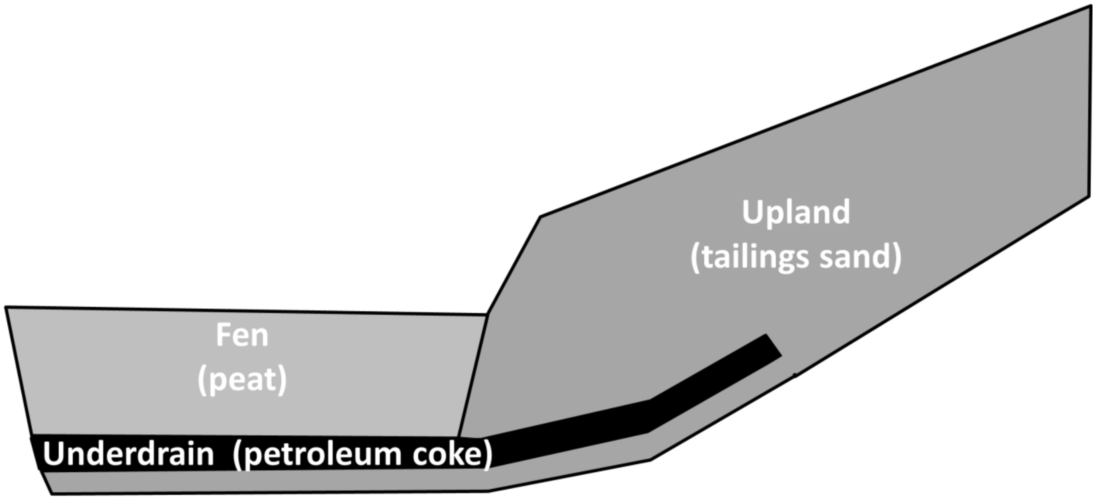

Figure 2.1 – Schematic cross section of the Nikanotee Fen watershed (not to scale). In brackets is the material name that composes the section. Upland depth varies from 2m to 3m close to the fen. The thickness of fen is 2m and of the underdrain is 0.5m.

2.2 Materials and methods

2.2.1 Study area

The Nikanotee Fen watershed was constructed in a post-mining landscape within an oil sands mining operation, located approximately 40 km north of Fort McMurray, Alberta (56°55.944'N 111°25.035'W). The designed fen-upland system was built between reclaimed slopes to the east, southeast and west and a natural slope to the south of the system (Fig. 2.2). All solid materials used for the construction of the Nikanotee Fen watershed were obtained from the mine lease before placement and triplicate samples of each material were collected and sealed in 20 L HDPE containers. Tailings sand was used to construct the upland and to protect the geosynthetic barrier from the underdrain layer (Fig. 2.1). It was taken from a dry tailings pond to the south of the watershed. Raw petroleum coke used for the underdrain layer was taken from a coker plant, which is located on the south side of the Athabasca River. The peat used for the fen was moderately decomposed rich fen, sedge peat, taken from a donor fen prior to stripping the overburden material to expose the oil sands deposits (Price et al., 2011; Daly et al., 2012; Nwaishi et al., 2015).

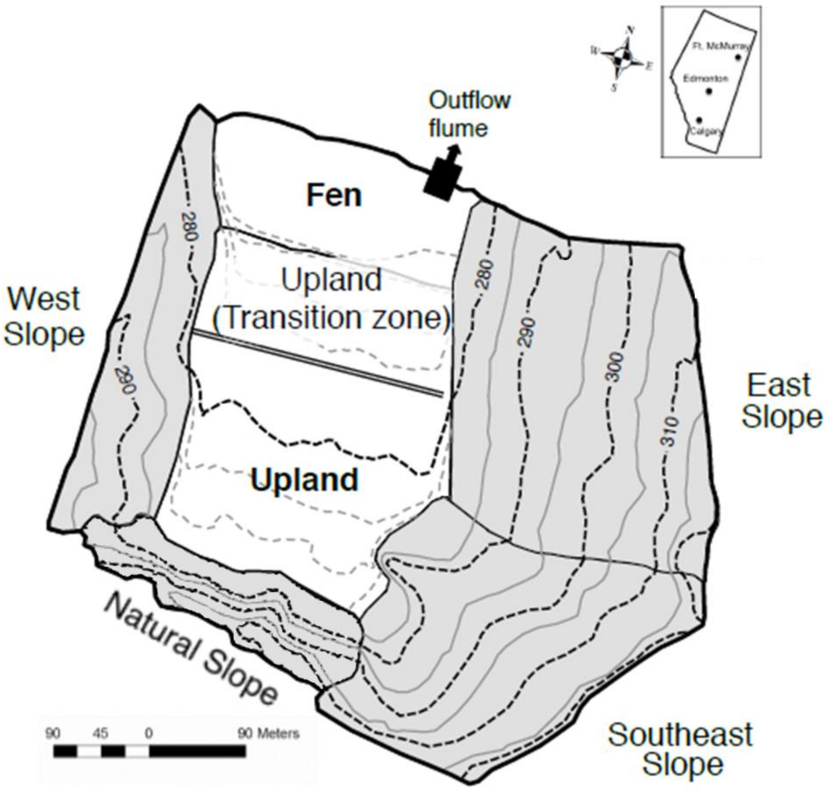

Figure 2.2 - Map of the Nikanotee Fen watershed. Modified from Ketcheson et al. (2016).

2.2.2 Solid material characterization

2.2.2.1 Microwave acid digestion

Solid material acid digestion was conducted on original construction materials (tailings sand, petroleum coke and peat) using a microwave oven (Multiwave 3000, Anton Paar, USA) to determine the concentration of analyte elements within each material. All containers of each material (~60 L total) were mixed by placing them on a polyethylene sheet and mixing by hand with nitrile gloves to increase homogeneity before sampling. Samples from all solid materials were freeze-dried and homogenized using a standard 500 µm soil mesh sieve.

All glassware and plasticware were soaked in 2% HNO_3 solution and rinsed with 18.2 MΩ·cm water prior to use. Coke (~ 0.1 g), was placed in Teflon tubes followed by additions of digest reagents 5 ml of 70% HNO_3 (Purified, Sigma-Aldrich, USA), and 1 ml H_2O_2 (30%, Sigma-Aldrich, USA). After acid additions, the tubes were sealed and microwaved for 1 hour (200 ^{o}C for 40 minutes, 220-240 ^{o}C for the next 20 minutes at a maximum pressure of 2.5-4.0 MPa) (modified procedure from Wang et al., 2004). Upon cooling, the solutions were filtered through a 0.45 µm PTFE syringe filter (Millex, Sigma-Aldrich, USA) into 15 ml polypropylene centrifuge tubes and evaporated under an IR lamp. Certified reference materials (CRM) were used to verify the results of the digestion procedure. The CRM's for coke were Coal (Bituminous, 1632d, National Institute of Standards and Technology (NIST)) and Coal Fly Ash (1633c, NIST). For Sand, standard method US EPA 3051a was used (US EPA 3051a). A CRM was used for validation (TLS-1, Canadian Certified Reference Materials Project (CCRMP)). CRM for peat was acquired from researchers created a peat CRM (Yafa et al., 2004). Peat (0.22 g) was placed in a teflon tube followed by the addition of 3 ml 70% HNO_3 (Purified, Sigma-Aldrich, USA) and 0.1 ml 48% HBF_4 acid (Sigma-Aldrich, USA) and microwaved for 76 minutes. Upon cooling, samples were transferred into 15 ml polypropylene centrifuge tubes and diluted with ultrapure Milli-Q water (Krachler et al., 2002). All digested samples were sent to the Water Quality Centre at Trent

University in Canada and analyzed for B, Na, Mg, Al, K, S, Ca and Fe concentrations via Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) analysis (XSeries2, Thermo, Germany).

2.2.2.2 Powder X-ray diffraction (XRD) analysis

Powder XRD analysis was conducted on coke and tailing sand to identify crystalline mineral phases. Samples were first wet-ground in a McCrone micronizing mill before analysis using a Bruker D5000 equipped with a Kevex Si(Li) solid detector and a Cu Ka1 þ 2 radiation source. Intensities were recorded at 25^{o}C over a range of 5-60^{o} 2θ (sand) and 5-90^{o} 2θ (coke) both with a step interval of 0.026 2θ and a counting time of 5 s per step. Full-widths at half-maximum intensity (fwhm) were determined for diffraction maxima using the EVA program (Bruker).

2.2.2.3 Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS)

Images were collected using scanning electron microscopy via a back-scattered electron (BSE) detector (Quanta FEG 200F). Energy dispersive spectroscopy (EDS) is used to determine relative elemental concentrations (> 0.1 wt%) and is coupled to the SEM so that imaging and elemental analysis is performed in parallel. Samples were prepared by depositing the sieved (≤ 500 µm) peat, tailings sand and petroleum coke onto carbon tape-coated aluminum stubs. All analyses were performed under high vacuum conditions and the BSE images and EDS spectra were collected at accelerating voltages of 10 kV and 25 kV, respectively.

2.2.3 Leaching experiment

A leaching experiment was conducted to elucidate the potential for contaminant release from the construction materials over time under the geochemical conditions (i.e., anaerobic, low temperature and dark) expected deeper in the constructed fen.

2.2.3.1 Incubation solutions preparation

3 type of incubation solutions were prepared using a cascading extraction scheme designed to simulate water movement and changes to its chemical composition as it flows through the upland-fen system. The sequence was based on the design structure of the system in which flows are from upland (i.e., sand) → underdrain (i.e., coke) → fen (i.e., peat) (Daly et al., 2012; see appendix A.1). Hence, each solid material was incubated with a solution that represented water that passed through the previous material layers. For example, the solution used for coke was derived from an incubation of a base solution with sand. All solutions were prepared using a solution to solid ratio of 2:1. Each solution was incubated for 7 days and was stirred 3 times daily to promote equilibration of the solution with the solid phase.

The base solution for all treatments was prepared under aerobic conditions to mimic a surface soil environment by incubating ultra-pure water (18.2 MΩ·cm) with LFH mineral soil mix (LFH). LFH is a mix of overstripped parent material and organic soil horizons (L, F and H) containing organic matter in various stages of decomposition, commonly used for reclamation purposes in Alberta (Naeth et al., 2013). In the Nikanotee Fen watershed, it is used as a cover material for the upland that provides soil to support vegetation; water must infiltrate the LFH to recharge the underlying tailings-sand aquifer. The resulting base solution was purged with nitrogen gas filtered through a 0.2 µm filter (Acro 50, PALL Corp., USA) for 2 hours, and then placed in an anaerobic chamber overnight to ensure the removal of any traces of oxygen (see appendix A.1). 18L of each incubation solution was prepared and used in the experiment.

All cascading solutions prepared inside the anaerobic chamber were covered with aluminum foil to prevent photochemical reactions. Incubation solutions were not buffered, thereby allowing for the solid phase to set the pH as would occur in the constructed system.

2.2.3.2 Leaching experiment procedure

For each material separately, all obtained material was mixed together thoroughly before sampling to increase homogeneity and reduce variability as much as possible. Different coke size fractions were used to evaluate the potential impact of particle size and surface area on contaminant leaching. The coke was sieved using standard soil sieves to determine the petroleum coke fraction composition and the 3 smallest fractions (0-6.35, 6.35-10 and 10-15 mm) were used for the experiment. The samples for the experiment were composed of ~50 g of field moist solid material and 120 ml of incubation solution. Solid samples were placed into 250 ml wide cap, glass mason jars and were kept inside an anaerobic chamber (Coy Laboratory products, <1 ppmv O_2 in N_2 with 3% H_2) and left to equilibrate with the chamber's atmosphere overnight prior to the addition of the solution. After the addition of the incubation solutions, the jars were sealed, removed from the anaerobic chamber and agitated continuously on a shaker table (MaxQ 3000, Thermo scientific) at a temperature of 3 ^{o}C for 56 days (see appendix A.1).

Prior to the experiment, the anaerobic stability (i.e., impermeability of the lid to O_2 diffusion) of the mason jars were tested by monitoring moistened anaerobic indicator strips (Becton Dickinson, catalog # 271051) in jars that were initially sealed in the anaerobic chamber and moved to a refrigerator for one month. The test strips showed no change in color thereby ensuring that the selected experimental vessel remained anaerobic. Moreover, the test jars remained in the refrigerator for the duration of the experiment (i.e., 2 months) and showed no further color change.

At time 0, aqueous samples from each incubation solution were collected, using vacuum filtration with a 0.7 µm glass microfiber 47 mm diameter pre-filter (GF/F, Whatman, USA) followed by a 0.2 µm membrane filter 47 mm in diameter (PES, Millipore Express PLUS, Fischer Scientific, USA). All subsequent samples were filtered using the same type of filters. In order to establish a baseline of elemental concentrations from which to compare to the leaching experiment samples. Moreover, aqueous samples were collected from each experimental vessel containing the construction materials using sacrificial sampling at 0.5, 1 , 7 , 28 and 56 days. At each interval, 18 vessels were sacrificed and comprised triplicates of a) the incubation solution, which served as a control, b) peat, c) tailing sand; and d) three size fractions of petroleum coke.

Extraction samples were filtered in the anaerobic chamber (model B Vinyl Anaerobic Chamber, COY, USA). An aliquot was diluted and acidified with 2% V/V HNO_3 (70%, purified , Sigma-Aldrich) for analysis of B, Na, Mg, Al, K, S, Ca and Fe concentrations using inductively-coupled mass spectrometry (ICP-MS) at the Water Quality Centre at Trent University (XSeries2, Thermo, Germany). Anion concentrations (i.e., F^-, Cl^-, NO_2^-, SO_4^{-2} and NO_3^-) were measured on filtrates using ion chromatography, (ICS-5000, Dionex, USA). Alkalinity was analyzed using an autoanalyzer (APA6000, Hach, USA). Electrical conductivity (EC) and pH were measured using an EC electrode (RK-35820-32, Cole-Parmer, USA) and a pH electrode (RK-59001-65, Cole-Parmer, USA), respectively. All reagents were of ACS reagent grade from Sigma-Aldrich, USA unless otherwise stated. All glassware and plastic ware were acid washed in 2% HNO_3 and rinsed with 18.2 MΩ·cm water prior to use. Presented values represent the net contribution of the solids to the solutions. These values were obtained by adjusting the result to account for the dilution effect of the added solution, followed by subtracting the concentrations measured in control solutions from the values obtained from incubation with solids. All statistical analysis has been done with SPSS V.20 (IBM Corp., 2011) using one-way ANOVA with a 95% confidence level ($\alpha=0.05$). Normal distribution of data was checked and confirmed using the Kolmogorov–Smirnov test. Levene's test of homogeneity of variances has found that for some variables the homogeneity of the variances does not exist, and therefore posthoc analysis for all variables was done using Tamhane's T2 test, which does not assume variance homogeneity. All reported values are the mean and the standard error of the mean.

2.2.4 Bulk density

Peat and sand bulk density values were taken from measurements done on field samples (Ketcheson, 2015). Since no field samples exist for coke due to the depth and unconsolidated nature of the layer, 5 samples for each fraction size of coke were determined gravimetrically based on an oven-dry mass basis for samples dried at 80 ^{0}C for a period of a week (Gardner, 1986). Since these fractions account for 52% of the composition of the coke samples (not shown), the results of all analyzed fractions were averaged together giving a total of 15 samples, as a closer representation of the coke layer bulk density (Bd).

2.2.5 Solute mass balance

The purpose of the mass balance is to calculate the mass of an leachable solute in a specific layer ($M_{\text{avail-}x}$, in mg) which is calculated from the concentration of leachable solute ($C_{\text{avail-}x}$, mg/kg) and the mass of the layer (M_{layer}, kg) as:

$$M_{\text{avail-}x} = C_{\text{avail-}x} \times M_{\text{layer}} \qquad \text{(Eq.2.1)}$$

where the mass of the layer (M_{layer}) is given by the bulk density of the layer (Bd_{layer}) times the volume of the layer (V_{layer}), whereas the concentration of the leachable solute ($C_{\text{avail-}x}$, mg/kg) is determined by the aqueous concentrations of the solutes that originated from the solid materials in the leaching experiment. Using the sample mass (M_{sample}, in kg), the volume of incubation solution (V_{solution}, L), and the measured aqueous concentration of the solute of interest ((CS_x, mg/l), $C_{\text{avail-}x}$ is calculated using:

$$C_{\text{avail-}x} = CS_x \times V_{\text{solution}}/M_{\text{sample}} \qquad \text{(Eq.2.2)}$$

Consequently, $M_{\text{avail-}x}$ (i.e., Eq. 2.1) was determined using $C_{\text{avail-}x}$ calculated using Eq. 2.2, and M_{layer} calculated using the system dimensions such as layer depth and area reported by Ketcheson and Price (2016a).

The constructed system is more complex than originally reported by Price et al. (2010) since it is located within a previously reclaimed area with side slopes that were not accounted for in the original model (Ketcheson and Price, 2016a). Moreover, the heterogeneity of material properties inherent even in constructed systems, coupled with minor variations in layer geometry caused by placement and setting, requires simplifying assumptions. Consequently, the reliability of the mass balance based on laboratory analyses as a representation of the constructed site must be viewed accordingly. However, the calculation can provide insight on the design and its stated goal and has relevance to processes that may occur in the actual system. The assumptions used are: A) the calculation is done only for the main layers within the upland-fen system; B) leachable solutes in each solid material are homogeneously distributed within it; and C) lab based values are representative of the field system.

2.3 Results

2.3.1 Composition of solid materials

2.3.1.1 Solid Phase Analysis

SEM images of the bulk peat taken at low magnifications show a highly porous structure with an average size of 13.5±0.4 x 7.6±0.5 µm (n=8) in larger pores and 8.8±0.4 x 6.6±0.4 µm (n=7) in smaller pores (Fig. 2.3a and b). While particle size in the coke is variable (Fig. 2.3c), particles are larger and more uniformly distributed in the tailings sand (Fig. 2.3d). XRD analysis revealed the presence of quartz, potassium rich microcline feldspar, kaolinite and muscovite in the tailings sand. Furthermore, SEM-EDS analysis of the tailings sand also showed particles enriched in Fe and S which exhibited a frambroidal morphology characteristic of a reduced iron sulfide mineral phase such as pyrite (Fig. 2.4). XRD analysis of the coke sample only identified quartz as a mineral phase, however, SEM-EDS analysis of electron dense (i.e., bright) particles on the surface of the bulk phase show enrichment of Fe and S (Fig. 2.5).

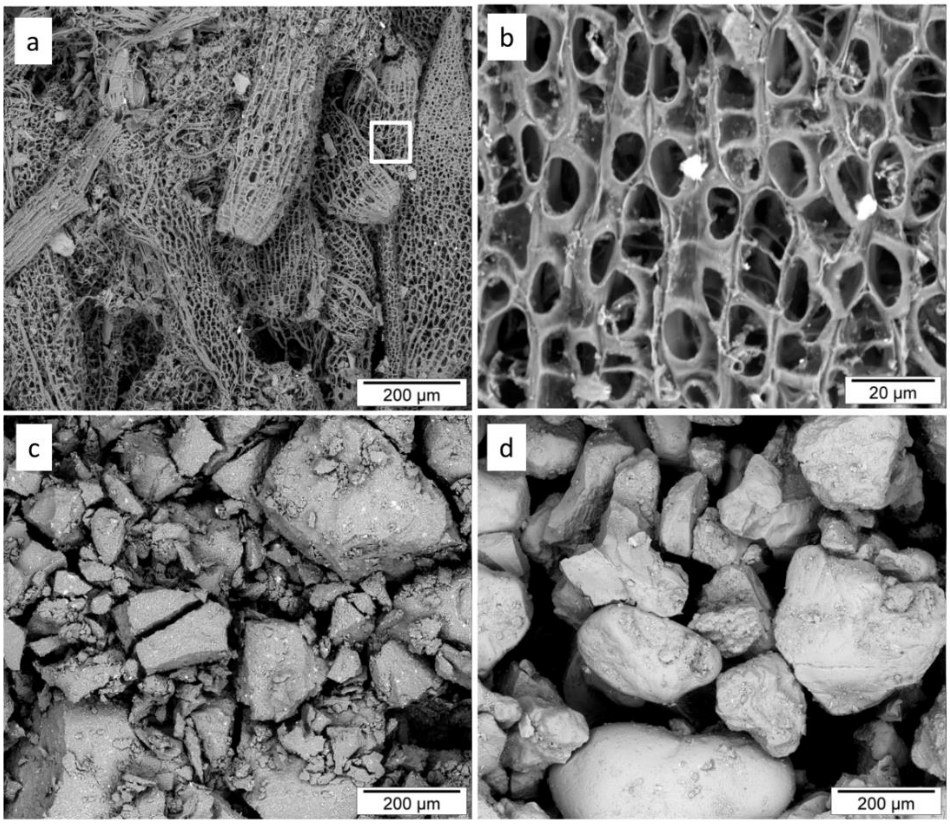

Figure 2.3 - Backscattered electron images were taken at 10 kV of a) peat; b) magnified area denoted by the white box in Fig. a; c) petroleum coke; and d) tailings sand.

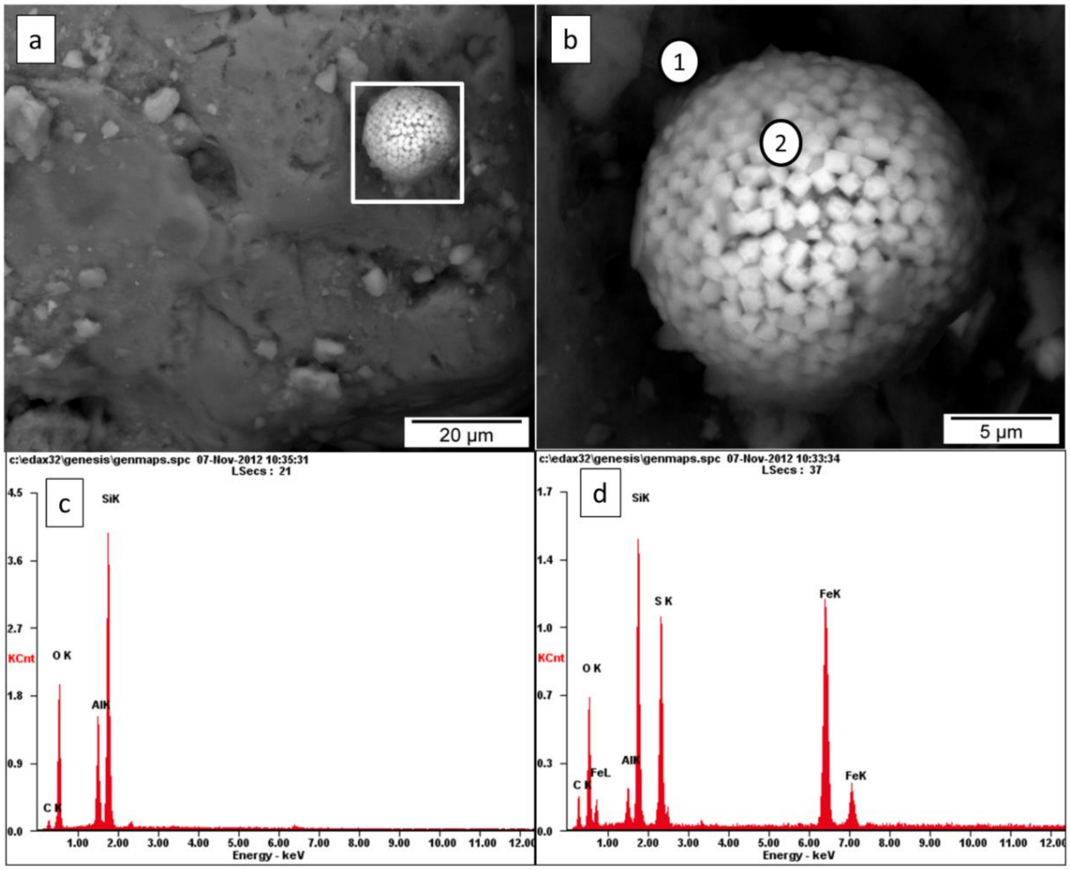

Figure 2.4 - Backscattered electron (BSE) images taken at 10 kV of a) tailings sand; b) magnified area of Fig. A denoted by the white box; c) and d) EDS spectra and relative elemental concentration (wt%) of locations 1 and 2, respectively.

