The Hydrogeochemistry of a Constructed Fen Peatland in a Post-Mined Landscape in the Athabasca Oil Sands Region, Alberta, Canada

by

Eric Kessel

A thesis

presented to the University of Waterloo

in fulfilment of the

thesis requirement for the degree of

Master of Science

in

Geography (Water)

Waterloo, Ontario, Canada, 2016

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Large areas of land within the Athabasca Oil Sands Region (AOSR) have been subjected to open pit mining to recover bitumenous oil sands. Following extraction, oil sands require the addition of solvents to optimize the solubility and separation of bitumen from sand. Consequently, the tailings sands, a byproduct of oil sands production, contain elevated residual concentrations of sodium (Na^+), amongst other constituents. In an attempt to reclaim post-mined landscape in the AOSR, a fen peatland system has been constructed, in which groundwater inputs are received from an upland aquifer constructed of tailings sands. The intent is to mimic the function of naturally occurring fens in which groundwater supplements precipitation inputs, especially important during periods of limited water availability, which are common in the AOSR. However, given the elevated concentrations of Na^+ in tailings materials, there is a concern that it will leach from the tailings sand and accumulate in the fen at concentrations toxic for the recently planted fen species. The purpose of this study was to determine the spatial distribution of Na^+ generated throughout the upland – fen system and to evaluate the hydrological processes controlling its transport from the upland to the fen.

Na^+ concentrations were highest within the tailings sand materials and petroleum coke underdrain and lowest within the fen peat deposit in all three years (2013 – 2015); however, there was considerable temporal variation in concentrations within all materials. Concentrations within the tailings sand upland and petroleum coke underdrain were generally the highest after the winter months which appeared to allow for elevated Na^+ concentrations in the absence of freshwater recharge. Following rainfall, Na^+ concentrations decreased within all construction materials. Upland recharge basins were important for detaining overland flow and encouraging upland freshwater recharge, which ultimately determined the trajectory for Na^+ re-distribution along the eastern region of the upland. High precipitation and recharge in 2013 and 2014 resulted in the highest fluxes towards the fen; however, allowed for dilution of upland groundwater which resulted in relatively low loads of Na^+ being received at the fen. A Na^+ plume was observed migrating from the upland into the petroleum coke underdrain and beneath the fen. Little upward migration of the Na^+ plume into the fen peat occurred in 2013 and 2014. In 2015, a lack of precipitation resulted in less groundwater dilution, which despite lower fluxes, resulted in greater loads of Na^+ being received at the fen. The Na^+ plume advanced throughout the petroleum coke underdrain. Considerable upwards migration of Na^+ into the peat deposit was observed, resulting in an increase in concentration, but mainly at depth. Evapo-concentration resulted in elevated concentrations at the fen surface by the end of the study.

This study documented the distribution and transport of Na^+ from a constructed tailings sand upland to the adjacent constructed fen within the first three years post-construction, and provides insight into the variability of salinity with location within reclamation materials, and the effects of weather conditions typical of the AOSR. This study also makes important fen construction design modifications and recommendations to minimize OSPW generation while simultaneously ensuring sub-surface storage. Success in reclaiming fen peatlands in the AOSR must account for the management and transport of solutes generated from the tailings sand materials.

Acknowledgements

Graduate school was a wonderful but challenging experience; a delicate balance between stress, caffeine, beer, field work, and countless hours at a computer. I was fortunate to have such a supportive and encouraging family and group of friends to keep me motivated during the frequent periods of self-doubt. For that I am forever thankful.

I am truly grateful to my supervisor, Dr. Jonathan Price, for the opportunity to be part of a wonderful laboratory group and his Fort McMurray research crew. Over the past several years Jonathan has shown me unforgettable guidance and patience. I would also like to thank Dr. Maria Strack, Dr. Richard Petrone, and Dr. David Cooper, whom all of which, along with Jonathan, were professional investigators on the Nikanotee Fen project.

The help with fieldwork, laboratory analysis, or general advice from James Sherwood, Corey Wells, Sarah Irvine, Julia Asten, Matthew Elmes, Dylan Price, Owen Sutton and Scott Ketcheson is much appreciated. We would also like to thank the Suncor Field Service's and Reclamation teams for their assistance in work logistics. This research would like to acknowledge and thank the Natural Sciences and Engineering Research Council of Canada, Northern Scientific Training Program, Esso Imperial Oil Ltd., Shell Canada Ltd., and Suncor Energy Inc. for their funding contributions.

Thank you to everyone else who has contributed in one way or another, small or large, along my journey as a graduate student.

To my loving grandparents:

Irene & Wolfgang Kessel

I literally could not have done this without your love and support.

Thank you.

Table of Contents

List of Figures

List of Tables

1.0 Introduction

The Athabasca Oil Sands Region (AOSR) is home to the third largest proven oil deposit (166 billion barrels as of 2014) in the world (Alberta Government, 2015; Woynillowicz *et al*., 2005). An estimated 4,800 km^2 of the AOSR has been deemed feasible for the recovery of near surface (~ 75 m) bituminous oil sands by open-pit surface mining techniques (Figure 1 – 1; Government of Alberta, 2015). The remaining areas require more complicated, 'in situ' techniques such as steam assisted gravity drainage (also known as SAGD) to recover deeper, less accessible bitumen oil sands (Government of Alberta, 2015). Both methods disturb, or in the case of open pit mines completely remove, natural wetland ecosystems within the AOSR (Rooney *et al*., 2012). As of December 2013, over 767 km^2 of the AOSR has been disturbed by oil sands extractions (Government of Alberta, 2015), which the oil companies responsible are required to return to equivalent land capability (OSWWG, 2000). Approximately 50% of the natural landscape of the Western Boreal Forest (WBF) in Northern Alberta is wetlands, of which ~ 90% are peatlands (fens and bogs; Vitt et al. 1996). The fen peatlands are important for water storage dynamics and interact with the surrounding upland forests to redistribute water (Devito