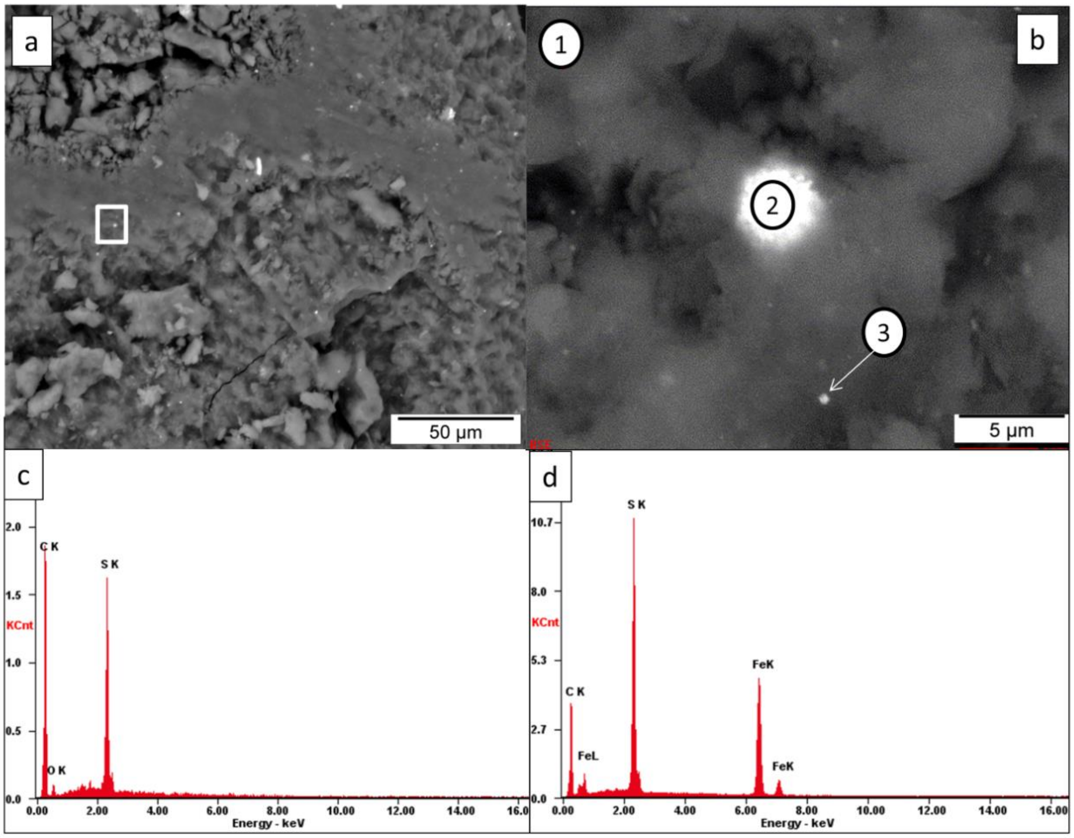

Figure 2.5 - Backscattered electron (BSE) images taken at 10 kV of A) petroleum coke; B) magnified area of Fig. A denoted by the white box; C) EDS spectra and relative elemental concentration taken at location 1; and D) EDS spectra of location 2 and relative elemental concentration (wt%) of locations 2 and 3.

2.3.1.2 Elemental analysis

Bulk analysis of digested solid materials composition showed that there were significant differences between the construction materials in total content of the selected elements (p-values<0.05), except for K, for which a significant difference in its content was found only between peat and coke or sand (p-value=0.01, see Table 2.1), but no statistical difference was present between K in coke and sand. Peat contained the highest total concentration of Na, Mg, Ca and S (Table 2.1). Moreover, SEM-EDS analysis of selected areas showed that relative concentrations of Ca and S varied spatially in the peat and was as high as 14.2 wt% and 6.5 wt%, respectively. Furthermore, Ca and S concentrations in peat were higher by 2 to 3 orders of magnitude than in sand and coke (Table 2.1). Additionally, peat contained 4 to 10 times the amount of Na, and ~9 and ~13 times higher Mg content than coke and sand, respectively (Table 2.1). In contrast, Al, K, and Fe concentration were lower in peat than sand or coke, with coke containing the highest concentrations (Table 2.1). Moreover, sand consistently had the lowest total concentration of all elements examined (Table 2.1).

Table 2.1- Total concentration results from the digestion analysis of Na, Mg, Al, K, Ca, Fe and S in the solid materials. Values are mean with a mean standard error.

	Element[mg/kg]							
Material	**Na**	**Mg**	**Al**	**K**	**Ca**	**Fe**	**S**	**N**
Sand	80±3	186±10	1708±65	254±23	41±3	912±82	320±29	4
Coke	220±12	281±9	2799±104	268±13	383±10	1302±24	950±82	6
Peat	445±13	2491±65	802±60	213±9	39548±1426	360±17	17000±289	4

2.3.2 Coke grain size impact on solute leaching

As part of the leaching experiment, 3 different coke grain sizes were examined to determine if this has an impact on solute concentrations. The assumption was that the higher specific surface area of the smaller particle size fraction would result in increased leaching. A significant statistical difference was found only in pH, EC, SO_4^{2-} and Cl^- concentrations in solution (Table 2.2). Post-hoc analysis revealed that the smallest fraction (< 6.35 mm) produced significantly higher EC and SO_4^{2-} than the other 2 fraction sizes, which were not different from each other. The pH and Cl^- data indicated that a significant difference was only found between the smallest and largest fraction examined with higher values measured in the smallest fraction (Table 2.2). These results suggest that grain size makes a contribution of OH^-, SO_4^{2-} and Cl^- to the solution with smaller grain size contributing more. However, since the absolute differences in the measured values are small, they do not represent a meaningful difference from a geo-chemical or biological perspective, and therefore the coke data were aggregated.

Table 2.2 - Comparison of variables from 3 different coke size fractions examined in the leaching experiment. All variables were found to be statistically different from each other (p-value < 0.05) with the exception of Cl^- and pH where only the smallest and largest sizes were different from each other. The presented values are mean with a mean standard error.

Coke grain size fraction [mm]	pH	EC [µS/cm]	Cl^- [mg/l]	SO_4^{2-} [mg/l]	N
X<6.35	8.22±0.06	632±7	9.8±0.4	127±1	15
10>X>6.35	8.06±0.05	568±9	8.4±0.7	103±3	15
15>X>10	7.95±0.05	559±7	7.6±0.7	102±3	15

2.3.3 Solute concentrations in coke, tailings sand and peat

The leaching experiment produced significantly different solution concentrations when exposed to sand, coke, and peat. Post-hoc analysis showed peat produced significantly lower pH and higher concentrations of SO_4^{2-}, Ca^{2+}, Cl^- than coke and sand (Fig. 2.6). A pattern of increasing SO_4^{2-}, Ca^{2+} and Mg^{2+} concentration in leachate occurred from sand to coke to peat (Fig. 2.6b). This pattern does not exist for Na^+, pH, Cl^- and K^+ where the solution with peat had the lowest average concentration (Fig. 2.6). Mean pH values were 7.87±0.07, 8.22±0.06 and 7.44±0.08 for sand, coke and peat respectively (Fig. 2.6a). In peat, removal of the control solution values resulted in negative K^+ concentrations, thereby indicating that K^+ was removed from the solution (Fig. 2.6a).

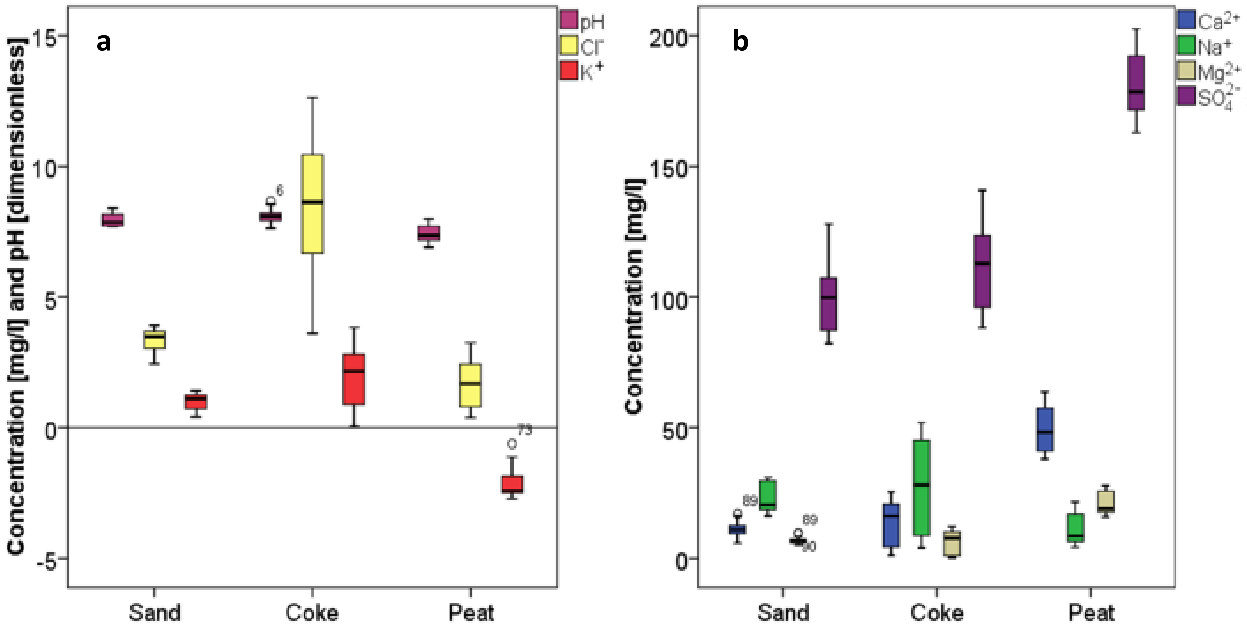

Figure 2.6 - Differences in pH, Na^+, Mg^{2+}, K^+, SO_4^{2-}, Ca^{2+} and Cl^- leached from the examined construction materials. Only peat was found to be statistically different from the other materials (p value < 0.05) except for Cl^- where sand and coke are also statistically different from each other. Each boxplot represent 15 samples for sand and peat and 45 samples for coke which were measured throughout the leaching experiment.

2.3.4 Solute concentration changes and relative leachability

Sacrificial sampling at selected time intervals was done to gain an understanding of the dynamics of solutes over time in the leaching experiment. The elements presented in this section are S, Ca, Na and Mg, which were found to have the largest increase in solution concentration. Fe was below detection level in the solution (not shown). For the purpose of quantifying leaching rates and calculating relative leachability, solute concentrations were converted from mg/l to mg/kg based on measured bulk density. Release rates represent the change in concentration over time from the initial concentration.

All the elements in this section exhibited an initial release of solute from the solid to the solution phase, shown by the rise in concentration. This was followed by either a more gradual increase in concentration over time or concentrations that remained stable (Fig. 2.7).

Based on the pattern found in the total digestions, where peat had the highest content of Na, Mg, Ca and S (Table 2.1) it was expected that these trends would also be apparent in the leaching experiment. However, this was not the case for Na, where peat leached the least amount (Fig. 2.7d); other elements in the leaching experiment followed the same trend found in the total content analysis.

Integrating the leaching experiment results with the digestion results reveals that peat has the lowest proportions of leachable fraction Na, Ca, S and Mg, followed by those in coke. Sand had the lowest total concentrations of Na, Ca, S and Mg, but the highest leachable fractions. By the end of the experiment about 11% of Na, 0.3% of Ca, 0.9% of S and 2.5% of Mg was leachable in peat. In contrast, there was 51%, 13.6%, 10.3% and 9.4% leachable from coke, respectively, and 90%, 96%, 31% 12% in sand, respectively.

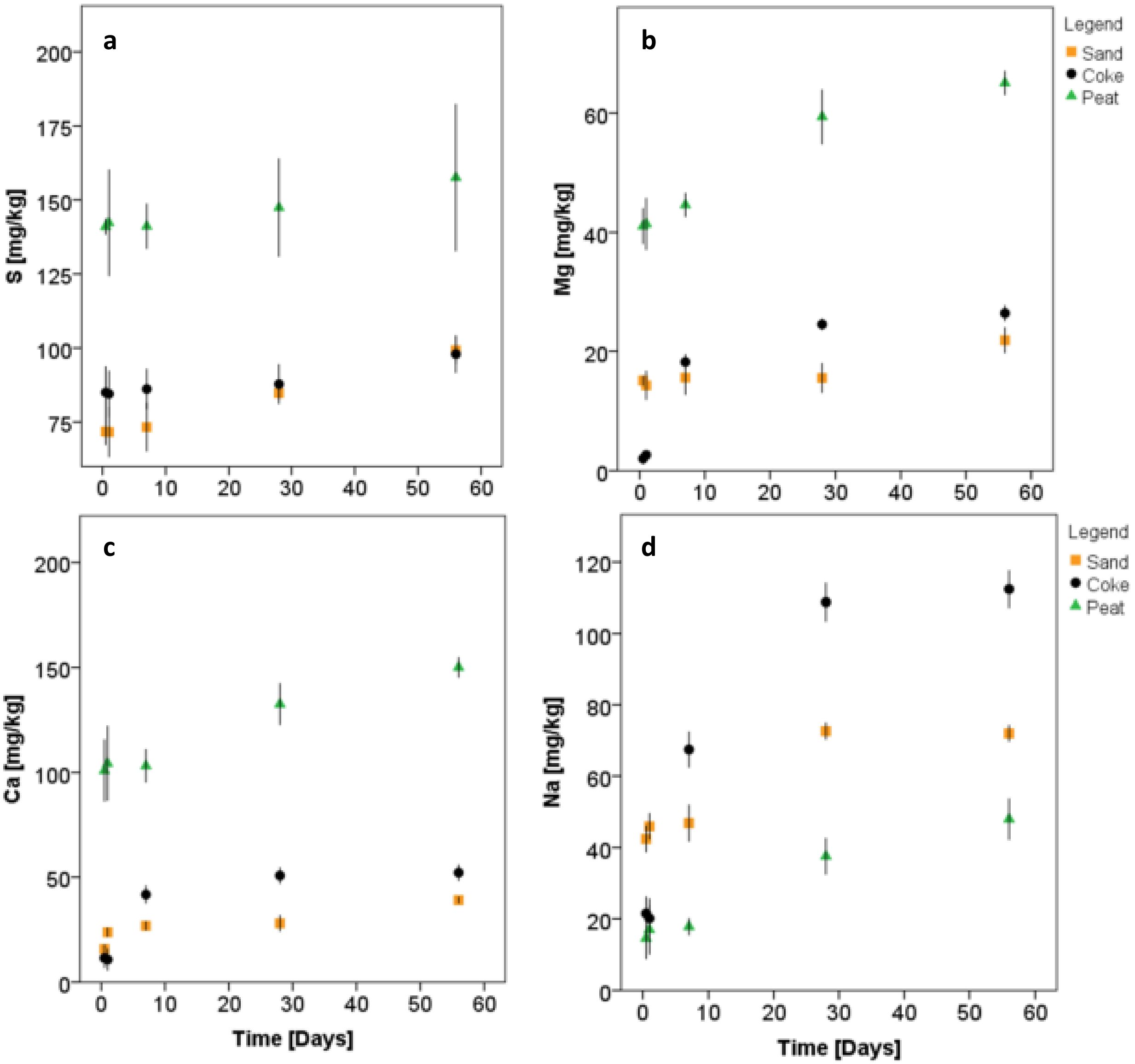

Figure 2.7 - Changes in aqueous concentration of S, Mg, Ca and Na over the duration of the incubation experiment for each solid material. Concentration values were converted from mg/l to mg/kg. For sand and peat each point is a mean of triplicates, for coke each point is a mean of 9 samples; error bars represent 2 standard errors. Note the different Y axis scale.

2.3.5 Solute pools and material dimensions

The bulk density of the materials was approximately 1.45, 0.64 and 0.21 g/cm^3, with the highest density for coke and lowest for peat (Table 2.3). Accounting for the sand beneath the fen as an extension of the upland and for the extension of the underdrain in the upland, we calculated the total volume of sand to be 2.4 x 10^5 m^3 (Table 2.3). This makes the volume of the upland the largest in the system, compared to 2.5 x 10^4 m^3 and 5.8 x 10^4 m^3 for coke and peat, respectively (Table 2.3). Based on this calculation the volume ratio between sand and peat is 4:1.

Table 2.3 - Material dimensions, volumes and bulk density. Dimensions and bulk density values were taken from Ketcheson (2015), except for coke bulk density, which was determined gravimetrically. The bottom sand row is accounting for an extension of the upland beneath the fen. Since the upland is sloped its depth varies from 2m the south to 3m near the fen, therefroe, the volume of sand placed was estimated based on Suncor (2014).

Material	layer type	Area [m^2]	Depth [m]	Volume [m^3]	Bulk density (g/cm^3)
Sand	**Upland**	7.9.E+04	2.8	2.2.E+05	1.45
Coke	**Underdrain**	4.9.E+04	0.5	2.5.E+04	0.64
Peat	**Fen**	2.9.E+04	2	5.8.E+04	0.21
Sand	**Under the fen**	2.9.E+04	0.5	1.5.E+04	1.45

The potential pool of leachable Na, Ca, S and Mg in the different fen constructions layers were calculated using Eqs. 2.1 and 2.2 using data from the digestion analysis and leaching data after 2 months of experiment. Table 2.4 shows that the upland contains the highest amounts of leachable Na, Ca, S and Mg. The fen has the smallest amount of leachable Na and Ca while the underdrain contains the smallest amount of soluble S and Mg (Table 2.4).

Table 2.4- Pool of leachable Na, Ca, S and Mg in the different layers of the Nikanotee Fen watershed.

Layer	Layer mass [t]	Leachable element [t]			
		Na	Ca	S	Mg
Upland (sand)	3.4.E+05	24.6	13.5	33.9	7.5
Underdrain (coke)	1.6.E+04	1.8	0.4	1.5	0.5
Fen (peat)	1.2.E+04	0.6	0.01	1.9	0.8

2.4 Discussion

2.4.1 Solid material composition

Of the three materials examined for total composition, which represents the overall concentration of a specific element within a material, not its leachability, peat is the only unprocessed material and comes from a nearby peatland that was stripped for operations (Bott, 2010; Daly et al., 2012). In contrast, tailing sand and petroleum coke are by-products of oil production (Bott, 2010) and therefore, a difference in the elemental content is expected. Furthermore, based solely on the industrial processes that produce the sand, it is reasonable to assume that sand contains the highest concentration of Na, Ca and S. However, sand was found to have the lowest content of all examined elements (Table 2.1). As shown in the result section (Fig. 2.4) sand is composed mainly of quartz which is a poor sorbent, therefore the solutes in the sand are likely either adsorbed to the fines (<2% of sand) or are salt precipitates on the surface of the grain; this means that the sand has a relatively small concentration of elements on a weight to weight basis. Additionally, a possible explanation might be found in the fact that the sand was piled in the open for ~6 years before it was excavated for the Nikanotee Fen watershed (Joshua Martin, personal communication). Exposure to the freshwater precipitation can cause dissolution of salts on the surface of the quartz grain, causing flushing or washing of the sand. This could result in accumulation of solutes at the bottom of the sand pile. Since samples were taken from the surface of the deposit, they may have had a lower concentration.

The unprocessed peat contained the highest concentration of Na, Mg, Ca and S (Table 2.1) with Ca and S found in very high concentrations (~40 000 mg/kg of Ca and 17 000 mg/kg of S) compared to coke and sand (Table 2.1). For peat, the high concentrations of Ca and S are related to their role as plant nutrients, and consequently they are found in elevated concentrations in the tissue of plants that formed the peat; this was confirmed in the donor peat via SEM (Fig. 2.3) (see also White & Broadley, 2003; Subbarao et al., 2003; Hopkins and Huner, 2008). The donor fen was a rich fen (Price et al., 2011; Daly et al., 2012) where peat formed in a relatively solute-rich environment (Shotyk, 1988). Moreover, the donor fen was drained for 2 years prior to peat extraction, during which time the peat was exposed to aerobic conditions (Nwaishi et al., 2015), causing rapid decomposition (Gorham, 1991). Decomposition resulted in increased element concentrations associated with the mineralization of organic matter and is reflected in its increased bulk density (Wells and Williams, 1996; Sundstrom et al., 2000; Macrae et al., 2013). Furthermore, deposition of S, Na, Ca and Mg due to the proximity of the donor fen to the upgrading plant may have some contribution to the elevated concentrations found. Atmospheric deposition of the aforementioned elements in the AOSR has the highest contribution within 20 km from the source and declines with distance (Fenn et al., 2015); the donor site is located ~ 12 km southeast from the upgrading plant. Vermaat et al. (2016) found that for peat, atmospheric deposition was important but was only a third of the amount of S released by mineralization via peat decomposition under aerobic conditions. Although, the digestion data indicates a high content of Na, Mg, Ca and S, it does not necessarily follow that peat is a greater source of the aforementioned solutes than is sand or coke when looking at the percent of leachable element out of the total pool and placement volumes in the system.

2.4.2 Impact of coke fraction size on leaching

While there was a significant statistical difference in pH, EC, Cl^- and SO_4^{2-} for the different size fractions (Table 2.2), the differences are small and are unlikely to affect the geochemical conditions in the solutions at the field scale.

Raw petroleum coke contains deposits on its surface, smoothing it and blocking pores, which results in a greatly reduced specific surface area (Chen and Hashisho, 2012). This further minimizes the effect of particle size on leaching. Given that the fractions used in the leaching experiment account for 52% of the composition of the acquired coke samples (not shown), and the similarity of their effect on the solution, data gained from all fraction sizes analysis were aggregated to represent coke in the leaching experiment for further analyses.

2.4.3 Leachability of ions from coke, sand and peat

Peat had the highest contribution of Ca^{2+}, Mg^{2+} and SO_4^{2-}, followed by coke and sand (Fig. 2.6b). This trend is similar to that in the digestion results for Ca, Mg and S (Table 2.1), suggesting that the peat originates from a solute-rich environment. The median pH of 7.4 measured in the leaching experiment (Fig. 2.6a) falls within the pH range of 7-8.5 associated with extreme rich fens (Shotyk, 1988). Leachable Ca^{2+}, Mg^{2+} and Na^+ (Fig. 2.6b) were all within 7 mg/l of field values reported by Zoltai and Vitt (1995) for extreme rich fens.

2.4.4 Solute dynamics

All the elements in this section exhibited an initial release followed by an increase over time in only some of the elements (Fig. 2.7). The initial release indicates that part of the mass of solutes is weakly bound whereas the continued increase in concentration suggests that part of the reserve takes longer to migrate to the solution (Fig. 2.7). Generally, desorption is a quick process, with a time scale of minutes to hours (Millward and Liu, 2009). In comparison, the rate of mineral dissolution varies and is dependent on many factors such as concentrations in the solution, temperature, flow rate, surface area (Holzheid, 2016) and therefore is usually a slower process than desorption. However, the sampling resolution was not high enough to allow for distinction between release mechanisms. The aforementioned pattern was evident in all but sulfur in the peat treatment, where there was no significant change in concentration over time beyond the initial release, indicating that the leachable sulfur in peat is released quickly. This release is likely due to the increased S leachability in the pores due to peat decomposition (Shotyk, 1988). The high Ca, S and Mg solution concentrations in the peat treatment relative to the other solids (Fig. 2.7) is in part because peat has the highest content of these elements, by an order of magnitude (Table 2.1). Even with the low leachability, the large reserve generates a relatively large contribution. For example, peat contains 39,548 mg/kg of Ca but only 0.3% was found to be leachable (based on 56 days of leaching), which manifested as ~150 mg/kg Ca release. Furthermore, since the bulk density of the peat is significantly smaller than for sand and coke (Table 2.3), its surface area for a given mass is substantially higher. Poots and McKay (1979) found that the specific surface area of peat was ~27 m^2/g, with very little variation due to particle size. In contrast, the specific surface area of raw coke, from the same source as placed in the Nikanotee Fen watershed, was 3 m^2/g and deemed “ineffective for adsorption” (Chen and Hashisho, 2012). Sand and silt used in the Nikanotee Fen watershed, with over 90% of particle sizes between 2-0.1 mm (O’Kane, 2011), has a low specific surface area. Leamnson et al. (1969) found the surface area for ~ 0.1 mm quartz grains to be 0.1 m^2/g.

The relatively low leachability of Na, S, Ca and Mg in peat, compared to the total pool is because they are part of the recalcitrant peat matrix. These elements are important to the biogeochemical function of plants (White & Broadley, 2003; Hopkins and Huner, 2008). Sulfur is essential in the formation of amino acids, proteins and oils and is necessary for chlorophyll formation (Hopkins and Huner, 2008). Ca has an important role in cell walls and membranes and is also important to various enzymatic, metabolic and hormonal processes in plants (White & Broadley, 2003). Mg is an essential part of the structure of chlorophyll, enzymes that are part of carbon fixation and in ATP related processes (Hopkins and Huner, 2008). Na is not considered an essential nutrient and little is known about its function in plants (Subbarao et al., 2003). However, a few functions have been identified and it is now considered a functional nutrient (Subbarao et al., 2003). Among the functions identified is maintaining turgor pressure within the plant stem, replacing potassium if it is deficient, and in C4 plants it is important for photosynthesis (Subbarao et al., 2003). Given the structure of plant cell and the relatively recalcitrant lignin from, which they are composed (Sorensen, 1962; Hopkins and Huner, 2008) it is no surprise that there is a large reserve of elements that are mostly unleachable since they are locked into organic complexes.

The high leachability of Na and Ca in tailings sand is partly due to its structure, which has previously been reported to consist of a quartz core covered with silt-sized grains (Scott, 2007; O'Kane, 2011). Although quartz has a low specific surface area and sorption site density additional crystalline minerals including microcline feldspar, kaolinite and muscovite were identified in the sand sample by XRD. These minerals have greater surface areas than quartz allowing for greater sorption of elements such as Na and Ca. Adsorbed Na and Ca can subsequently desorb with changes in pH or ionic strength.

Tailings pond water contains a high concentration of Na^+ & SO_4^{2-}, while Mg^{2+}, Ca^{2+} are present in small amounts (Leung et al., 2001; MacKinnon et al., 2001; Frank, 2008; Whitby, 2010; Holden et al., 2011). Over time, the anaerobic environment in the pond results in a reduction of SO_4^{2-} to S^{2-}, which reacts with various metals and the resulting mineral precipitates; one example of this is FeS precipitation (Salloum and Dudas, 2002) of which evidence was found in the SEM/EDS analysis (Fig. 2.4). Furthermore, as water in the pond evaporates, leaving the solution while the solutes remain, the solute concentrations increase and salts start to precipitate, covering the sand grain (Scott, 2007; Holden et al., 2011). Later on, when these materials are used in reclamation projects, the exposure to fresh water, such as rain, causes the salts to dissolve. In contrast, if aerobic conditions are present, FeS oxidizes, releasing Fe and S to the solution. The solution composition and pH determine further interactions (Schippers and Jorgensen, 2002; Stephenson, 2012; Stasik et al., 2014; Vermaat et al., 2016). Moreover, FeS is often poorly crystalline and would likely not be identified through XRD analysis in low concentrations (Herbert et al., 1998). Accordingly, particles enriched in Fe and S in the sand (Fig. 2.4) and the coke (Fig. 2.5) via SEM/EDS were not identified by XRD because they were either amorphous or below detection limits (~ 2 wt%) and represent a pool of oxidizable S. The main salts reported in tailings sands are NaCl, Na and Mg-SO_4, Ca-NAs , Na-NAs and $CaSO_4$ (Leung et al., 2001; MacKinnon et al., 2001; Frank, 2008; Whitby, 2010; Holden et al., 2011). These salts have varying solubility; some such as NaCl will dissolve quickly and some such as Na-NAs dissolve slowly (Frank, 2008; Holden et al., 2011) resulting in an extended release.

2.4.5 Solute pools

The mass balance calculation indicates that there are large pools of leachable Ca, Na, S and Mg in the construction materials (Table 2.4). The total leachable mass of each element in the entire fen-upland system is 27.1 t of Na, 13.5 t of Ca, 37.5 t of S and 8.8 t of Mg (Table 2.4). About 90% of Na, 99% of Ca, 90% of S and 83% of Mg are stored in the upland and originate from the incorporation of tailings sands into the system (Table 2.4). The large volume difference between the upland and fen (a ratio of 4:1) coupled with the high ion leachability in the sand and low leachability in peat, result in a large leachable pool of Na, Ca, S and Mg in the upland relative to the fen. Peat is known to attenuate solute flows, especially cations such as Na^+ (Rezanezhad et al., 2012a, Rezanezhad et al., 2016) based on its dual-porosity structure and negative surface charge. However, little is known about its ability to attenuate S. Furthermore, because the placed peat is disturbed and decomposed (Nwaishi et al., 2015), its water flow pathways are likely erratic (Ketcheson, 2015), and its ability to attenuate solute flows are uncertain.

Based on the results, recharge water in the Nikanotee Fen watershed will be enriched with Na, S, Ca and Mg in contact with sand. The ions will be transported with the water to the coke layer and peat (Fig. 2.6). Although, peat has a high cation exchange capacity that will remove some of the ions from the solution (Shotyk, 1988), the amount of bonding sites is finite. Furthermore, competition between ions on bonding sites may result in the release of bonded ions (Shotyk, 1988). For example, divalent cations such as Ca^{2+} have a stronger affinity to bonding site than monovalent cations like Na^+ (Shotyk, 1988), thus limiting its bonding and even displacing Na^+ into solution. The large leachable mass of Na, S, Ca and Mg in the upland means the influx of solutes with water is continuous, resulting in a major movement of solutes to the fen. The rate of this process will be dictated by the flow rate, solution composition and adsorption-desorption capacity, which is currently being investigated.

It is important to note that the large solute pools in the upland are finite, and since fresh water via rain, snowmelt (Ketcheson and Price, 2016a) and surface runoff from the adjacent reclaimed slopes (Ketcheson and Price, 2016b) are the only source of input to the system, eventually they will be flushed from the system. However, flushing from the system can only occur via surface runoff, which accounted for 28% of water losses from the fen (Ketcheson, 2015). The main water output from the system is evapotranspiration (Ketcheson, 2015). The implications are that there is a potential for substantial, perhaps periodic, build-up of salts on or near the surface of the fen. The difference between flushing of solutes and the transport rate from the upland to fen, and upwards through the peat, will determine the accumulation rate of solutes. This is not yet known, although at the end of 2015 there was no evidence these solutes have arrived from the upland via the underdrain into the rooting zone of the fen (unpublished project data).

2.4.6 Limitations

The purpose of this work is to gain an understanding of which of the constituents within the fen construction materials will be released and move through the system.. The samples size of 60 L per material is miniscule compared to the amount of material that was placed (see total volumes in Table 2.3), The materials were brought from different locations and were stockpiled in some cases, meaning a gradient of solutes concentrations could have developed. Therefore, while the materials analyzed were sampled from those used to construct the system, it is almost certain that the heterogeneity of the solid materials was not represented. Furthermore, scaling between laboratory and field is always problematic for similar issues of field based heterogeneity and complex process that are simplified in a lab scale experiment. For example, the leaching experiment required incubation of solutions in a closed container, which can give a different release rate than having fresh water flowing over the material (Akratanakulet al., 1983). The relative leachability may differ and reported release rates might be different from those in the field. Consequently, the values determined from these experiments are likely within the range found in the materials used, but not necessarily an accurate characterization of them as they are placed.

2.5 Conclusions and recommendations

The goal of this study was to gain insight into the fen construction material composition, and characterize the major leachable ions in the system. Cross reference of data gathered with known literature values identified the donor fen as rich fen (Zoltai and Vitt, 1995). The most leachable elements were found to be Na, S, Ca and Mg. These results can help focus the monitoring effort to the elements most likely to migrate through the system. Based on the solution concentrations found, as water flows from layer to layer, over time progressive enrichment of S, Ca, Na and Mg in the peat layer will occur. The time required for this process to happen is dependent on the flow rate, solution concentrations and surface interactions, which are currently being studied. Peat contained the highest total concentrations of Na, S, Ca and Mg, but exhibited the lowest leachability; in contrast tailings sand contained the lowest total concentrations of these elements but they were found to have the highest leachability.

Acknowledging the limitations of applying laboratory data to the field setting, the data show that incorporation of tailings sand in the design of the Nikanotee Fen introduces a large pool of Na, Ca, S and Mg into the fen-upland system. Since the fen-upland system water egress is primarily by evapotranspiration, evapo-accumulation of solutes on the surface may occur. The accumulation rate is dependent on the difference between solute input from the upland and surface outflow. The transport rates of solutes in the system in general, and in the unsaturated zone of the fen specifically, have not yet been established. This is critical to estimate the timeframe over which solutes may accumulate, and to the concentration they achieve. If solute efflux from the fen does not keep pace with flushing from the upland, there may be a vegetation succession towards more salt tolerant plants used in the revegetation scheme. Knowledge on the transport rates from upland to fen, and within the unsaturated zone in the peat, is imperative for the ability to assess the system's ecological trajectory and the time scales involved.

2.6 Acknowledgements

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3 Assessment of metals leaching from petroleum coke incorporated in the Nikanotee Fen watershed.

3.1 Introduction

Petroleum coke (coke) is a byproduct of oil production, designed to remove excess carbon and impurities during upgrading of bitumen to crude oil (Squires, 2005; Bott, 2010). The impurities include organic molecules such as naphthenic acids, and metals such as vanadium (V) and nickel (Ni), while carbon and sulfur (S) compose most of the coke with ~85% and ~6%, respectively (Squires, 2005; Chmelar, 2006; El-Din et al., 2011). Although coke is highly porous, the impurities within it block pores, making its surface relatively smooth and thus reducing its surface area (Chen and Hashisho, 2012; Fig. 3.1). Coke has some commercial and operational uses; however, due to its high production rate and limited demand, excess coke is stockpiled on site (Squires, 2005; Puttaswamy and Liber, 2012). Fedorak and Coy (2006) calculated that during the lifespan of oil sands production, ~1 billion m^3 of coke will be produced. It was estimated that by 2008, 60 million tons of coke were stockpiled in the Athabasca oil sands region (AOSR) (Baker et al., 2012).

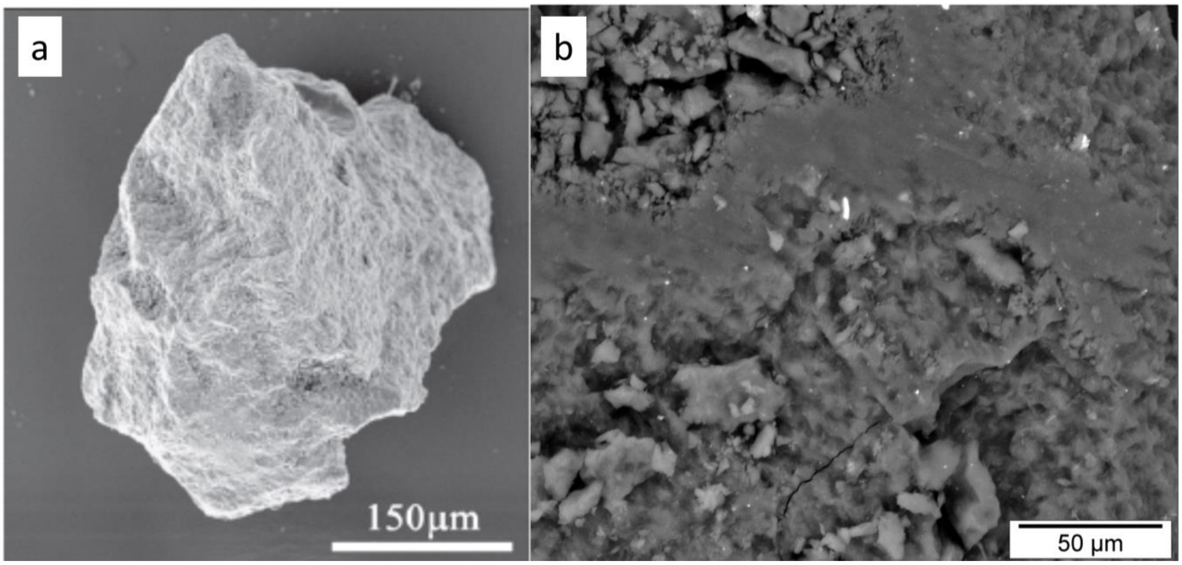

Figure 3.1 – Scanning electron microscope (SEM) pictures of raw petroleum coke. Picture "a" adapted from Chen and Hashisho (2012); Picture "b" is an SEM scan of raw coke used in this work. Picture modified from Chapter 2. In b, note that most of the surface is covered with a deposit.

Stockpiled coke exposed to the elements raises environmental concerns related to its increased weathering, flushing and release of contaminants (Fedorak and Coy, 2006; Jautzy et al., 2015). There are not many studies on the interaction between coke and the environment in general, and on its long-term impact (Luna-Wolter, 2012). However, Jack et al. (1979) found that V and Ni have the highest leaching potential when coke undergoes acidic extraction. Squires (2005) found that leaching of cobalt (Co), copper (Cu), manganese (Mn), molybdenum (Mo), Ni, V and zinc (Zn) under a range of pH and oxygen contents exceeded the Canadian water quality guidelines for the protection of aquatic life. Puttaswamy et al. (2010) found that over a 20-month incubation experiment, coke stockpiles leached aluminum (Al), Mn, V and Ni, causing acute toxicity to *Ceriodaphnia dubia,* a zooplankton used in toxicity testing. Puttaswamy and Liber (2011) examined coke leachates and concluded that Ni and V are the main sources of toxicity and called for long term monitoring of metals in coke stockpile leachates. When mining operations are completed, site closure regulations require companies to return the sites to a land capability equivalent to that prior to disturbance (Government of Alberta, 2016). Therefore, finding a safe and effective way to incorporate coke into landscape designs is needed (ERCB, 2009).

The coke stockpiles in the AOSR are to be reclaimed or incorporated into other reclamation projects as part of the closure plans of oil sands operators (Puttaswamy and Liber, 2011; Nakata et al., 2011). Oil sands companies have started to incorporate coke in reclamation projects as an added means of handling the large reserve (Luna-Wolter, 2012). However, the ecological and biogeochemical impact of incorporating coke in reclamation projects is not well understood. Nakata (2007) found that plants commonly used for reclamation in the AOSR that were grown on coke, suffered from reduced biomass, photosynthetic activity and transpiration along with water stress and nutrient deficiency, potentially due to metal toxicity. Nakata et al. (2011) concluded that *Triticum aestivum* and *Deschampsia caespitosa* could be grown directly on a coke substrate but elevated concentrations of Ni, V and Mo caused plant stress (Nakata et al., 2011). The impact of coke as a cover layer embedded in a wetland was explored by Baker et al. (2012), who found evidence for uptake of V and Ni by aquatic algae and invertebrates.

As part of the mine closure, the regulatory framework (EPEA approval 94-02-00) required the oil sands companies to examine the feasibility of incorporating constructed peatlands into the reclaimed landscape. Previously, this was considered infeasible since peatlands take thousands of years to form naturally (Clymo, 1983); consequently, reclamation of wetlands focused mainly on marshes (Harris, 2007). However, peatlands in the region comprise >50% of the landscape (Vitt et al., 1996) thus have an important role in sequestering and long term storage of carbon (Vitt et al., 2000; Blodau, 2002). Additionally, they buffer the periodic droughts as they supply water to upland areas via clonal aspen root systems (Petrone et al., 2008). The approach to construct a peatland for landscape reclamation in the AOSR using locally available overburden and tailings materials is based on a conceptual model outlined by Price et al. (2010), who used a numerical model coupled with historical climate records to test the optimal geometry and material hydraulic properties required to sustain a level of wetness assumed to adequately sustain peat formation processes. This guided the design and construction of the Nikanotee Fen watershed, incorporating earth materials present on the mine lease (Price et al., 2011; Daly et al., 2012).

The design of the fen-upland system consists of an upland aquifer constructed primarily of tailings sand that discharges into a fen constructed with salvaged peat. The system uses a permeable underdrain constructed of coke to enhance the connection between the upland and fen and to more evenly distribute the hydraulic pressures (thus water and solute flows) beneath the fen (Price et al., 2011; Daly et al., 2012) (Fig. 3.2). The building materials used in the project lie over a geosynthetic barrier that prevents deep recharge (Fig. 3.2). Coke and sand contain elevated concentrations of inorganic ions such as sodium, metalloids, metals and organic constituents that could potentially affect plants in the system (Leung et al., 2001; MacKinnon et al., 2001; Scott, 2007; Frank, 2008; Whitby, 2010; Holden et al., 2011). A study examining the bulk elemental composition of the materials used to build the Nikanotee Fen watershed found large pools of leachable Na, Ca and S. The pools were found to be located mainly in the upland and mainly originated from incorporation of sand in the design.

Additionally, the pH of the peat was ~7.4 while the pH of coke was ~8.1 (Chapter 2, section 2.3.3).

This paper focuses on the implications of petroleum coke in the Nikanotee Fen watershed to determine which metals are most likely to be transported to the rooting zone of the fen peatland. The objectives of this paper are to A) understand the metal composition of the building materials, mainly of coke; B) identify which metals, if any, will leach; and C) evaluate the risk of incorporating coke into the fen-upland system.

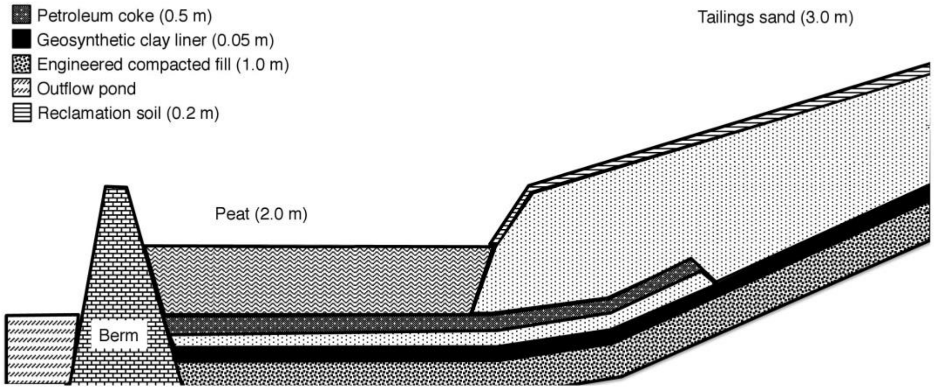

Figure 3.2 - Cross section of the Nikanotee Fen watershed (modified from Ketcheson, 2015).

3.2 Materials and methods

For a more detailed explanation on: a) the site and Nikanotee Fen or b) methods and procedures found in the solid material characterization and leaching experiment sections, the reader is referred to section 2.2 in chapter 2. All digested solid and field water samples (details below) were analyzed for Ti, V, Ni, Pb, Mn, Cu, Zn, U and Cd concentrations using Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) analysis (XSeries2, Thermo, Germany) in the Water Quality Centre at Trent University in Canada. Detection limits (respective element in brackets), in µg/l, were 0.05 (Ti), 0.5 (V), 1 (Ni), 0.5 (Pb), 2 (Mn), 1 (Cu), 10 (Zn), 0.1 (U) and 0.1 (Cd). Values with a relative standard deviation > 5% were not used. CRM recoveries, in %, were 96 (Ti), 95 (V), 96 (Ni), 95 (Pb), 94 (Mn), 92 (Cu), 93 (Zn), 92 (U) and 90 (Cd). Statistical comparisons between mean values was done with one way ANOVA with a 95% confidence level ($\alpha=0.05$) using SPSS V.20 (SPSS, 2011). Normal distribution of data was checked and confirmed using Kolmogorov–Smirnov test. All values reported are mean and standard error of the mean.

3.2.1 Study area

The Nikanotee Fen watershed was constructed in a post-mining landscape within the mine lease at the oil sands mining operations, approximately 40 km north of Fort McMurray, Alberta (56°55.944'N 111°25.035'W). The fen-upland system was built between preexisting natural and reclaimed slopes as reported in chapter 2 section 2.2.1. The main solid materials used for the construction, included tailings sand, petroleum coke and peat that were collected from within the lease area. To build the upland and to protect the geosynthetic barrier from the underdrain layer, tailings sand was used (Fig. 3.2). For the underdrain layer, raw petroleum coke was taken from a coker plant. For the fen, moderately decomposed rich fen, sedge peat was taken from a donor fen site (Price et al., 2011; Daly et al., 2012; Nwaishi et al., 2015).

3.2.2 Solid material characterization

All solid materials used for the construction of the Nikanotee Fen watershed were obtained from the mine lease before placement and triplicate samples of each material were collected and sealed in 20 L HDPE containers. Tailings sand was taken from a dry tailings pond to the south of the watershed. Raw petroleum coke was taken from a coker plant. The peat was taken from a donor fen prior to stripping the overburden material to expose the oil sands deposits; it was a moderately decomposed rich fen, sedge peat (Price et al., 2011; Daly et al., 2012; Nwaishi et al., 2015).

3.2.2.1 Microwave acid digestion

To determine the concentration of targeted elements within each material, solid material digestion was conducted on the sand, coke and peat, using a microwave digester system (Multiwave 3000, Anton Paar, USA). All plastic and glassware were soaked in 2% HNO_3 solution and rinsed with 18.2 MΩ·cm water prior to use. Each material had a different digestion method, for coke and peat the method was modified from Wang et al. (2004) and Krachler et al. (2002), respectively. For sand, an unmodified standard method was used (US EPA 3051a). For each material digestion, a certified reference material (CRM) was added for quality control. Coke had two CRMs to cover the expected range of metals of interest Coal (Bituminous, 1632d, National Institute of Standards and Technology (NIST)) and Coal Fly Ash (1633c, NIST). The CRM for sand was TLS-1 (Canadian Certified Reference Materials Project (CCRMP)). And for peat a CRM was obtained from researchers that composed it (Yafa et al., 2004).

3.2.3 Leaching experiment

A leaching experiment was conducted to determine the potential leaching of metals over time from the construction materials into solution, under the slight alkaline to alkaline pH, between 7.4 – 8.1 (chapter 2; section 2.3.3), anaerobic, low temperature (3°C ± 1°C) and dark conditions simulating the bottom parts of the Nikanotee Fen watershed.

Incubation solutions were prepared using a cascading extraction based on the designed water flow of the system from upland (tailing sand) → underdrain (coke) → fen (peat) (Price et al., 2010). To account for the expected conditions in each layer of the Nikanotee Fen watershed the solutions were prepared in an anaerobic chamber (Coy Laboratory products, <1 ppmv O_2 in N_2 with 3% H_2) (see appendix A.1).

Prior to sampling for leaching experiment, the 3 containers of each material were mixed thoroughly to increase homogeneity. Each sample was composed of 50g ± 1g of field moist solid material and 120 ml of a corresponding incubation solution. Samples were prepared inside an anaerobic chamber (Coy Laboratory products, <1 ppmv O_2 in N_2 with 3% H_2) and contained in 250 ml wide cap, glass mason jars. After the addition of the incubation solutions, the jars were sealed, removed from the anaerobic chamber and agitated continuously on shaker table (MaxQ 3000, Thermo scientific) at a temperature of $3^{o}C \pm 1^{o}C$ for 56 days. Samples were removed and solute was extracted from the slurry after 12 h, 24 h, 1 week, 1 month and 2 months. Each sampling interval consisted of 18 samples.

Solute extraction was executed inside an anaerobic chamber; samples were filtered through a 0.7 µm glass microfiber 47 mm diameter pre-filter (GF/F, Whatman, USA) followed by a 0.2 µm membrane filter 47 mm diameter (Millipore Express PLUS, Fischer Scientific, USA). Filtrates were diluted and acidified with 2% V/V HNO_3 (70%, purified, Sigma-Aldrich) for concentrations analysis of Ti, V, Ni, Pb, Mn, Cu, Zn, U and Cd using an ICP-MS. Presented values represent the net contribution of the solids to the solutions after adjusting result to account for the dilution effect of the added solution, followed by removal of the incubation solution control values (i.e. removal of the measured values measured in solutions without the addition of solids).

3.2.4 Field samples

Field based water samples were collected to quantify the metals leaching in the Nikanotee Fen watershed. The data were used as a snapshot of the system after 3 years of operation and as a cross-reference to the results of the leaching experiment. Ten water samples were taken from both the coke layer and from the overlaying peat. All water samples were collected from piezometer nests with coke and peat samples collected from the same nest. The peat water samples were from the deepest piezometers representing the bottom of the peat layer, directly above the coke (Fig. 3.2). Since the coke layer slopes and the fen thickness is uneven, the sample depth changes over the site. For coke, one sample was taken from 215 cm below the surface, 7 from 225 cm and 2 from 275 cm. For peat, 8 samples were taken from 150 cm below the surface and 2 from 225 cm below the surface. The piezometers were purged 3 times before sampling. Samples were drawn and filtered via a 0.2 µm membrane filter, 47 mm in diameter (Millipore Express PLUS, Fischer Scientific, USA) into 15 ml polypropylene centrifuge tubes (CLS430791, Corning, Sigma-Aldrich). The filtrated samples were diluted and acidified with 2% V/V HNO_3 (70%, purified, Sigma-Aldrich) for preservation.

Data gathered were compered to Alberta Environment and Sustainable Resource Development Environmental Quality Guidelines for Alberta Surface Waters (ESRD, 2014) or to the British Columbia Approved Water Quality Guidelines (BC WQGs, 2016) if an Alberta guideline could not be found. If several guidelines for an element were found, the stricter guideline was used. Hardness dependent guidelines were calculated under an assumed low hardness of 50 mg/l of $CaCO_3$ for a stricter guideline value.

3.3 Results

3.3.1 Content in solid materials

Digestion analysis of solid materials composition showed that coke contained the highest amount of Ti, V, Ni and Pb and peat contained the highest concentration of Mn, Cu, Zn and Cd (Table 3.1). The digestion analysis for sand materials exhibited low concentration of the targeted elements (Table 3.1). Examination of the values reveals that coke contains 1 to 3 orders of magnitude more V, Ni and Ti than peat and sand, while the peat contained between 3 to 10 times more Mn, Cu and Zn than coke and sand materials (Table 3.1).

Table 3.1 - Total concentration results from the digestion procedure of Ti, V, Mn, Ni, Cu, Zn, Cd, Pb and U in the solid materials. Values are mean and standard error of mean. For sand and peat n=4, for coke n=6. [a] marks a significant statistical difference between the value found in the specific material to the other materials' concentrations (p-value<0.05); element name marked with [b] means the specific element concentrations were significantly different between all materials (p-value<0.05). ND = not detected.

Mat.	Element [mg/kg]								
	Ti[b]	V[b]	Mn	Ni	Cu[b]	Zn	Cd[b]	Pb	U[b]
Sand	37±2	2.6±0.2	22.3±1.3	1.7±0.2	3.2±0.1	5.0±0.3	0.02±0.001	1.34±0.03	0.16±0.01
Coke	159±2	1062±22	20.4±0.5	389±8.5*	10.1±0.8	5.8±1.4	ND	5.50±0.1[a]	ND
Peat	50±2	1.18±0.03	93.7±4.1*	0.79±0.06	40.2±1.2	29.6±0.8*	0.11±0.001	2.10±0.1	0.05±0.001

3.3.2 Concentrations in the leaching experiment

Analysis of Mn, Zn, Ni, Cu, V, Ti, Cd and U concentrations in solutions from the leaching experiment presented little significant differences in solution composition between tested materials. Leachate from sand and coke were not significantly different from each other (Fig. 3.3). However, leachate from sand and coke had more Mn than that from peat (Fig. 3.3), while that from peat had higher amounts of Zn than that from sand and coke (Fig. 3.3). All statistical differences had a p-value<0.05. Ti, V, Cd, U and Cu in the solutions with different solids were defined mainly by non-detected concentrations with over 75% of samples below the detection limit (represented in Fig. 3.3 as a line close to 0). Fe was screened as well but was below detection limit (not shown).

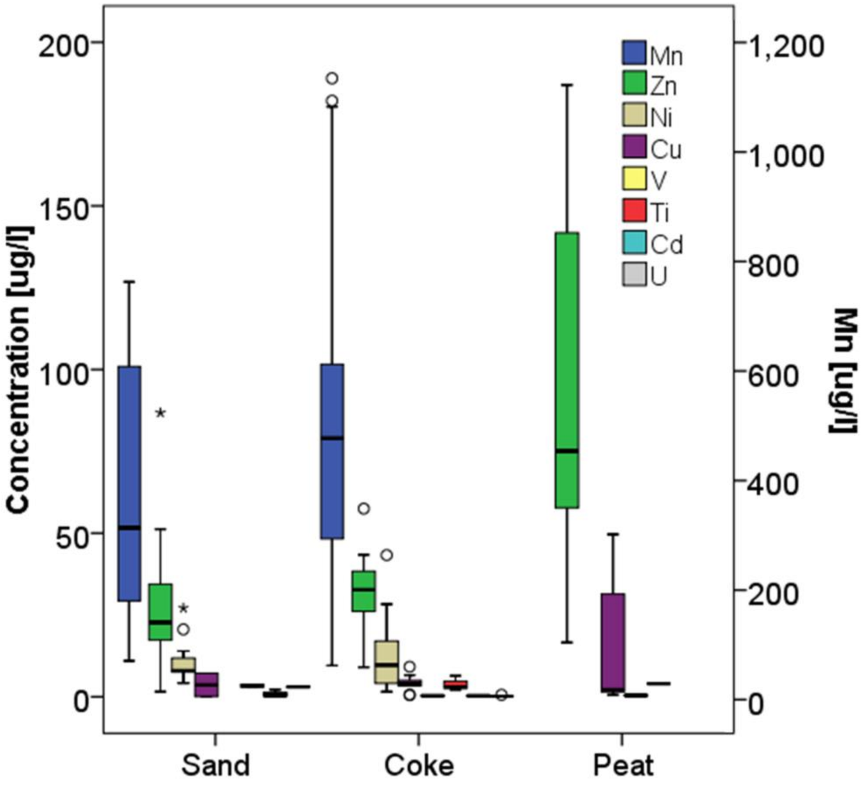

Figure 3.3 Aqueous Mn, Zn, Ni, Cu, V, Ti, Cd and U concentrations at 56 days in the leaching experiment for each solid material. Note different y-axis for Mn. For Cu, V, Ti, Cd and U groups are defined more by values below detection limit (over 75% of samples) and are shown as a line close to 0. For Mn and Ni, n=45 for coke and 15 for sand or peat. For Zn, n= 11, 16 and 15 for sand, coke and peat, respectively.

3.3.3 Concentrations in the field samples

Analysis was done to gain an understanding of the leaching potential of Mn, Zn, Ni, Cu, V, Ti, Cd and U over a longer duration than the leaching experiment by examining field conditions. Since the hydrological gradients in the Nikanotee Fen watershed dictate flow from the coke to the peat (Ketcheson, 2015) and because coke had the highest potential to act as a source for metals, samples were collected from the coke layer and the overlying peat. As in the leaching experiment, Fe in the field samples was below detection limit (not shown). Pore-water from the coke layer contained more Mn, Ni and U than those sampled in peat ($p\text{-value} < 0.05$; Fig. 3.4). No significant differences were found in Cu or V concentrations between coke and peat. Furthermore, 70% of samples did not contain measurable V concentrations. Similarly, in all samples no measurable concentrations of Zn, Ti and Cd were detected (Fig. 3.4).

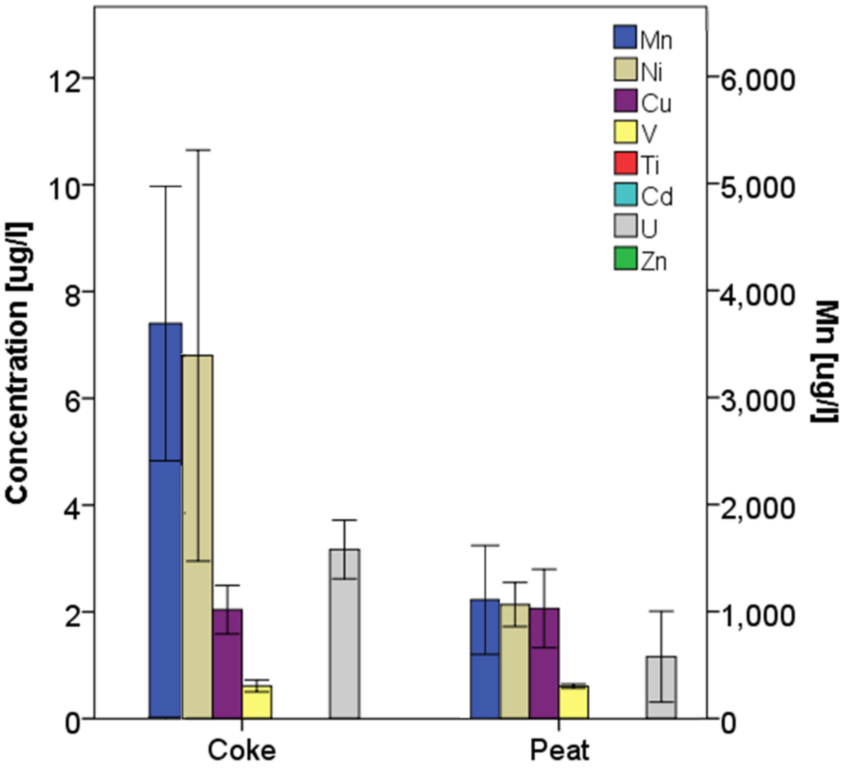

Figure 3.4 – Pore-water concentrations of Mn, Ni, Cu, V, Ti, Cd, U and Zn in coke and overlaying peat from the Nikanotee Fen watershed after 3 years of operation. All samples had Zn, Ti, and Cd concentrations below detection limit and are represented for comparison with the leaching experiment. Similarly, in 70% of samples V was below detection limit (n=3 and 2 for coke and peat, respectively). Note the different y-axis for Mn. Bars are mean and error bars are 2 standard errors of mean. For Mn, n=10 for coke and peat. For Ni and U, n= 10 in coke and 8 in peat. For Cu, n= 5 and 8 for coke and peat respectively.

3.3.4 Comparison to guidelines

Data from the leaching experiment and field samples were compared to water quality guidelines (ESRD, 2014; BC WQGs, 2016; Table 3.2). Comparisons show that for all samples, concentrations of Ni, V and U were within the guidelines limits (Table 3.2). Zn, Cu, Cd and Ti were above the guidelines in the samples from the leaching experiment, but below the guideline limit in the field samples (Table 3.2). In contrast, Mn values were below the guideline limit in the leaching experiment samples and above it in the field samples (Table 3.2).

Table 3.2 – Comparison of Ti, V, Mn, Ni, Cu, Zn, Cd and U values from the Nikanotee Fen watershed and leaching experiment to water quality guidelines. All values are in µg/l. Research derived data are mean ± S.E. For fen samples n=10 to each material. For leaching experiment n=15 for sand and peat; n=45 for coke. All guidelines used are Alberta Environment & Sustainable Resource Development Environmental Quality Guidelines for Alberta Surface Waters (ESRD, 2014) unless marked. In case several values were available the stricter values were used. Green highlights values below guideline limit, orange highlights values above guideline limit. ND = not detected. See footnote for marks.

Element [µg/l]		**Guideline limits**	**Leaching Experiment**			**Fen Water Samples**	
			Sand	**Coke**	**Peat**	**Coke**	**Peat**
Mn*[a]	Mean	825	382±62	509±42	ND	3743±651	1110±253
	ND N		0	0	15	0	0
Zn	Mean	30	30±7	32±3	94±14	ND	ND
	ND N		4	29	0	10	10
Ni*	Mean	29	10.7±1.7	11.3±1.3	ND	6.8±1.9	2.1±0.2
	ND N		1	0	15	0	2
Cu*	Mean	8.1	3.7±3.6	4.2±0.9	16.9±7.8	2.0±0.2	2.1±0.4
	ND N		13	36	8	5	2
V[a]	Mean	6	ND	0.32±0.03	0.4	0.61±0.06	0.61±0.02
	ND N		15	39	14	7	8

Ti[a]	Mean	2	3.4±0.4	3.8±1.3	4.0	ND	ND
	ND N		13	42	14	10	10
Cd*	Mean	0.09	0.9±0.7	0.33±0.07	ND	ND	ND
	ND N		12	43	15	10	10
U	Mean	15	3.0	0.24±0.06	ND	3.2±0.3	1.2±0.4
	ND N		14	37	15	0	2

*marks hardness dependent value; hardness assumed as 50 mg/l of $CaCO_3$.

[a] British Columbia Approved Water Quality Guidelines 2016 Edition.

3.4 Discussion

3.4.1 Reserve in solid materials

Samples of the three main materials used in the construction of the Nikanotee Fen watershed were digested for quantification of metals content. The Ti, V and Ni concentrations in coke (159, 1062 and 389 mg/kg, respectively) were orders of magnitude larger than that of peat (50, 1.18, 0.79 mg/kg, respectively) or sand (37, 2.6, 1.7 mg/kg, respectively; Table 3.1). The observed reserves of Ti, V and Ni mark coke as a high potential for metal leaching. The high content of these elements in coke is a product of a selective industrial process designed to remove impurities from the bitumen during upgrading (Al-Haj-Ibrahim and Morsi, 1992; Squires, 2005; Bott 2010). Initially, bitumen is heated to 500 ^{0}C to decrease viscosity, large carbon chains break down to smaller ones and crude oil separates from heavier constituents (Squires, 2005; Bott 2010). This stage is also designed to remove metal impurities that interfere with the catalysts used in the following stages (Squires, 2005; Bott 2010), effectively enriching their concentrations in the end by-product. The separated solids settle and form petroleum coke while the crude oil continues to the next stage of purification (Squires, 2005; Bott 2010).

The composition of the coke will vary as a function of changes in the source layer and different extraction and coking practices (Squires, 2005). Generally, coke is mainly composed of carbon (~85%), S (~7%), metals and hydrocarbons (Squires, 2005; Chmelar, 2006; El-Din et al., 2011).

3.4.2 Metals in leaching experiment

The very large reserve of Ni and V in coke did not manifest in the leaching experiment (Fig. 3.3). The leaching experiment was conducted under anaerobic conditions with slight-alkaline to alkaline pH (chapter 2, section 2.3.3). Under these conditions the examined metals exhibited low leachability, <0.2% out of the total reserve, with the exception of Mn (Table 3.1; Fig. 3.3). Studies show that at pH=8 cationic metals' leachability is reduced as adsorption and precipitation is enhanced (Chuan et al., 1996; Matos et al., 2001). Chuan et al. (1996) also concluded that pH is more important in regulating metals' leachability than redox. Furthermore, although Fe-Mn oxyhydroxides will undergo dissolution under reducing condition, releasing surface sorbed metals, under alkaline conditions the released metals would complex with the reduced sulfur and form insoluble precipitates or adsorb to Fe-hydroxides (Chuan et al., 1996; Charlatchka and Cambier, 2000; Zheng and Zhang, 2011). V is most mobile under acidic pH and anoxic conditions (Wehrli and Stumm, 1989). Anoxic conditions and alkaline pH will substantially limit V mobility as dependent on the dominant species of V (Breit and Wanty, 1991; Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989). Therefore, V, other metals and sulfur speciation should be studied at the Nikanotee Fen watershed as part of regular monitoring to advance our understanding of the system and governing geochemical controls.

Additional limitation of leaching from the potential reserve may be found in the structure of the coke, which locks in potential contaminants within the coke matrix. The process that forms the coke is designed to remove impurities from the crude oil (Al-Haj-Ibrahim and Morsi, 1992; Squires, 2005). As the coke solidifies the impurities settle, blocking pores and smoothing the surface (Chen and Hashisho, 2012). For comparison, the image of raw coke used in the presented research shows that the surface of the coke used is covered with a deposit (Fig. 3.1b). Chen and Hashisho (2012) concluded that the explanation for lack of pores on the surface is clogging of pores by impurities (Fig. 3.1a). Zhang et al. (2015) found that raw coke had effectively no measurable micropore volume while mesopore volume was 0.026 cm^3 per one gram of coke. Furthermore, Karimi et al. (2013) reported that the surface area of raw coke from the same source was $0.2m^3/g$; this value was for the largest particle size range used (0.3-0.6 mm). For comparison, the smallest ranged used in this study was <6.35 mm and accounted for ~20% of the coke composition (chapter 2, section 2.3.2). The low micropore volume and smoothed, clogged pore spaces offer a low surface area from which metals can be leached.

The data gained in this experiment suggests that under the alkaline pH and anoxic conditions leaching of the examined metals is limited, on a timescale of two months. To strengthen our conclusions we sought to validate them through analysis of samples exposed to years of potential leaching, based on water sampled from the field.

3.4.3 Concentrations found at the Nikanotee Fen watershed

Similar to the leaching experiment, Mn concentrations were orders of magnitude higher than other examined elements (Fig. 3.3 and Fig. 3.4). Biological reduction of Mn provides part of a possible explanation since reduced Mn can be released from complexes (Lovley and Phillips, 1988). Additionally, high sulfate (SO_4^{2-}) concentrations are a probable contributor to elevated Mn concentrations in the coke field samples compared to the leaching results.

Puttaswamy and Liber (2012) found SO_4^{2-} acts a ligand, detaching metals sorbed to weak bonding sites on the surface of coke, increasing their concentration in solution. The average SO_4^{2-} concentration at sampling points in the coke layer of the Nikanotee Fen watershed was 1132 ± 118 mg /l (Kessel, 2016) with a concentration of 3.7 mg/l of Mn (Table 3.2). For comparison, the average SO_4^{2-} concentration found in coke treatment of the leaching experiment was ~125 mg/l (chapter 2, section 2.3.4) while the average Mn value was 0.51 mg/l (Fig. 3.4). The role of S as a control on trace metals, through complexation and precipitation in anoxic conditions is well known (Shotyk, 1988; Billon et al., 2001; Brucker et al., 2011) and could partially explain the results. Phillips and Chao (1977) found that coke contains 7.5% sulfur (weight basis) out of which 99.6% as part of organic molecules and 0.4% as inorganic pyritic mineral. However, tailings sand contains a large amount of SO_4^{2-} due to the addition of $CaSO_4$ to the tailings ponds to expedite settling of fines (Chalaturnyk et al., 2002). Since the upland is composed of tailings sand and is the aquifer for the fen, distributing the water through the coke layer (Price et al., 2011; Daly et al., 2012; Ketcheson, 2015), SO_4^{2-} is transported from it to the coke layer. Measured methane values in the Nikanotee Fen watershed (Nwaishi, 2016) indicate that the redox potential is low enough to allow for methanogenesis. Therefore, water in the coke layer of the Nikanotee Fen watershed likely contain a mix of SO_4^{2-} and S^{2-} due to sulfate reduction, although sulfur speciation was not done and is required for verification.

Similar to the leaching experiment, low field concentrations of V and Ni were found (Fig. 3.4), which is not consistent with their respective reserve in the coke. In bitumen, Ni is bound to organic molecules (Lewan and Maynard, 1982) thus limiting its leachability. Furthermore, S^{2-} reacts with Ni to form NiS precipitates (Billon et al., 2001). For V, the combination of alkaline anaerobic conditions and the V species in bitumen limits leaching. V species in bitumen are mainly Vanadyl (V(IV)), which is immobile in alkaline anaerobic conditions, and some vanadate (V(V)) which is the mobile and toxic form of V and is the dominant V form in alkaline, aerobic environments (Millson et al., 1966; Hocking and Premovic, 1978; Carpentier and Sandra, 2003; Ortiz-Bernad et al., 2004; Li et al., 2007; Wright and Kenneth, 2010). However, under the geochemical conditions expected in the fen V(V) may be biologically reduced to V(IV), which precipitates as a solid (Carpentier and Sandra, 2003; Ortiz-Bernad et al. 2004; Li et al. 2007; Wright and Kenneth, 2010). This process may effectively remove V resulting in undetectable concentrations (Carpentier and Sandra, 2003).

Zn concentrations were below detection limit in all field samples (Fig. 3.4). S^{2-} could control Zn concentration since Zn and S^{2-} form a ZnS precipitate (Billon et al., 2001). Although only SO_4^{2-} was analyzed in the system, in the anaerobic conditions of the saturated layers of the fen upland system part of the S would speciate as S^{2-} through biological reduction (Koch et al., 1990). Furthermore, Cu and Cd react with S^{2-} in anoxic sediments resulting in precipitates (Billon et al., 2001). Our results emphasize the importance of investigating the biogeochemical controls on metal mobility in the Nikanotee Fen watershed via S speciation and distribution. S dynamics at the fen-upland system are not well known and are currently being investigated. This information would provide insight on S control of metal and their fate in the system.

3.4.4 Comparison to guideline limits

To understand the meaning of the detected metal concentrations, values were compared to water quality guideline limits (ESRD, 2014; BC WQGs, 2016), if a few guidelines were available the strictest limit was chosen. Concentrations of Ti, V, Ni, Cu, Zn, Cd and U from both peat and coke in the Nikanotee Fen watershed were below the guidelines limit while Mn concentration was above the guideline limits (Table 3.2). Since the peat water samples were taken from the base of the peat layer directly overlaying the coke samples and since they were taken 3 years into the system's completion, the reduced concentrations seem to indicate removal of these elements from the water by the peat.

High Mn values in the coke layer and no detectable Mn concentration in the overlying peat (Table 2) suggest the peat is acting as a retarding layer. Peat is known to remove cationic metals from water through its high cation exchange capacity (CEC) at high pH (Crist et al., 1996). At a pH of 7 and above, CEC is the dominant form of metal removal rather than complexation with humic molecules due to a reduction in H^+ and an increase in negatively charged surfaces (Crist et al., 1996; Sposito, 2008). Furthermore, Crist et al. (1996) found a decreasing rate of sorption where Pb>> Cu>> Zn>> Mn >Mg; meaning that Zn, Cu and Pb have a higher affinity to bonding sites than Mn and Mg, and thus more easily displace other cations. However, optimal adsorption is pH dependent and varies for each metal; generally, pH values from 3.5 to 6.5 are considered optimal (Ho et al., 1995; Brown et al., 2000). The pH of the peat used in the Nikanotee Fen watershed is 7.4 (chapter 2, section 2.3.3); it is therefore likely that CEC is not the sole control on metal concentration. Lalancette and Coupal, (1972) concluded that high S content in peat favors removal of metals through the formation of low solubility metal-S^{2-} complexes, though this mechanism does not apply to Mn^{2+}. Smieja-Król et al., (2010) examined the behavior of Pb, Zn, Cd, Cu and Fe and found that metal chemistry in peat is controlled by mineral dissolution/precipitation due to complexation reactions with SO_4^{2-} or S^{2-}.

The number of bonding sites in peat is finite (Brown et al., 2000) and metals compete over available bonding sites (McLellan and Rock, 1987). Furthermore, high concentrations of Na^+ and Ca^{2+} reduce the adsorption capacity for other cations and may displace metals back to the solution due to larger affinity to the bonding sites (Shotyk, 1988; Crist et al., 1996; Sposito, 2008). Given the large concentration of Na^+ and Ca^{2+} in the Nikanotee Fen watershed (chapter 2, section 2.3.5), the adsorption capacity for metals is reduced, while the large concentration of S in the system (chapter 2, section 2.3.5) likely controls metals solution concentrations. Although the only metal that exceeds the guidelines was Mn, if it transported to the top 30 cm of the fen where the water table fluctuates, under the circumneutral pH and the periodic presence of oxygen (Nwaishi et al., 2016), Mn would form oxides, biotically and abiotically, and precipitate out of solution (Sposito, 2008). Thus, the risk from metals leaching from coke under the alkaline anoxic conditions detailed is considered low, including from Mn which will likely precipitate if transported to an oxic layer. It is important to note that this assessment holds true only if the examined geochemical conditions are constantly maintained. However, long term changes potentially increase the risk of enhanced leaching of metals. The tailing sand used to build the Nikanotee Fen watershed has low alkalinity (ranging between 21 to 40 mg/l of CO_3, (see appendix A.2) therefore; its ability to withstand pH changes is low. Considering the acidic rain pH in the AOSR and the constant downward flushing based on the gradients of the design the pH in the upland will eventually change from alkaline to acidic. This would mean that the coke layer will be flushed by acidic water. Though the coke buffering capacity is currently unknown, the alkalinity in the coke layer ranges between 36 to 57 mg/l of CO_3 (see appendix

A.2). Since pH impacts metal leaching more than redox (Chuan et al., 1996) an influx of acidic water would cause a release of metals.

When dealing with landscape reclamation it is part of the scientific communities' responsibility to consider the possible long-term changes that may occur tens and even hundreds of years past the construction of the systems, and how these changes may impact future generations. A change in the pH and release of metals might not be critical in the pilot scale but in a landscape scale it can have more severe implications. Furthermore, the companies are required to store coke in a manner that would allow easy access for removal as a potentially future fuel source (ERCB, 2009). This would mean that incorporation of coke into landscape reclamation might be not only questionable in terms of metal leaching but also in an environmental and economical term. With these considerations in mind, incorporation of coke in landscape reclamation cannot be recommended based on current knowledge. Nonetheless, the presented research does open a path to research safer storage conditions for coke.

3.5 Summary and conclusions

The goal of this research was to assess metal contamination risk due to incorporation of petroleum coke in the Nikanotee Fen watershed. Initial characterization found high total Ni and V concentrations in coke (Fig. 3.3). A leaching experiment showed Mn leached from coke along with small concentrations of Ni and V. The results could be explained by a combination of the chemistry of the examined metals under the slight alkaline pH, anaerobic conditions along with high concentrations of S and the physical properties of the coke which limit leaching by locking in potential leachates. Consequently, we conclude that coke can be stored under the alkaline, anoxic conditions with little risk of metal leaching. Field samples were gathered for comparison and the data showed that the average concentrations of Ti, V, Ni, Cu, Zn, Cd and U were under 8 µg/l while average Mn concentration was ~3800 µg/l in coke and ~1100 µg/l in peat (Fig. 3.4); comparison to water quality guidelines that showed all elements were below the guideline values with the exception of Mn, which was above it.

Although peat has a large cation exchange capacity, the high concentrations of Na^+ and Ca^{2+} limit metal bonding. Therefore, adsorption alone cannot explain the reduction in metal concentrations at the transition from coke to peat. Hence, under the alkaline pH and anoxic environment along with high concentrations of S, it is likely that S dynamics plays an important role as a control on most metals, except Mn, in the fen system.

In the Nikanotee Fen watershed, changes in pH and oxygen content as the water table fluctuates within the top 30 cm of the fen may cause transported Mn to form Mn oxides and precipitate, further reducing Mn solution concentration to a level below the guideline. Therefore, the large concentration of leachable Na^+ and Ca^{2+} (chapter 2, section 2.3.5) is likely to have more of an impact on the plants in the fen than Mn. Our results emphasize the importance of researching S, metals speciation and spatial distribution in the Nikanotee Fen watershed to improve our understanding of the long-term consequences of incorporating coke in reclamation projects in general and specifically with possible changes to the pH of the system which would increase metal leaching. The data suggest that incorporation of raw coke as a deep buried layer, under stable alkaline pH and anaerobic conditions, minimizes the risk of metals leaching and should be further explored as a low risk substitute for stockpiling.

3.6 Acknowledgements

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4 Transport properties of peat from the Nikanotee Fen watershed at the Athabasca Oil Sands Region, Alberta.

4.1 Introduction

The incorporation of large quantities of tailings sand into the design of the Nikanotee Fen Watershed as part of a novel attempt at landscape reclamation in the oil sands region, introduced a large pool of leachable Na, Ca and S (chapter 2, section 2.3.5). Near surface accumulation and potential impact of these solutes on the vegetation is controlled by the transport rate from the upland to the fen and the rate of flushing out of the system, which are currently under investigation (chapter 2, section 2.5). In constructed peatlands designed for oil sands reclamation landscapes, water quality is a concern due to incorporation of process-affected materials (Price et al., 2011; Daly et al., 2012). In this context a better understanding of the transport processes through peat and solute accumulation in the rooting zone of the fen is needed.

Peat is thought to attenuate solutes by mass exchanges between mobile and immobile phases (Hoag and Price, 1997; Rezanezhad et al., 2012), as well as by adsorption of reactive solutes (Rezanezhad et al., 2012; 2016). Peat has a continuous profile where deep peat layers are generally more decomposed (Clymo, 1983), as is peat subjected to drainage (e.g., Nwaishi et al., 2015). Moreover, fen peat and bog peat have different hydrophysical properties including water retention characteristics and bulk density (Boelter and Verry, 1977) and wettability (Caron et al. 2015). In addition to pore-scale effects, the systematic layered heterogeneity common in natural peatlands influences mixing and transport (Hoag and Price, 1995); in constructed peatlands this is destroyed (Fig. 4.1; Nwaishi et al., 2015), and flows become less predictable (Ketcheson, 2016).

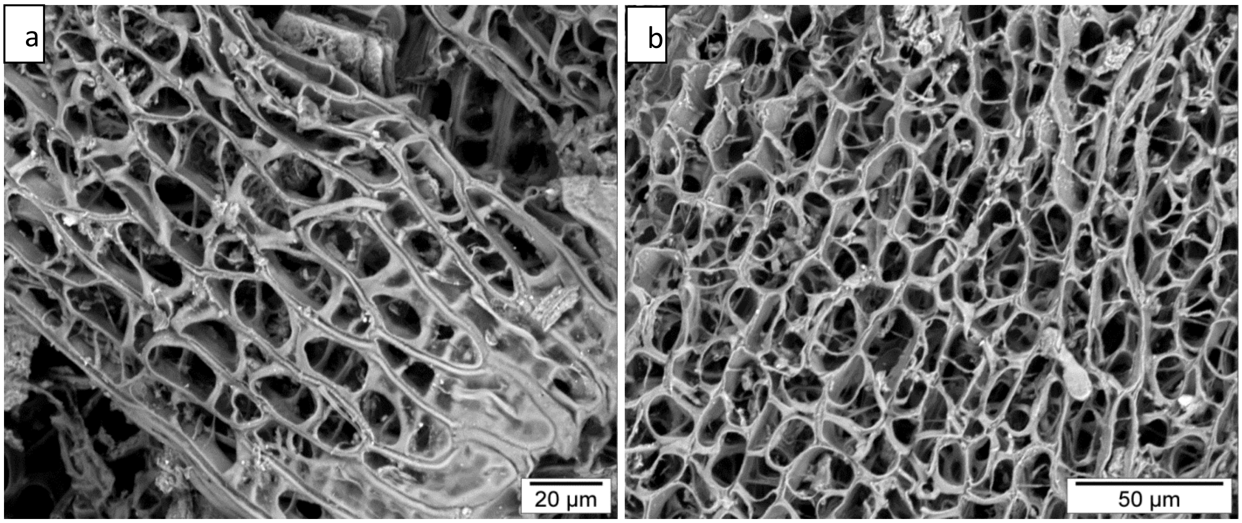

Figure 4.1 – Scanning electron microscope pictures of samples of the peat used in this study. a) Moss with hyaline cells, note cells with intact membrane at bottom right corner and larger pore spaces in bottom left and top right corners. b) Moss cells, Note that membranes are missing and a view through the skeleton is evident. Modified from Rezanezhad et al., (2016)

Solute transport in the subsurface may be subject to physical and chemical non-equilibrium (Nielsen et al., 1986) invalidating the use of the conventional convection dispersion equation (CDE) to simulate it. Physical non-equilibrium is thought to be a process of a heterogeneous flow field with spatial differences in hydraulic conductivity due to dead-end pores (Coats and Smith, 1964, Zurmühl and Durner, 1996), non-moving intra-aggregate water (Philip, 1968; Passioura, 1971), or stagnant water in thin liquid films around soil particles (Nielsen et al. 1986). In this mobile-immobile model (MIM, Coats and Smith, 1964; van Genuchten and Wierenga, 1976) the liquid phase is partitioned into a mobile and an immobile region. Convective-dispersive transport occurs only in the mobile zone, while solute transport into the immobile region is by diffusion, the rate of which can be determined by experiments and inverse estimation of transport parameters (Vanderborght et al., 1997). In chemical non-equilibrium models, it is assumed that sorption at the pore-water solid particle interface is kinetically controlled (Cameron and Klute, 1977; Nkedi-Kizza et al. 1989). Both non-equilibrium models may additionally account for chemical equilibrium adsorption (Toride et al. 1993).

To distinguish between the governing solute transport process, models can be fitted (e.g. with CXTFIT v2.0) to describe solute breakthrough experiments, which can be done for observations of reactive as well as non-reactive solutes (Nkedi-Kizza et al., 1984). In the notation of the convection dispersion equation in breakthrough experiments (as calculated in CXTFIT), retardation is strictly referred and attributed to equilibrium adsorption. As a factor (R) it is a function of bulk density, the adsorption isotherm, and volumetric water content (Toride et al., 1995). To date the only literature reports with experiments of NaCl breakthrough on saturated peat columns conducted in the laboratory are from Price and Woo (1988), Ours et al. (1997), Hoag and Price (1997) and Rezanezhad et al. (2012). Ours et al. (1997) speculate that observed prolonged tailings of NaCl are a result of a mobile and immobile zone influence with solutes diffusing into the immobile zone. However, neither batch adsorption tests with the potential to exclude kinetic chemical sorption are presented, nor were solute transport models fitted to breakthrough curves, leaving their conclusions tentative.

Hoag and Price (1997) successfully describe their observations with the conventional convection dispersion equation (CDE). However, they used a measured value of effective porosity (n_e) to calculate velocity (v) ($v=q/n_e$, where q is specific discharge), which results in a higher value than had it been calculated using total porosity, ϕ. In fitting breakthrough curves for non-reactive Cl^-, their retardation factor, R, reflecting v_{water}/v_{solute} was close to the ratio of ϕ to n_e, and they attributed (and modeled) the delay in solute transport to physical non-equilibrium processes whereby solutes were abstracted from the flowing solution by diffusive loss into the inactive pores (i.e. solute transfer from the mobile to the immobile region). This differs from the classical understanding where diffusion into the immobile zone is described by a kinetic constant, while R assumes chemical equilibrium of solutes with sorption sites (Coats and Smith, 1964; van Genuchten and Wierenga, 1976).

Therefore, we investigated if the choice of a physical mobile-immobile model can be substantiated for fen peat with *Sphagnum* remains. We approach this by testing various equilibrium and non-equilibrium models, by fitting them to observed NaCl breakthrough curves. For this Cl^- was used as it is generally uninvolved in chemical reactions in peat except in ultra-saline conditions (Ours et al., 1997), and its counter-ion, Na^+, was used because it is a prominent solute in the post oil sands mining landscape and of research concern (chapter 2, section 2.1).

The goal of the study is to expand our understanding of the transport processes in the vadose zone of the Nikanotee Fen by testing various transport models and scrutinizing the common assumption that mobile-immobile transport models best reflect the processes in saturated and unsaturated peat. To compare models, breakthrough curves with conservative and non-conservative solutes were conducted in the lab on saturated soil flow chambers, and model parameters were estimated using inverse modelling (CXTFIT). Comparison was based on a statistical analysis to investigate the information content of the data collected and a careful assessment of the underlying processes.

The resulting parameters and selected models were used to simulate unsaturated column experiments using HYDRUS-1D and compared to the observations, testing if the model selection and parameterization based on saturated experiments can be used to predict unsaturated solute transport. No inverse fitting was done for the unsaturated transport of the non-reactive solute, while inverse fitting for the reactive solute was only done for the unknown Freundlich-Langmuir parameters. A sensitivity analyses was then carried out to account for the potential error caused by using parameters derived from saturated transport to the unsaturated case.

4.2 Materials and methods

4.2.1 Research approach

Four soil physical experiments were conducted to estimate the hydraulic properties and solute transport characteristics of the fen peat material. The experiments were: 1) Transient evaporation; 2) Water retention characteristics using tension disks; 3) Saturated breakthrough; and 4) Unsaturated breakthrough. Initially, the peat was cleaned from woody plant material such as leaves and stems to ensure replicability. Furthermore, to reduce variations in moisture content between samples, the peat was thoroughly mixed before a sample was packed (see appendix A.3). Prior to experimentation samples were saturated from the bottom using ultra-pure water in small increments over a 24-hour period. All experiments were conducted at a target bulk density, (ρ_B; g/cm^3), of 0.122. All water used was 18.2MΩ·cm. Experiments were conducted in triplicates, except for the tension disk experiments which were conducted on 4 samples. For the determination of the solute transport properties, Cl^- was used as a non-reactive solute and Na^+ as a reactive solute. All breakthrough experiments were performed using a solution of 200 mg/l Na^+ and 300 mg/l Cl^- corresponding to values measured by Kessel (2016) in the Nikanotee Fen watershed under the peat layer. This solution was prepared by mixing 500 mg of NaCl (1.06404.055, ACS grade, Merck, Germany) per 1L of ultra-pure water.

4.2.2 Soil hydraulic properties

To determine the soil hydraulic properties, we conducted transient evaporation experiments (Schindler, 1980, Peters et al., 2015) for the retention properties and supplemented them with tension disk experiments. Tension disk experiments are considered to be a more reliable method to determine the unsaturated conductivity in the wet range (Klute and Dirksen, 1986), because transient evaporation experiments contain limited information at pressures heads between 0 and -60 cm for the unsaturated conductivity curve (Peters and Durner, 2008). Water retention and unsaturated hydraulic conductivity were determined with the tension disk experiments using 10 cm i.d. and 5 cm high peat samples at -2.5, -5, -7.5, -10, -15, -20, -25 cm pressure head (h; cm) steps, which was also the order in which the experiment was conducted. Outflow during each pressure step was monitored by scales with an accuracy of 0.1 g and logged at 1-minute intervals. The unsaturated hydraulic conductivity was calculated from the Darcy-Buckingham equation (Swartzendruber, 1969) based on the outflow discharge rate. The transient evaporation experiment was also conducted on the same samples to determine the retention properties using commercial UMS HYPROP devices (UMS GmbH, Munich, Germany). The water retention and unsaturated hydraulic conductivity data were used to inversely fit parameters as described in Peters and Durner (2008), using the unimodal van Genuchten-Mualem model combination (van Genuchten, 1980; Mualem, 1976; see appendix A.4) and the bimodal variant (Ross and Smettem, 1993). Estimation was done in R.3.2.1 (R Core Team 2015) with implementation of the differential evolution optimiser to minimise the sum of squared errors for the retention and hydraulic conductivity curves (Mullen et al., 2011).

Saturated hydraulic conductivity (Ks; cm d^{-1}) was determined with a constant head test (Freeze and Cherry, 1979) using flow-through chambers described below and a 1 cm hydraulic gradient.

Volumetric water content, θ, was determined gravimetrically as the difference between sample weight and the oven-dry mass for samples dried at 80°C until no difference in weight was measured (Gardner, 1986). Bulk density was determined as the ratio of dry weight to the original sample volume. Volumetric water content at saturation, θ_s, was assumed to be equivalent to the sample total porosity.

4.2.3 Soil solute transport properties

Saturated breakthrough experiments were conducted in 10 cm long, 10 cm i.d. Plexiglas^{TM} (785 cm^3) flow-through chambers, fitted at each end with 2.5x15x15 cm HDPE end-plates with silicon gaskets. A polypropylene fiber pad was placed between the plate and the sample to enhance the distribution of the solution beneath the sample (see appendix A.3). The NaCl solute source was a 20 L magnetically stirred solution reservoir pumped at a steady rate of 5 ml/min (0.064 cm/min) using a peristaltic pump (WT600-3J, LongerPump, China) and the outflow solute concentration monitored continuously (e.g. Skaggs and Leij, 2002). Prior to the breakthrough experiment, the samples were flushed with 2 chamber volumes of the NaCl solution to reduce potential changes to the pore sizes as a result of swelling (Price and Woo, 1988; Ours et al., 1997) or clogging due to flocculation. Subsequently, the samples were inverted and flushed with ultra-pure water (18.2MΩ·cm) for 6 chamber volumes to remove the solutes that were introduced. To determine sampling times and the end of the experiment an EC electrode (11388-372, SympHony, VWR, USA) connected to a portable meter (SP80PC, SympHony, VWR, USA) was used. The EC meter was calibrated using a 2-point calibration with

84 µS/cm and 1413 µS/cm conductivity calibration solutions (HI-7033 and HI-7031, respectively (Hanna instruments, USA). EC was checked every 5-10 minutes depending on the trend observed. Sampling was done with observed changes in EC and the experiment was continued until 1 hour after the outflow EC value was similar to the inflow. Samples were collected in 1.5 ml polypropylene micro centrifuge tubes (Z336769, Sigma Aldrich, USA) and kept frozen until analysed. Water samples were analysed for Na^+ and Cl^- at the Biogeochemistry Laboratory at the University of Waterloo using an ion chromatograph (IC) (DIONEX ICS 3000, IonPac AS18 and CS16 analytical columns). Apparatus blank corrections were done as described in Rajendran et al. (2008), where no transport model describing the apparatus blank was assumed but correction values were generated using hermite cubic splines.

4.2.4 Saturated solute transport models

Two different parametric solute transport model types were used to describe the observed breakthrough data of Cl^- and a third additional model for the Na^+ data. The first two consisted of the mobile immobile equation (MIM; Eq. 4.1 and 4.2; van Genuchten and Wagenet, 1989) and the classical convection dispersion equation (CDE; Eq. 4.3; van Genuchten and Alves, 1982, Nielsen et al., 1986), and the third the one-site adsorption equation (OSA; Eq. 4.5 and 4.6; van Genuchten et al., 1974, Nielsen et al., 1986) only used for Na^+.

The MIM for a non-reactive solute with instantaneous equilibration is given by

$$\beta\theta\frac{\partial c_m}{\partial t} = D\frac{\partial^2 c_m}{\partial^2 x} - v\frac{\partial c_m}{\partial x} - \alpha_{MIM}(c_m - c_{im}) \qquad \text{(Eq.4.1)}$$

$$(1-\beta)\theta\frac{\partial c_{im}}{\partial t} = \alpha_{MIM}(c_m - c_{im}) \quad \text{(Eq.4.2)}$$

where β is the ratio of the water content of the mobile region to the total water content, θ (L^3/L^3), C_m and C_{im} are the concentrations in the water phase of the mobile and immobile regions (M/L^3), respectively, D is the dispersion coefficient (L^2/T), v is the average linear pore water velocity (L/T), and α_{MIM} is the first order rate coefficient between the mobile and immobile region (T^{-1}).

The CDE is given by

$$\frac{\partial c}{\partial t} = \frac{D}{R}\frac{\partial^2 c}{\partial^2 z} - \frac{v}{R}\frac{\partial c}{\partial z} \quad \text{(Eq.4.3)}$$

Where c is the concentration of the total water phase (M/L^3), D is the dispersion coefficient (L^2/T), and R is a retardation factor for equilibrium adsorption, which for a non-reactive solute is typically assumed to be 1 (but see Hoag and Price, 1997). In the classical interpretation, R is related to the adsorption distribution coefficient, K_d (M^3/L^3), by $R = 1 + \rho_B K_d/\theta$. The MIM reduces to the CDE equation under certain conditions, which can be analysed by the dimensionless Damkohler number (D_a; Vanderborght et al., 1997, Eq. 4.4), given by

$$D_a = \frac{\alpha L}{v(1-\beta)\theta} \quad \text{(Eq.4.4)}$$

where L is the column length (L). Large D_a values indicate very fast equilibration between the regions. From inspection of Eq. 4.4 it becomes clear that $\lim_{\beta\to 1} D_a \to \infty$, and as α increases, D_a increases proportionally, signifying instantaneous equilibration, thus a differentiation between the two regions cannot be determined. For example, Parker and Valocchi (1986) could show that the CDE may also be applicable when a considerable part of the solute dispersion is caused by diffusion into the immobile region.

In physical non-equilibrium the attenuation of both reactive and non-reactive solutes is affected. However, if only the reactive solute shows long tailing, then it can be assumed that chemical non-equilibrium is affecting the flow process. In NaCl breakthrough experiments (Rezanezhad et al., 2012), only Na^+ showed long tailings in fen peat so that the physical non-equilibrium model should not be employed. For this case, first-order kinetic chemical non-equilibrium models may be chosen. One typical model for solute transport in porous media is the one-site adsorption equation which is an expansion of the CDE with the addition of a kinetic adsorption member and is given by:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial^2 z} - v\frac{\partial c}{\partial z} - \alpha_{OSA}[(R-1)c - \frac{\rho_B}{\theta}s] \qquad \text{(Eq.4.5)}$$

Where

$$\frac{\rho_B}{\theta}\frac{\partial s}{\partial t} = \alpha_{OSA}[(R-1)c - \frac{\rho_B}{\theta}s] \qquad \text{(Eq.4.6)}$$

where s is the kinetically sorbed concentration to the solid (M), and α_{OSA} is the first order rate coefficient between dissolved and adsorbed concentration (T^{-1}) which has been found to be a function of pore water velocity and cannot be derived by batch experiments individually (Nielsen et al., 1986).

Following the traditional approach for solute transport parameterization in peat, we initially assumed the MIM model and compared it with the performance of the CDE for the non-reactive solute. For Na^+, transport parameters were additionally estimated with a one-site chemical adsorption model. The data used for the fitting were averages of three replicates. Parameterization of the model was done with CXTFIT (V2.0; Toride et al., 1995), which minimises the least-squares. We estimated the following parameters: v and D for the CDE, v, D, β, and α_{MIM} for MIM, and R and α_{OSA} for the OSA model. The estimated D and v from the Cl^- data fit was used for the Na^+ simulations since dispersion is a physical material property, and R can only be determined if v is fixed from knowledge of a conservative solute experiment. Using various starting values, we ensured that the global minimum was found. CXTFIT calculates the variance-covariance matrix, which is required for the calculation of the standard errors of the parameters and the parameter correlation matrix.

The root-mean-squared-weighted error was used as an index for model performance calculated for each of the tested models (Eq. 14 in Weber et al, 2016). The corrected Akaike Information Criterion (AICc; Eq. 2 in Ye et al. 2008) was used as a method of model comparison where the model with the smallest AICc is to be favored. It is a statistically robust and commonly used index to compare models in soil physics (e.g. Weber et al., 2016).

4.2.5 Unsaturated Column Experiment

The unsaturated solute breakthrough experiments were designed as six steady state evaporation columns 23 cm high and 10 cm i.d. (Fig.4.2). Peat samples were placed in a column constructed with a grooved HDPE base plate with an inlet, a silicon washer and polypropylene fibre pad and open at the top (see appendix A.3). The columns were slowly saturated from the bottom in small increments over 48 hours to minimize trapped gas bubbles. Once saturated the columns were flushed with 2 column volumes with the NaCl solution to reduce potential changes in hydraulic properties, as previously described. This was followed by flushing 6 column volumes of ultra-pure water (18.2MΩ·cm) to remove the Na^+ and Cl^-, with the water overflowing from the top of the sample. Flushing of Na^+ did not remove all present concentrations, resulting in 40 mg/l of Na^+ remaining in the time 0 samples taken at the bottom 8 cm of the column. Nevertheless, these concentrations were accounted for in the HYDRUS simulation. Columns were then drained overnight with 0 cm pressure head at the bottom of the sample, and connected to a Marriot device containing ultra-pure water. The water table was set to the base of the peat column, and the columns were left to settle for 11 days, after which the columns were instrumented with the soil tensiometers and water samplers (further details below).

Each Marriot device was fitted with a low flow 12-volt mini water pump to circulate the water within it for 5 minutes every two hours, to prevent solute stratification. Three Marriot devices were filled with an 8.9 mM solution of NaCl as treatment and three with 18.2MΩ·deionised water. The columns were fitted with 4 unsaturated soil water samplers at 2.5, 7.5, 12.5 and 17.5 cm above the water table (19.21.05, Rhizon, Rhizonsphere, Germany), and with 2 two tensiometers filled with ultra-pure water at 10 cm (LM) 23 cm (UM), to determine if the water pressure deviated from hydrostatic conditions (see appendix A.5). Tensiometers were composed of a porous clay cup and a flexible silicon tube, which was open to the atmosphere. The experiment was run for 120 days; evaporation was calculated based on changes to the water level in the Marriot device (see appendix A.5). The experiment was conducted in a room with controlled humidity maintained at ~45%, assisted by a fan to mix the air in the chamber. Relative humidity (RH) and temperature were measured every 10 minutes (ECT, Decagon, USA) (see appendix A.5).

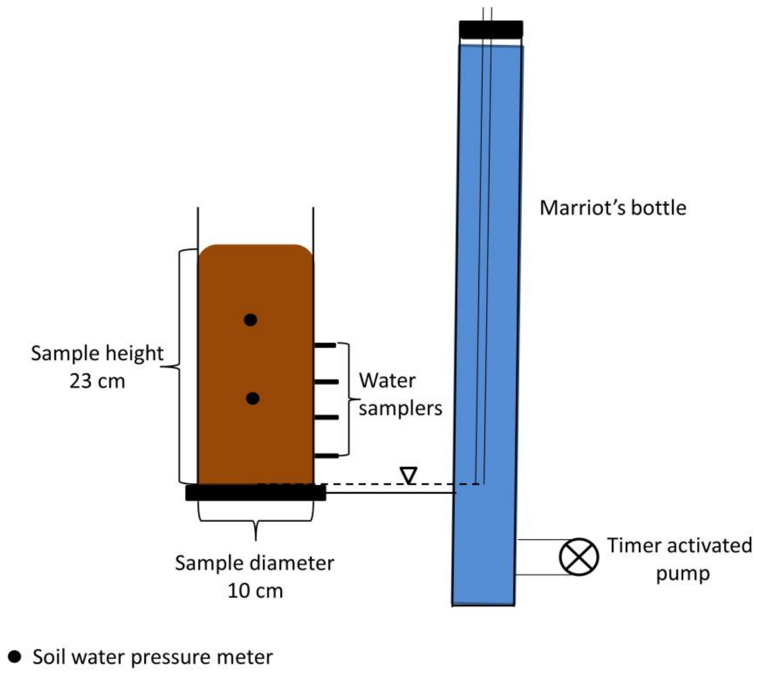

Figure 4.2 – Unsaturated column experiment column and water reserve setup.

NaCl solution was introduced at the base of the column and drawn upwards by evaporation. Marriot devices were attached to supply water over the bottom boundary for each column. The pressure head at the lower boundary was fixed to a pressure head of 0 cm for the duration of the experiment. Daily measurements of the water level in the Marriot were measured with a measuring tape, and the evaporative water flux over the upper boundary was calculated by dividing the water lost by the surface area of the column (see appendix A.5).

Pore-water samples were taken weekly from each sample height through the Rhizon samplers. On average, 5.5 ml of water was drawn from each sampler using a dedicated 30 ml polypropylene syringe (Z683647, Sigma-Aldrich, USA). To insure equal pull on each sampling point, 6x4x4 cm HDPE spacers were fabricated and placed within the syringe body and piston. Only samples from time steps 0, 21, 42, 63, 84 and 120 days were analysed. After the experiment ended the cores were frozen then sliced to ~2 cm thick sections using a band saw. Sections were measured with callipers, weighed and placed in pre-weighed, food grade and heat resistant bags. The slices were than thawed and ultra-pure water, twice the weight of the slice, was added to extract the solutes and placed on a table shaker (MaxQ 3000, Thermo scientific) for 48 hours. All samples were frozen until analysed for Na^+ and Cl^- via IC at the Biogeochemistry Laboratory at the University of Waterloo (DIONEX ICS 3000, IonPac AS18 and CS16 analytical columns). Results were adjusted to account for the dilution effect of the added water.

4.2.5.1 Numerical Simulations and sensitivity analyses

The steady state unsaturated evaporation experiment with solute transport was simulated with HYDRUS-1D (Simunek et al., 2008), which numerically solves the Richard's equation for water flow and the solute transport equations. For the water flow, the soil hydraulic properties are the necessary input and were parameterized with a unimodal van Genuchten-Mualem equation using data collected in the tension disk experiments and transient evaporation experiments. The model domain represented the 23-cm high column with a spatial discretization of 0.5 cm.

The lower boundary condition for the water flow was a constant zero pressure representing the water table. The upper boundary condition was a flux boundary based on measured evaporation rates. For the solute transport, the lower boundary was a fixed concentration in the liquid phase and the upper boundary condition was a zero flux. To account for the soil solution sampling (that would otherwise lead to a misrepresentation of water flow and solute transport), we used the Root Water Uptake function in HYDRUS by specifying an individual root at the height of each of the four Rhizon samplers. The total water volume extracted per sampling day was taken to be equal at each root node. The root water uptake model (Feddes et al., 1978) assumes no salinity stress, no pressure dependent reduction of given water uptake quantity, and a quasi-infinite maximum allowed concentration for passive root solute uptake.

Dispersion is dependent on the average linear velocity, which in turn is dependent on the water content (Perkins and Johnston, 1963). To date, HYDRUS does not account for changes in D in unsaturated flow as a result of changing water content in the profile; therefore, a sensitivity analysis of D in the unsaturated model was done to assess its influence on the model performance, when based on a value from a saturated experiment. To gauge the range of values for the sensitivity analysis, a calculation of the change in D was performed using data gathered from the unsaturated columns. The calculation used the equation for D in capillary flow under unsaturated conditions in soils as a function of v by Fried and Combarnous (1971) (not shown). The equation connects D to changes in water content, C/C0 over time and the distance of the measurement from the source point. As such it allows calculation of changes in D due to changes in water content. Comparison of the calculated values provided with a range of change in D. Calculations indicated that the change in D ranged from 8% to 15%. Therefore, to add extra range the sensitivity analysis for the HYDRUS model was performed using ±20% and a ±100% change in D.

4.3 Results and discussion

4.3.1 Soil physical properties

The bulk density and porosity of the peat used in the various experiments was similar (Table 4.1). The retention curve does not have the classical shape that indicates a difference between active and inactive pores (cf. Rezanezhad et al., 2016). Measured water retention and hydraulic conductivity data closely fit the van Genuchten-Mualem unimodal and bimodal models (RMSE of 0.03 and 0.01, respectively; Fig. 4.3; Table 4.2). While the lower RMSE and AICc values (Table 4.2) for the bimodal model indicate a closer fit, it requires three additional parameters to do so. Furthermore, the estimated Ks value of the bimodal fit (454 cm/d; Table 4.2) is much greater than the measured value (100 cm/d; Table 4.1), or that predicted by the unimodel model (106 cm/d: Table 4.2). Given the simplicity of the unimodal approach and the closer fit to Ks, it was considered to be the better choice for simulation.

Table 4.1 - Soil physical and hydraulic properties of prepared peat cores from different experiments. Values are averages and standard errors. Porosity was calculated using particle density from Ketcheson and Price (2016).

Samples origin experiment	n	ρ_B (g/cm^3)	K_s (cm/d)	Porosity
Saturated breakthrough	3	0.12±0.002	99.7±0.021	0.93±0.012
Unsaturated columns	6	0.12±0.005		0.93±0.026
Retention	4	0.12±0.004		0.93±0.026

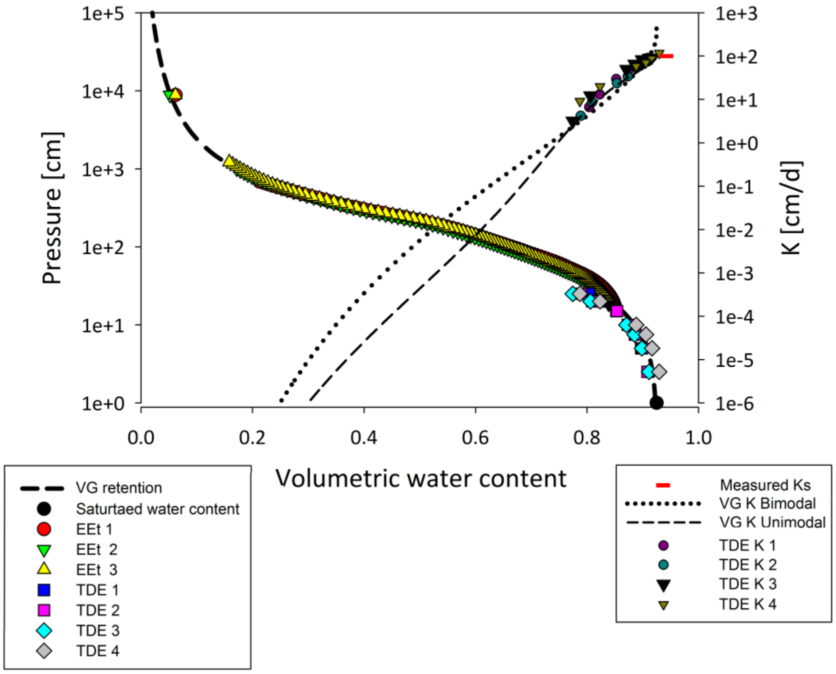

Figure 4.3 – Soil water retention and hydraulic conductivity curves with measurement results of the transient evaporation experiments (EEt) and Tension Disk Experiments (TDE) and parameterizations for the unimodal and bimodal van Genuchten-Mualem model. Negative pressure was used for the retention experiment.

Table 4.2– Parameter results for the soil hydraulic properties functions of the unimodal and bimodal functions; the parameter names are explained in the text.

model	θ_r	θ_s	a_1	n_1	K_s	τ	w_2	a_2	n_2	n_p	RMSE θ (h)	RMSE $\log_{10}$ K(h)	AICc
	-	-	1/cm	-	cm/d	-	-	1/cm	-	-	-	cm/d	-
uni	0	0.93	0.015	1.6	106	10	-	-	-	5	0.03	0.19	-342
bi	0	0.93	0.054	1.4	454	7.6	0.52	0.005	2.2	8	0.01	0.16	-374

4.3.2 Saturated breakthrough experiment

Cl^- breakthrough started around ~60 minutes with C/C_0=0.5 arriving 97 minutes from the start of the experiment (Fig. 4.4). Complete Cl^- breakthrough (C/C_0=1) was achieved after 300 min. Similar to Cl^-, initial Na^+ breakthrough began ~60 minutes from the start of the experiment (Fig. 4.4). However, C/C_0=0.5 was not achieved until ~250 minutes, with only ~0.85 breakthrough at the end of the experiment that had prolonged tailing, indicating non-equilibrium process. The EC curve is similar in shape to that of Cl^-, but took longer to reach the full breakthrough. Attenuation of Na^+ compared to Cl^- is evident by the greater time until $C/C_0=0.5$ (Fig. 4.4), is attributed mainly to the high adsorption capacity of peat (Ho and McKay, 2000). In contrast, Cl^- attenuation in peat is mainly due to mechanical dispersion and diffusion into dead-end pores and not adsorption (Price and Woo, 1988). The dissimilarity of the EC breakthrough curve to that of Na^+ (Fig. 4.4) demonstrates the limitation of using EC as an indicator for reactive solutes. This limitation is due to enrichment of ions in the solution from the soil and cation exchange with the medium, which changes the solution concentration of the cation of interest; therefore, EC can be a good estimator for non-reactive solutes but is limited as an indicator for cation transport (Olsen et al., 2000; Vogeler et al., 2000).

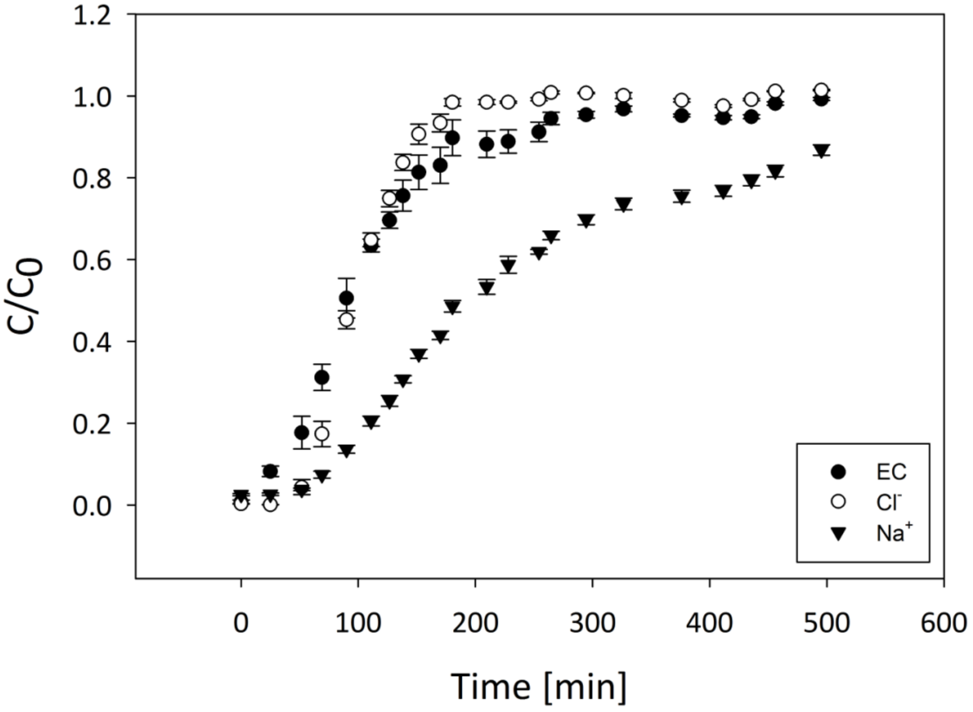

Figure 4.4 – EC, Cl^- and Na^+ corrected saturated breakthrough curves in saturated peat over time. Each point is an average of 3 samples, error bars are standard error of mean. Errors were not accounted for in the fitting.

4.3.3 Unsaturated column experiment

The calculated evaporation rate of the experiment was 3mm/day (not shown, see appendix A.5). As expected, Cl$^-$ was transported faster than Na$^+$ as evident by the more rapid rise of Cl$^-$ in the peat profile (Fig. 4.5). C/C$_0$=0.5 of Cl$^-$ reached 7.5 cm above water table within 21 days (Fig. 4.5a) and by 42 days C/C$_0$=0.5 reached 17.5cm (Fig. 4.5a). Complete breakthrough (C/C$_0$=1) of Cl$^-$ was achieved between 63 to 84 days from start of experiment (Fig. 4.5a).

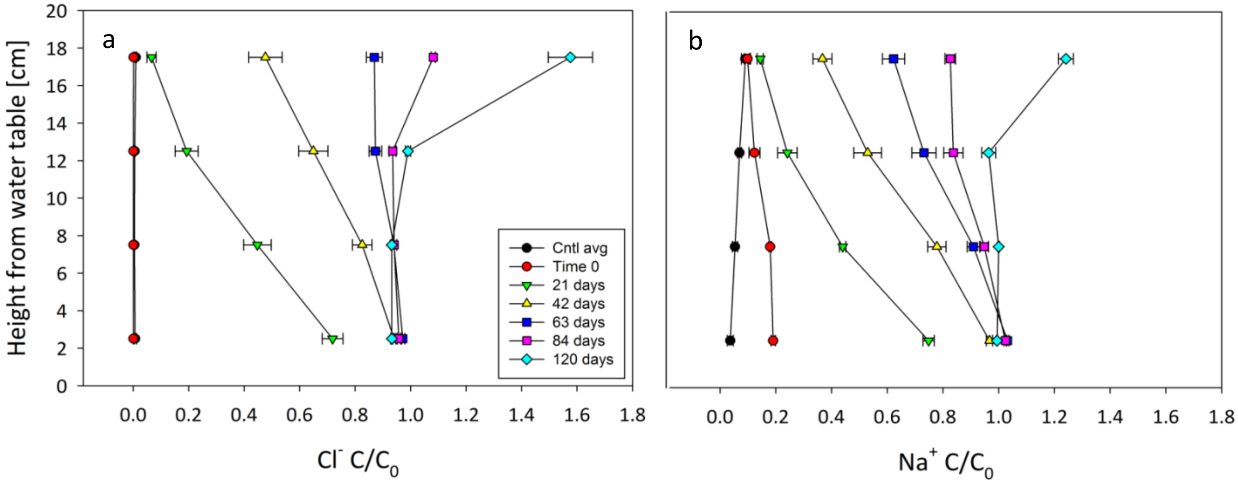

Figure 4.5 - Breakthrough curves of solutes in the unsaturated columns profile. a) of Cl$^-$, and b) of Na$^+$. Values presented are averages and standard errors. "Cntl avg" represents the average of control measurements; for this aim, all measurements in a specific height were averaged with each point representing 18 measurements. For the treatment, each point is an average of 3 measurements. Each treatment curve represents a different sampling time from start of experiment. 0 cm is the water table location.

Comparably, Na$^+$ C/C$_0$=0.5 reached 7.5 cm within 21 days (Fig. 4.5b). After 42 days, the C/C$_0$=0.5 was located between 12.5 to 17.5 cm from the water table (Fig. 4.5b). Complete Na$^+$ breakthrough occurred later than did Cl$^-$, sometime after 84 days but before 120 days (Fig. 4.5b). The accumulation of both elements above inflow concentrations (C/C0>1) at 17.5cm after 120 days (Fig. 4.5b), indicates evaporative accumulation occurred as water molecules left the column while solute molecules remained (Tsypkin, 2003). Therefore, evaporative accumulation enhances the breakthrough rate as ions remain in the soil while water evaporates; thus, producing a faster accumulation rate than if the breakthrough was estimated using a saturated flow system where the solutes would leave the system with the carrying solution. Nevertheless, this effect is a basic product of evaporation controlled transport (Elrick et al., 1994; Tsypkin, 2003).

4.3.4 Simulations

4.3.4.1 Saturated transport fitting

For all models, the fitted parameters and associated uncertainties, AICc, and RMSE values are given in Table 4.3. The CDE and MIM model for Cl^- fit the data well (Fig. 6a), and have identical RMSE (0.032 mg/l). However, the AICc is slightly more favorable for the CDE fit, and the MIM model estimated parameters (v, D and β) had much larger coefficients of variation, with β varying by 1510% (Table 4.3). During fitting, α_{MIM} ran into the CXTFIT internal upper boundary, further suggesting that the MIM is less suitable than the CDE transport model for this type of fen peat. Also, the MIM has two additional parameters than the CDE model, which makes the simpler CDE model preferable (Cavanaugh 1997).

The Peclet number for the fitted Cl^- breakthrough data, which is the ratio of advective vs diffusive transfer, was 33.9. In systems with values > 2 diffusion is considered negligible (Huysmans and Dassargues, 2005). Moreover, with $\beta \rightarrow 1$ (Table 4.3), the Damkohler number, D_a approaches infinity, so that the equilibration between the mobile and immobile zones is considered instantaneous (Wehrer and Totsche, 2005; Vanderborght et al., 1997). In other words, D_a indicates the system does not require the MIM to achieve a fit, but rather the simpler CDE concept applies. The significance of this is that the physical non-equilibrium approach may be excluded for these samples. A few reasons can provide a possible explanation for lack of a significant immobile phase. One reason is that the peat used in the Nikanotee Fen watershed was sedge peat containing only small amounts of *Sphagnum* moss (Nwaishi et al., 2015). It is the *Sphagnum* mosses that contain the hyaline cells, which are the main structure of the dead end pores (Hayward and Clymo, 1982). Therefore, with only a small part of the Nikanotee Fen watershed peat originating from *Sphagnum*, the potential for dead end pores was small compared to peat that originates mainly from *Sphagnum* moss. Additionally, evidence found in the SEM scans of the peat used in this study (Fig. 4.1), shows that the cell walls have decayed, with only the skeleton of the cell remaining, while the skeleton itself hasn't yet collapsed. These results contradict the hitherto assumption that solute transport in peat has to be simulated using the MIM, but rather asses the use of the assumption based on gathered data. For example, the retention curve data can indicate the existence of two flow phases, which may indicate whether MIM is present or not.

As the CDE model provides a good description of the saturated Cl^- breakthrough, and physical non-equilibrium can be discarded as the underlying process, the non-equilibrium effect observed in the Na^+ breakthrough (Fig. 4.6b), must be due to chemical processes. Having shown that the MIM is not parsimonious in its parameters and the robust estimates of v and D for the CDE, these were fixed when fitting the remaining model parameters of the CDE and one-site adsorption model for Na^+. First, the CDE was fitted with R to the Na^+ data; the resulting curve shows that equilibrium adsorption does not fit (Fig. 4.6b). In comparison, the one-site adsorption model fit well (Fig. 4.6b) and had a lower RMSE and a considerably lower AICc value (Table 4.3). Based on the estimated R-value of the one-site adsorption model, the K_d value of Na^+ was 15.6 l/kg. The parameters from the CDE for Cl^- and from one-site adsorption for Na^+ were then used for the HYDRUS simulation of the unsaturated columns.

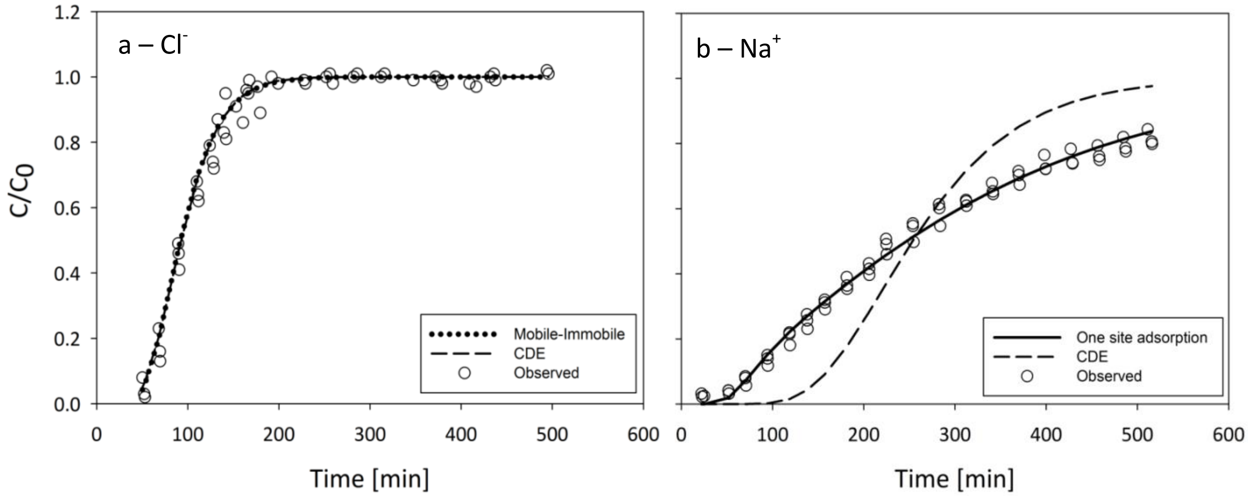

Figure 4.6 –Breakthrough curves of observed values and fitted models. a) of Cl^-; b) of Na^+.

Table 4.3 – Estimated saturated transport parameters and the models' goodness of fit data. N.A. = not applicable. Estimated values are presented with a standard error, percentages in brackets are the coefficient of variation.

Solute	Model	v	D	R	β	α	RMSE	AICc
		cm/min	cm^2/min	-	-	1/min	(mg/l)	(-)
Cl^-	MIM	$9.81*10^{-2}$ (91%)	$6.66*10^{-2}$ (19%)	fixed to 1	1.00 (1510%)	$6.05*10^{-1}$ (0%)	0.032	-406
	CDE	$9.79*10^{-2}$ (1%)	$6.66*10^{-2}$ (7%)	fixed to 1	N.A.	N.A.	0.032	-408
Na^+	CDE	fixed	fixed	2.65 (3%)	N.A.	N.A.	0.145	-229
	OSA	fixed	fixed	3.07 (1%)	N.A.	$6.71*10^{-4}$ (3%)	0.024	-443

4.3.4.2 Unsaturated column simulation

The HYDRUS predictions of solute concentrations at the four observation points were good for both solutes (Fig. 4.7), even though the solute transport model parameterization was based on the saturated experiments. Plotting of the concentrations from the solute extractions for the upper part of the core at the end of the experiment reaffirmed the models' generally good fit for both solutes (Fig. 4.7), although in both cases the models underestimate the measured concentration at the very top of the soil profile (Table 4.4).

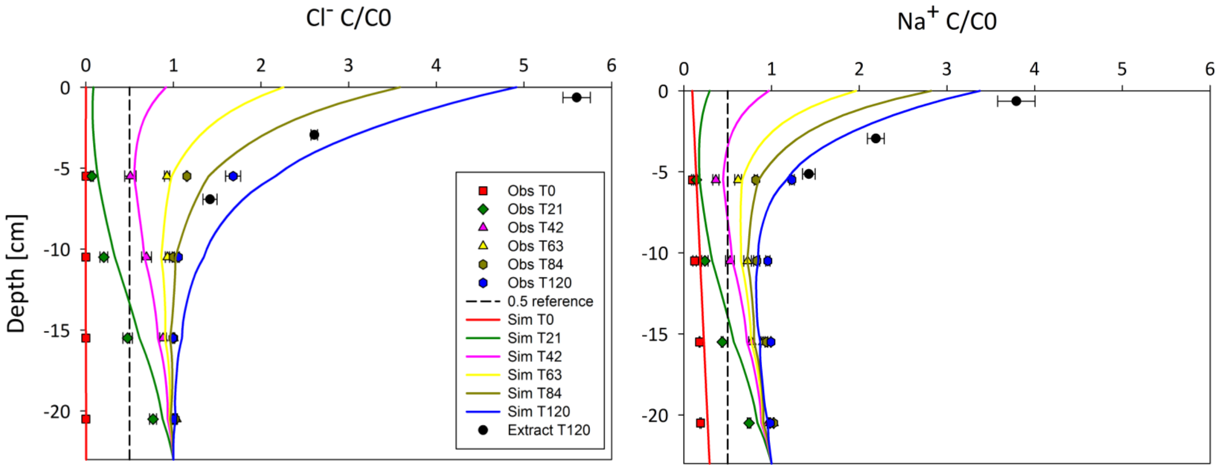

Figure 4.7 - Observed values from the unsaturated column experiment vs simulated values of a) Cl$^-$; and b) Na$^+$. Observed values are averages and standard error, n=3. T stands for time and the number that follows is the number of days. Extract T120 represents values measured via extraction as part of post experiment processing. Zero (0)0 depth marks the surface of the column. Dashed reference line marks C/C0=0.5.

Table 4.4 - Unsaturated transport parameters used in or estimated by HYDRUS and models' goodness of fit data. -- = not applicable. Estimated values are presented with a standard error. Diff. W is the molecular diffusion coefficient of the solutes.

	Cl^-	Na^+
D [cm²/min]	$6.81*10^{-2}$	$6.81*10^{-2}$
Kd [l/kg]	0	15.6
***Diff.W [cm²/min]**	$1.22*10^{-4}$	$7.98*10^{-5}$
α [1/min]	--	$1.11*10^{-2} \pm 9.8*10^{-3}$
β	--	$1.00 \pm 1.24*10^{-1}$
RMSE [mg/l]	15.65	10.19

* taken from Appelo & Postma (2004).

Given that the dispersion coefficient for the unsaturated modeling was based on measurements in the saturated flow-through chambers, a sensitivity analysis was performed with HYDRUS to determine its impact on the simulations. It indicates that a ±20% change in the dispersion coefficient resulted in a ±1.2% and a ±4.1% change in the final concentration of Cl^- and Na^+, respectively (Fig. 4.9). Further, an analysis with a ±100% change in the dispersion coefficient altered the final concentrations by -5% to 6.5% for Cl^- and by 9% to -17% for Na^+. The analysis demonstrates unsaturated transport is not highly sensitive to changes in the dispersion coefficient under the experimental conditions used. Furthermore, since the differences in water contents were not large, ranging between 0.93 at full saturation to 0.84 at the top of the column, the dispersion coefficient probably did not vary a lot. Coupled with the model's insensitivity to dispersion coefficient, using the parameter derived from saturated transport experiments had little impact on the simulation.

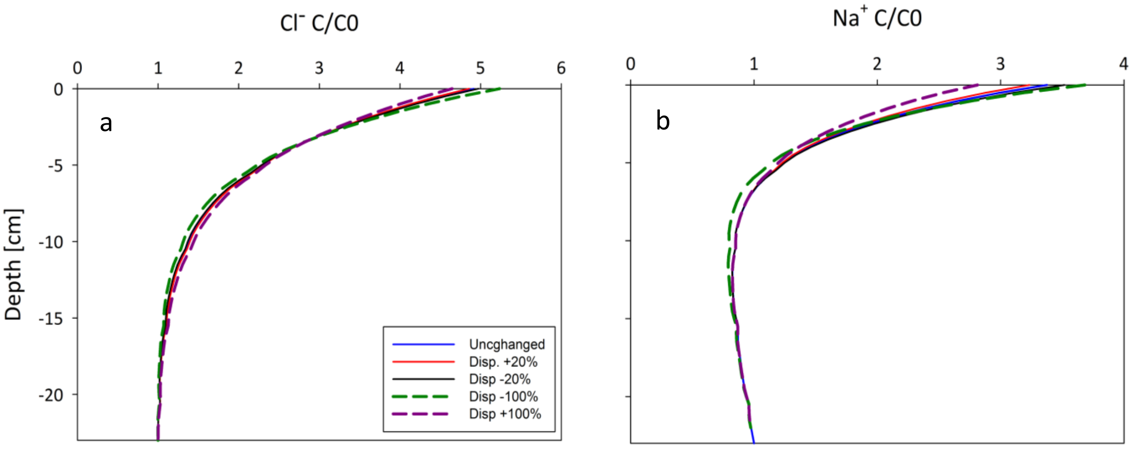

Figure 4.9 – Sensitivity analysis of unsaturated transport for changes in the dispersion coefficient. a) in Cl^- transport, b) in Na^+.

4.4 Conclusions

Saturated breakthrough experiments were conducted in the laboratory using conservative and reactive solutes. With this, the physical equilibrium concept to describe solute breakthrough in fen peat was tested as applicable. Water retention data measured did not contain evidence of a physical dual porosity structure. Based on inverse modelling and robust statistical evaluation, the MIM model was found to be an over-parameterization, since very good results were found using the simpler CDE for Cl^-. For this reason, it can be deduced that the Na^+ attenuation in the fen peat is chemically based, as the physical non-equilibrium (i.e. MIM) approach would have had an effect on both solutes. Na^+ showed distinct chemical non-equilibrium adsorption process, which could be described using the one-site adsorption model, and still fulfilling the requirement of parsimony.

Thus, further experiments under different initial and boundary conditions and sample sizes are required to strengthen and validate our results. Additionally, adsorption-desorption experiments would allow better accuracy by reducing the need to inversely estimate solute reaction parameters. The use of EC as an indirect measurement for a reactive solute will result in overestimation of breakthrough if the solute interacts with the solid phase.

This research implies that automatically assuming mobile and immobile regions in peat is incorrect. The sedge peat with remnants of *Sphagnum* moss used in the Nikanotee Fen watershed (Nwaishi et al., 2015) had limited potential of containing dead end pores, due to the low content of moss with hyaline cells. Furthermore, evidence suggests that the peat used in the Nikanotee Fen watershed has decayed enough to lose the cell walls but not enough to break the cell skeleton, and is likely why the peat lacks the classically assumed MIM regions. The decomposition may have been enhanced by aeration of the peat in the donor fen (Nwaishi et al., 2015). Additionally, it is concluded that transport parameters gathered in saturated breakthrough experiments can be used to simulate transport in slightly unsaturated media under near steady state conditions. Data gathered show that the accumulation of solutes via evaporation causes concentration to rise quickly above the initial concentration.

To further understand the rates of the evaporative accumulation, a more complex numerical transport model including flushing due to precipitation and runoff, using the parameters reported in this study along with various weather scenarios should be done. Scaling issues require that parameters are measured in the field site to drive a site scale model. However, just as this work added to our understanding of the peat used to construct the Nikanotee Fen watershed, a flushing study will widen that understanding further. The results are in contrast to the commonly accepted MIM behavior of peat samples. The significance of this is that while reactive solutes may be heavily attenuated in peat, conservative solutes are not necessarily retarded (Hoag and Price, 1997). In this case the degraded structure of the peat (Fig. 4.1) eliminated many of the enclosed spaces commonly visible is less decomposed *Sphagnum* peat (see Hoag and Price, 1997; Rezanezhad et al., 2016).

While these results are valid for the described boundary conditions and initial conditions, the fate of salt accumulation is not clear when regarding more natural conditions such as complex meteorological evapotranspiration-precipitation cycles, with, for example, surface inundation and overland flow export of solutes. Additionally, different salt concentration levels at the lower boundary of the experiment were not investigated, which has been documented in the case of the Nikanotee Fen watershed (Kessel, 2016). While the simulated water contents in the steady state evaporation experiment showed a small range (0.84-0.93) close to saturation, they were not verified with gravimetrically determined water contents, nor do they necessarily represent all water contents typical to the field. As a first assessment of the effect D has on salt accumulation, a synthetic parameter sensitivity analyses was carried out for Na^+. However, the effect of water content and velocity on the type of underlying transport process (saturated and unsaturated) has not been shown. Considering the complex hydraulic retention and conductivity properties of *Sphagnum* mosses and peat, it is conceivable that a wide range of tested water contents could affect the choice of the underlying transport process. Additionally, the experiment was carried out under steady state conditions, unlike the complex meteorological patterns in the field. Finally, the implications for reclamation projects are that if one of the goals is to enhance solutes attenuation, the origin and composition of the peat, its water retention properties along with its decomposition state should be characterized as not all peats will perform equally. From the industry perspective, choosing and peat with dead end pores would allow a potential for significant attenuation.

4.5 Acknowledgements

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5 Summary

This thesis represents an interdisciplinary evaluation of: a) the potential contaminants, both major ions and trace metals, that were introduced into the Nikanotee Fen watershed through the incorporation of locally available materials into the design of the system; and b) the transport properties of the fen peat to understand the potential accumulation of solutes at the top of the fen. The data gathered represent a first comprehensive effort in the understanding of the implications of incorporation of excavation, extraction and upgrading affected materials in the novel reclamation of a post-mined landscape that is the Nikanotee Fen watershed. As such, this work advances our knowledge of the effect of incorporation of the construction materials in the design.

Chapter 2 presented a detailed characterization of the elemental composition of the main building materials and the leachable pool of inorganic ions. By considering the design of the system along with quantification of the leachable elements within them, the research indicates that large leachable pools of sulfur, sodium, calcium and magnesium exist in the system. These pools are located mainly in the constructed upland and originate from the incorporation of tailings sand in the design. Smaller solute pools were also found in the underdrain layer (petroleum coke) and in the fen (peat). However, these pools are negligible when compared to the large pools in the upland. The fate of these pools are determined by the transport rate, and accumulation rate which in turn are determined by the difference between solute input from the upland and surface outflow, flushing out solutes. Since the fen-upland system water egress is primarily by evapotranspiration, evapo-accumulation of solutes on the surface may occur impacting the plant community towards a salt tolerant one. Mosses are less likely to survive, and since they are more resistant to decomposition than sedges, the long-term carbon accumulation rate of the fen may be affected.

Chapter 3 explored the risk assessment of incorporation of petroleum coke in the design. This goal was achieved through material composition analysis, leaching experiments and comparison to field samples. The data indicated that a large reserve of metals exist in the coke. However, under the expected geochemical conditions of alkaline pH and anoxia, the metals examined, with the exception of Mn, were not found to be substantially mobile and were below strict fresh water quality guideline limits. The limited leaching was due to several factors including the chemistry of the metals under the specific geochemical conditions, the encapsulation of metals within the coke matrix due to its formation process, the limited surface area for interactions and the existence of large concentrations of sulfur. These factors combined control the potential leaching and solution concentrations. Based on the data the risk of incorporating raw petroleum coke in the design, under the existing conditions is considered minimal. However, long term changes in pH in the upland may cause a water flux with acidic pH to the coke layer. This in turn, can cause enhanced leaching of metals, with possible consequences to the environment, and human health. If coke is used extensively in landscape reclamation, recognition of the potential release of metals must be considered in the design, regarding flow pathways and source-water pH. Furthermore, since companies are required to store coke in an easily accessible location for future mining as a potential fuel source, they must weigh any potential benefits for its use in reclamation, accordingly. Given these environmental concerns, storing or using petroleum coke under the suggested optimal conditions shown in this research, should be explored further.

Chapter 4 explored the transport characteristics of the fen peat under saturated and unsaturated water contents. Breakthrough of a non-reactive tracer indicated that for the examined peat, the physical mobile-immobile transport regime was not a valid assumption. This result implies that dual porosity should not be automatically assumed in peat but rather need to be established via empirical evidence. Furthermore, breakthrough of a reactive tracer was successfully simulated using one-site adsorption, illustrating that the main retardation mechanism was surface adsorption/desorption reactions. In the case of the peat used in the Nikanotee Fen watershed, the small amount of *Sphagnum* moss in the sedge peat along with the decomposition of the cell membranes is offered as an explanation for the lack of MIM. Accumulation of solutes in the top 7 cm of peat in am unsaturated laboratory column increased exponentially. Within 4 months, solute concentrations at the top of the soil profile were 3 to 5 times higher than those at the water table, for reactive and non-reactive tracers, respectively. These experiments did not account for flushing of solutes, either out of the columns from run-off or down into the columns due precipitation. The results illustrate the importance of considering the composition of the peat used for reclamation projects if attenuation of solutes is a desired function.

Connecting the dots and implications for mosses

Based on this research, sodium, sulfur and calcium are the main solutes that are readily leachable and mobile. Based on the hydraulic gradients of the system, these pools will be transported mainly through the connecting layer to the bottom of the fen where they will start to rise to towards the surface. The existence of a relatively large reserve of metals in the connecting layer does not manifest into substantial solution concentrations, with the exception of Mn. This is due to the structure of raw petroleum coke, the chemistry of the metals under the alkaline, anoxic conditions and the influx of sulfur that helps to control the solution concentrations of the metals through precipitation of insoluble metal-sulfur complexes. The large leachable mass of sulfur and calcium, but mainly sodium, is likely to present a greater challenge to the fen ecology than Mn. There are crucial aspects of knowledge missing to give a specific time frame. Adsorption/desorption experiments for the main solutes found as large pools are required, to understand the possible surface interactions they may undergo. Similarly, breakthrough experiments can provide data on the ability of the peat to attenuate them. This will enable an estimate on the time for a contaminant present at the bottom of the fen to reach the water table. Once a contaminant reaches the water table, it would accumulate near the surface of the soil profile in concentrations that are several times higher than those at the water table. A flushing experiment is needed to quantify the ability to flush solutes from the peat. Finally, a comprehensive data base of metals, solutes and their species in the layers of the Nikanotee fen Fen watershed should be methodically collected and expanded by ongoing monitoring; this would allow analysis of long term temporal and spatial distributions and processes in the system.

One of the questions that arise from the presented data is what might be the implication for the mosses that were used to revegetate the system, if Na accumulation occurs in the rhizosphere? There are three main plant groups that have been planted in the fen, mosses, sedges and halophytes (Borkenhagen and Cooper, 2016). Out of the three groups, mosses are considered the most important for peat accumulation in fens since they decompose slowly, and store carbon for the long term (Graf and Rochefort, 2009; Vitt, 2015). The main moss species at the donor site were *Tomenthypnum nitens*, *Aulacomnium palustre, Sphagnum warnstorfii*, and *Sphagnum angustifolium* (Borkenhagen and Cooper, 2016). After two growing seasons, *Tomenthypnum nitens* is the most dominant species growing at the Nikanotee Fen watershed, accounting for 79% of the average total moss cover. The second most common species is *Ptychostomum pseudotriquetrum* (formerly called *Bryum pseudotriquetrum*; Vitt, 2015) which accounts for less than 1 % of the average total moss cover (Borkenhagen and Cooper, 2016).

The potential implications for mosses used to re-vegetate Nikanotee Fen watershed can be conceptualized on the basis of this research. Assuming a 20-cm deep water table, and neglecting flushing and water table fluctuations, Na concentrations at the top of the soil column could increase 3 times compared to its concentration at the water table, over a period of 3 months (approximately one growing season). High Na concentrations at the top of the soil profile, are toxic to mosses (Rezanezhad et al. 2012), since they do not have mechanisms such as a vacuole to actively mitigate unwanted solutes, and are therefore not tolerant to saline conditions (Boerner and Forman, 1975). For example, *Aulacomnium palustre* rapidly deteriorated and died within a 2 weeks of salt spray treatments, even though it was collected from a beach (Boerner and Forman, 1975). Pouliot et al. (2013) showed that long-term exposure (100 days) of *Bryum pseudotriquetrum* and *Tomentypnum nitens* to relatively low concentrations of Na (39 mg/l) resulted in reduced development of the plants, being more harmful to the plants than relatively short high concentration (100 mg/l) pulses. Prolonged exposure of *Aulacomnium palustre* and *Tomentypnum nitens* to Na at concentrations of 400 mg/l resulted in death to the plants at the end of the second growing season (Pouliot et al., 2012; Rezanezhad et al., 2012b). Research conducted simultaneously found no significant harm to vascular plants after two growing seasons (Pouliot et al., 2012; Rezanezhad et al., 2012b; Pouliot et al., 2013); this suggests vascular plants will come to dominate the vegetation community at Nikanotee Fen watershed over the medium-term. Importantly, fen peatlands can be dominated by sedge and shrub vegetation and still accumulate peat (Trites and Bayley, 2005).

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A.1 Appendix 1: Leaching experiment- cascade scheme, pictures

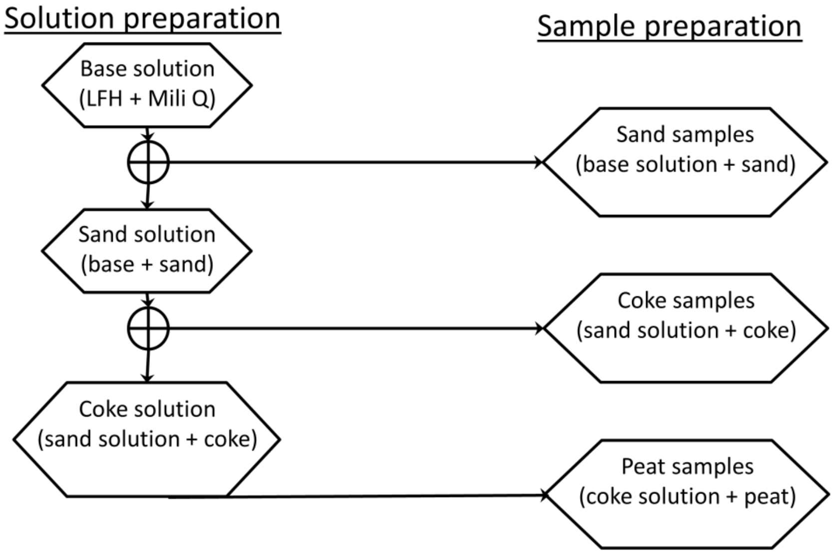

Figure A.1.1 - Flow chart schematic of incubation solution and samples of the leaching experiment.

Figure A.1.2 - Pictures of solution preparation from the leaching experiment. A) Base solution purging with N_2; B) The anaerobic chamber used for preparations and sampling, base solution bottles can be seen in back of chamber; C) Jars with

base solution and tailings sand (preparing sand solution); and D) Jars with coke and sand solution, jars were wrapped in foil to prevent photochemical reactions.

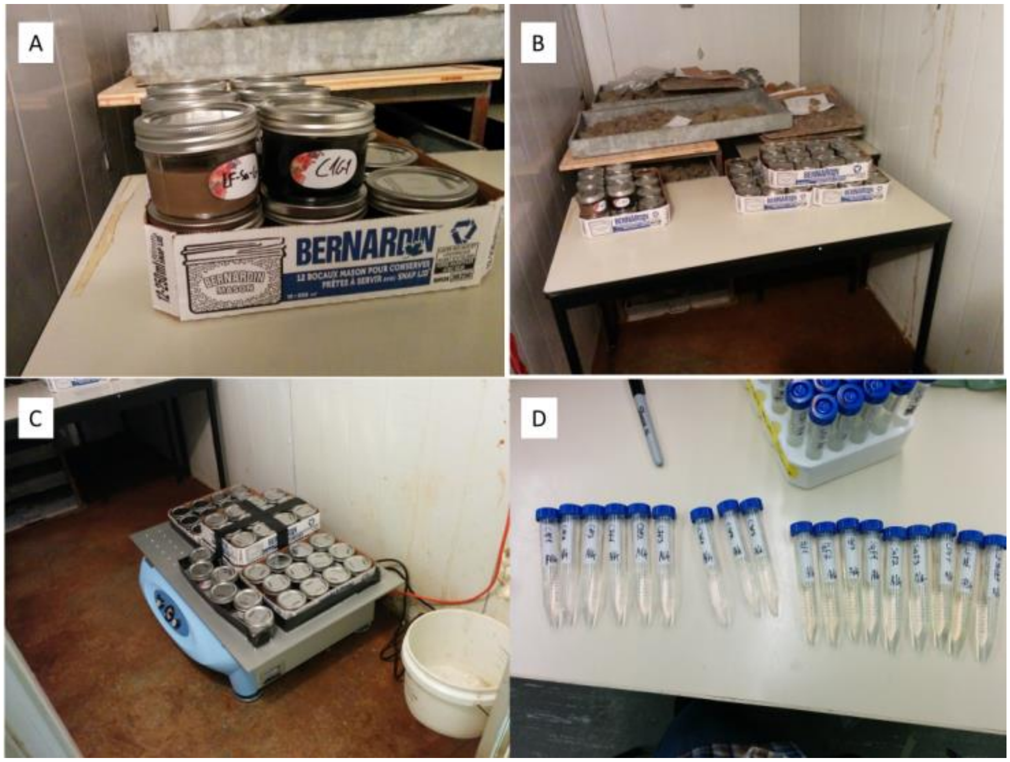

Figure A.1.3 - Pictures of incubation in the cold room from the leaching experiment. A) close up of incubation jars; B) all samples ; C) incubation jars on shaker; and D) samples after filtration and preservation for various analyses.

A.2 Appendix 2: Alkalinity, TN and DOC data.

	Material type	Sampling time	DOC	TN	Alkalinity CO_3
		days	mg/l	mg/l	mg/l
1	Coke <6.35mm	0.5	30.43	4.06	51
2	Coke <6.35mm	0.5	47.17	4.09	42
3	Coke <6.35mm	0.5	36.57	4.15	49
4	Coke <6.35mm	1	31.01	4.09	49
5	Coke <6.35mm	1	29.28	3.96	52
6	Coke <6.35mm	1	29.57	3.84	47
7	Coke <6.35mm	7	37.02	4.18	51
8	Coke <6.35mm	7	32.47	4.01	47
9	Coke <6.35mm	7	32.30	4.03	48
10	Coke <6.35mm	28	56.16	3.84	53
11	Coke <6.35mm	28	51.95	3.62	58
12	Coke <6.35mm	28	54.57	3.99	57
13	Coke <6.35mm	56	40.63	3.69	53
14	Coke <6.35mm	56	42.25	2.90	58
15	Coke <6.35mm	56	43.52	3.65	54
16	Coke 10>X>6.35mm	0.5	41.73	4.27	47
17	Coke 10>X>6.35mm	0.5	29.44	4.21	49
18	Coke 10>X>6.35mm	0.5	39.47	4.28	51
19	Coke 10>X>6.35mm	1	28.32	3.95	46
20	Coke 10>X>6.35mm	1	30.20	3.77	40
21	Coke 10>X>6.35mm	1	28.07	4.04	52
22	Coke 10>X>6.35mm	7	31.82	4.13	52
23	Coke 10>X>6.35mm	7	32.83	4.10	36
24	Coke 10>X>6.35mm	7	31.28	4.10	53
25	Coke 10>X>6.35mm	28	46.51	3.99	58
26	Coke 10>X>6.35mm	28	43.97	3.79	47
27	Coke 10>X>6.35mm	28	42.60	3.89	58
28	Coke 10>X>6.35mm	56	44.08	3.66	54
29	Coke 10>X>6.35mm	56	43.80	3.83	49
30	Coke 10>X>6.35mm	56	39.94	4.27	65
31	Coke 15>X>10mm	0.5	37.89	4.49	42
32	Coke 15>X>10mm	0.5	28.31	4.35	38
33	Coke 15>X>10mm	0.5	23.92	4.30	39
34	Coke 15>X>10mm	1	24.19	4.08	50
35	Coke 15>X>10mm	1	27.24	3.87	38
36	Coke 15>X>10mm	1	23.34	4.08	41
37	Coke 15>X>10mm	7	26.01	4.13	54
38	Coke 15>X>10mm	7	31.37	3.91	44

39	Coke 15>X>10mm	7	27.67	4.13	46
40	Coke 15>X>10mm	28	38.31	3.92	51
41	Coke 15>X>10mm	28	61.61	1.53	43
42	Coke 15>X>10mm	28	39.86	3.74	45
43	Coke 15>X>10mm	56	35.89	3.76	55
44	Coke 15>X>10mm	56	40.07	3.87	49
45	Coke 15>X>10mm	56	40.09	3.78	46
46	Peat	0.5	124.60	10.12	63
47	Peat	0.5	129.20	10.50	74
48	Peat	0.5	130.40	11.58	67
49	Peat	1	137.40	10.83	73
50	Peat	1	128.30	10.00	72
51	Peat	1	132.30	11.12	81
52	Peat	7	150.00	10.43	46
53	Peat	7	145.60	10.30	44
54	Peat	7	136.00	9.76	68
55	Peat	28	172.50	1.75	46
56	Peat	28	197.50	2.46	42
57	Peat	28	178.20	3.35	66
58	Peat	56	182.90	2.16	83
59	Peat	56	189.20	2.45	62
60	Peat	56	200.00	3.37	57
61	Tailing Sand	0.5	18.44	5.56	24
62	Tailing Sand	0.5	22.99	5.53	32
63	Tailing Sand	0.5	21.62	5.47	31
64	Tailing Sand	1	19.56	5.17	39
65	Tailing Sand	1	23.92	4.97	28
66	Tailing Sand	1	22.33	5.17	33
67	Tailing Sand	7	20.06	5.36	21
68	Tailing Sand	7	21.91	5.54	27
69	Tailing Sand	7	22.14	5.41	35
70	Tailing Sand	28	34.17	1.77	37
71	Tailing Sand	28	41.50	1.88	31
72	Tailing Sand	28	40.10	1.90	36
73	Tailing Sand	56	39.95	0.58	40
74	Tailing Sand	56	38.99	0.51	35
75	Tailing Sand	56	33.58	0.50	33

A.3 Appendix 3: Pictures of saturated and unsaturated experiments.

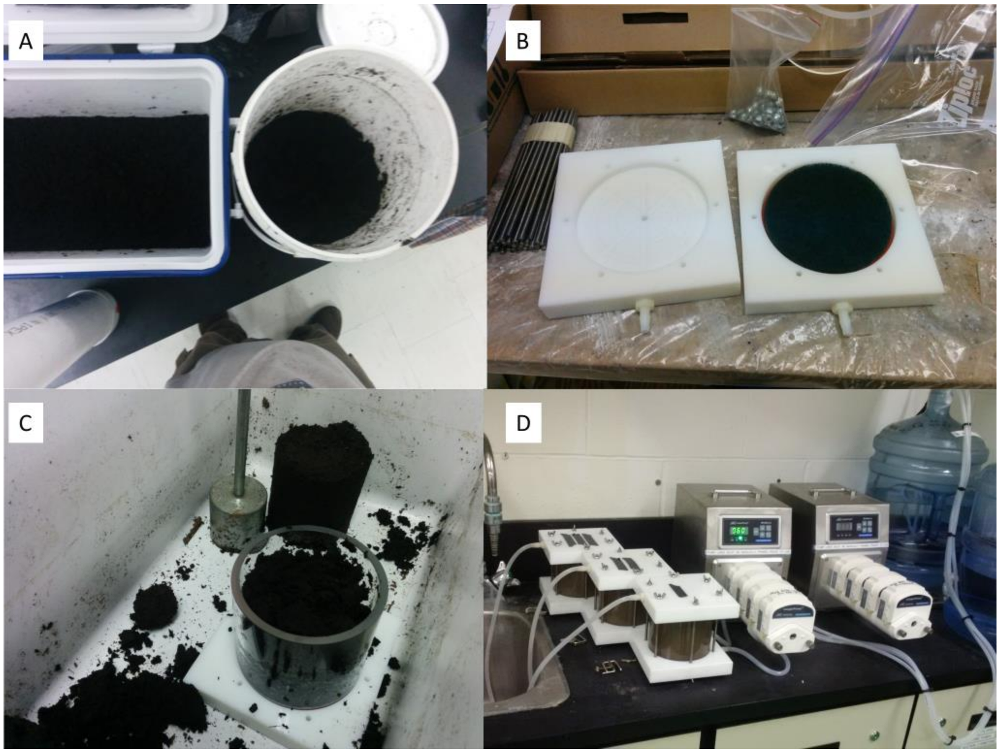

Figure A.3.1 - Pictures from saturated transport experiment. A) Cleaning and mixing the peat; B) flow through cells plates. The green pad is below the sample, redistributing the water beneath it; C) packing cell with peat; and D) flow through experiment setup, cells are connected to a pump drawing the solution from a container on a magnetic stirrer.

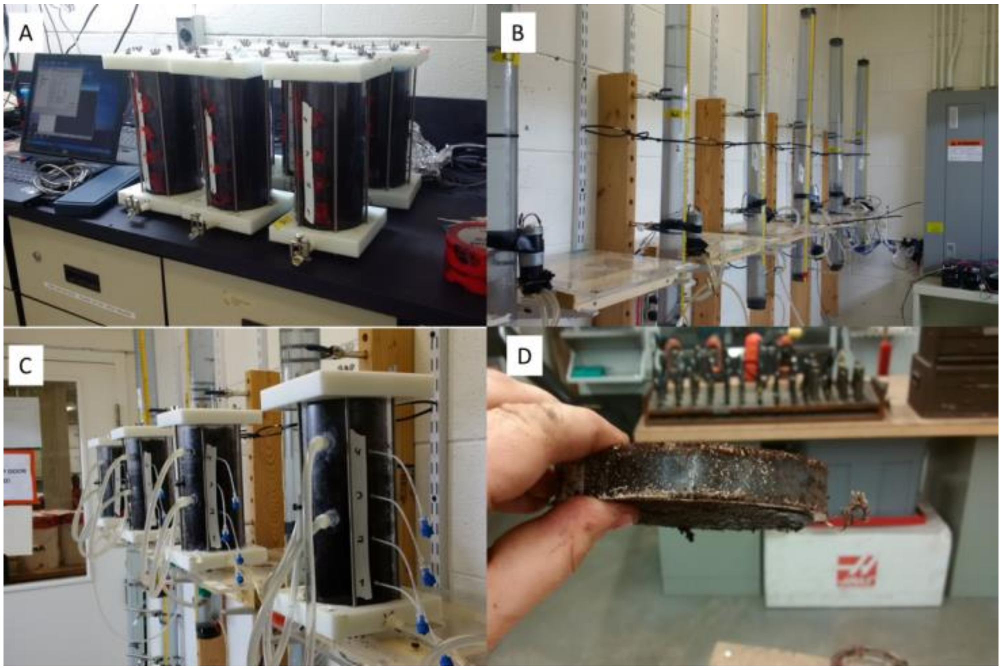

Figure A.3.2 - Pictures from the unsaturated transport experiment. A) columns with peat, note the laptop for scale; B) Marriot bottles and pumps; C) columns connected and instrumented, Blue caps are the soil pore water samplers, large tubes are the tensiometers; and D) slice of a peat column before extraction at end of experiment.

A.4 Appendix 4: Soil hydraulic properties

Measurements of water retention properties

The TDE was conducted on 10 cm i.d. and 5 cm high peat samples at seven different pressure steps under unsaturated unit gradient vertical flow conditions using a tension disk apparatus that used 15 µm Nytex screens to prevent air entry below the air entry pressure (~35 cm) (Price et al., 2008). Samples were initially saturated for 48h and two layers of cheese-cloth covered the top and bottom of the sample to maintain the integrity of the surfaces. The pressure steps (h; cm) were -2.5, -5, -7.5, -10, -15, -20, -25 cm, which was also the order in which the experiment was conducted. During the experiment, outflow was monitored for each pressure step by a scale with an accuracy of at least 0.1 g and logged at 1-minute intervals. The experiment stopped when there was no change from past measurements over a 30-min. period. After each step the weight of the sample was determined to enable calculation of the water content. From the outflow, the unsaturated hydraulic conductivity was calculated from the Darcy-Buckingham equation (Da Silva et al., 2007).

Saturated hydraulic conductivity

The FTC were used for the determination of the saturated conductivity (Ks; cm d^{-1}), too, which were connected to a Marriot's bottle supplying a constant pressure head. The adopted method was a constant head test (Freeze and Cherry, 1979) with a gradient of 0.5. Once the outflow stabilized, it was measured in a 250ml glass graduated cylinder (S63459, Fischer Scientific, USA) every 2 min over 20 min.

Transient evaporation experiment

The transient evaporation experiment (EEt) was conducted on the same samples as the TDE. With a 0 cm pressure head at the bottom prior EEt with the commercial UMS HYPROP device (UMS GmbH, Munich, Germany). The samples had a larger diameter than the UMS HYPROP device so that Plexiglas screens were used at the bottom to seal and prop the sample. The pressure head was directly related to the water content to obtain the retention information, which is a valid approximation at or near a linear pressure distribution (Becher, 1971). With this, the evaluation for conductivity is not possible.

Inverse fitting of soil hydraulic properties

The water retention and unsaturated hydraulic conductivity data were used to parameterize SHP models. We compare two models, the unimodal van Genuchten-Mualem model combination (van Genuchten, 1980; Mualem, 1976). Secondly, a bimodal expression as first proposed by Ross and Smettem (1993), superimposing two van Genuchten-Mualem equations. We used the analytical expression derived by Priesack and Durner (2006). The soil water retention function is given by

$$\theta(h) = \theta_r + (\theta_s - \theta_r)\,\Gamma(h) \qquad \text{(Eq.A.4.1)}$$

where θ_r is the residual and θ_s the saturated water content (cm³ cm^{-3}) and $\Gamma(h)$ (-) the effective saturation given by

$$\mathit{\Gamma}(h) = \sum_{i=1}^{k} \mathit{\Gamma}_i(h) = \sum_{i=1}^{k} w_i\,[1 + (-\alpha_i h)^{n_i}]^{m_i} \tag{Eq.A.4.2}$$

where, w_i is a weighting coefficient between the modal pore size distributions, and α_i (cm^{-1}) and n_i (-) are shape parameters, $m_i = 1 - 1/n_i$. The unimodal van Genuchten saturation function is obtained by $k = 1$ and the bimodal function by $k = 2$. The unsaturated hydraulic conductivity is expressed as

$$K(\Gamma) = K_s \Gamma^{\tau} \left(\sum_{i=1}^{k} w_i \alpha_i \right)^{-1} \left(\sum_{i=1}^{k} w_i \alpha_i \left[1 - \left(1 - (\Gamma)^{1/m_i} \right)^{m_i} \right] \right)^{2} \tag{Eq.A.4.3}$$

where K_s is the saturated hydraulic conductivity (cm d^{-1}).

Soil physical properties

All parameters were estimated except for θ_s, which was set to 0.925, i.e. the porosity value. Estimation was done in R.3.2.1 (R Core Team 2015) with implementation of the differential evolution optimiser to minimise the sum of squared errors for the retention and hydraulic conductivity curves (Mullen et al., 2011). The estimation of the soil hydraulic properties of the fen peat by inverse estimation was done as described in Peters and Durner (2008). After all procedures were concluded, bulk densities for all samples were determined gravimetrically based on an oven-dry mass basis for samples dried at 80°C until no difference in weight was measured (Gardner, 1986). From knowledge of the dry weight and experimental system weight water contents could be calculated for the soil hydraulic properties.

Statistical parameters

The root mean square error (RMSE) is used as a metric to describing the model prediction quality, such that

$$RMSE = \sqrt{\frac{1}{m}\sum_{l=1}^{m}(y_l - \hat{y_l})^2} \qquad \text{(Eq.A.4.4)}$$

where m is the number of observations, y_l is the observed and $\hat{y_l}$ the model predicted value (solute concentration, water content or hydraulic conductivity). The corrected Akaike Information Criterion (AICc; Ye et al. 2008)) was also used as a method of model comparison where the model with the smallest AICc is to be favored.

$$AICc = m\ \ln\left(\frac{1}{m}\sum_{l=1}^{m}(y_l - \hat{y_l})^2\right) + 2\,n_p + 2\,\frac{n_p(n_p+1)}{m-n_p-1} + C \qquad \text{(Eq.A.4.5)}$$

where n_p is the number of parameters of a respective model.

References (References that do not appear here can be found in the main reference list):

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A.5 Appendix 5: Unsaturated experiment conditions

Ambient conditions in the chamber where the experiment was conducted were stable with an average temperature of ~25±1 ^{0}C and an average RH of 41±0.02% (Fig. A.5.1). Additionally, water pressure profile in the soil did not vary much for each column; soil water pressure above the water table averaged -10.7±0.5 cm for the low meter and -19.5±0.5 cm for the high meter (Fig. A.5.2). Furthermore, data from all columns were in a similar range (Fig. A.5.2) meaning the columns were reasonable replicates in soil water pressure.

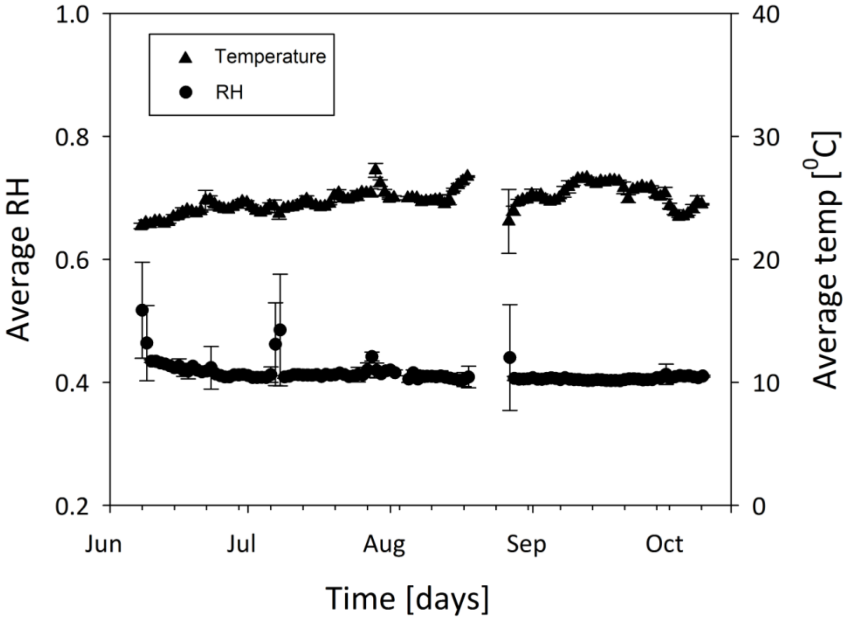

Figure A.5.1 – measured temperature and relative humidity during the unsaturated column experiment. Each point is a daily average of 144 measurements and corresponding standard error.

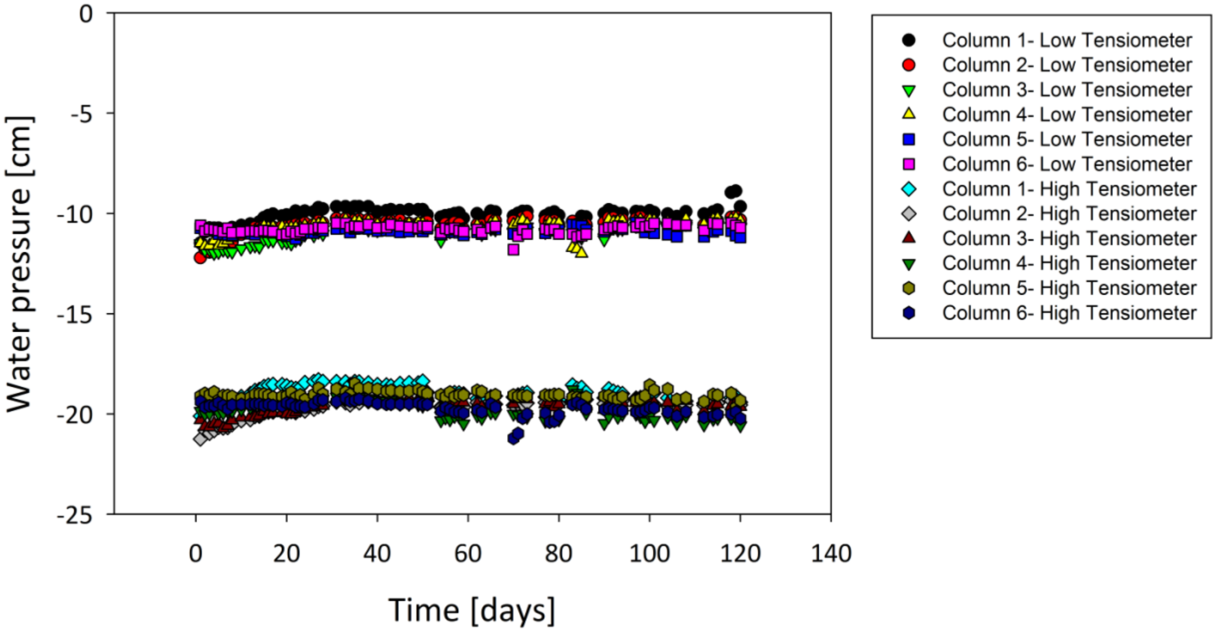

Figure A.5.2 – Soil water pressure measurements over time. 0 cm marks the water table. Values around the -10 cm mark are from the low pressure meters of all 6 columns; values around -20cm are from the high pressure meters.

Moreover, E data strengthen the conclusion that the columns were decent replicates with an overall low fluctuation in values averaging at 0.27±0.05 cm/day (Fig. A.5.3).

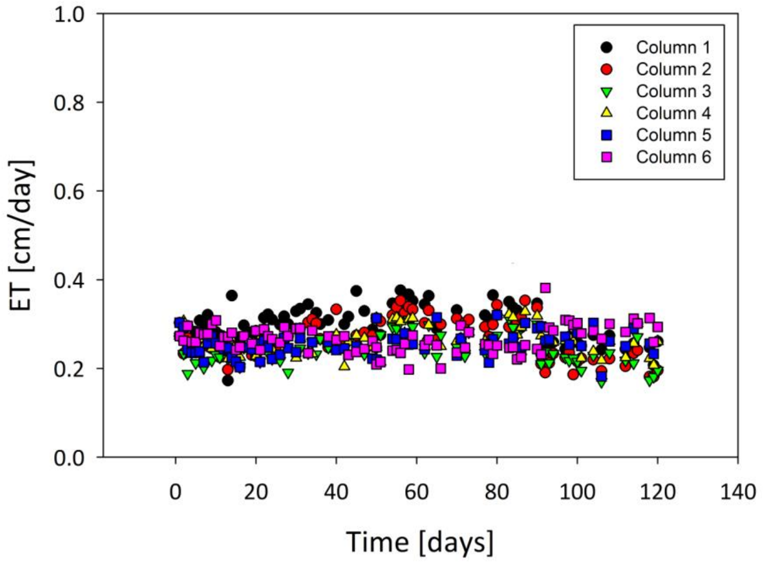

Figure A.5.3– Calculated ET during the experiment. Data presented is for each column separately (color coded, see legend).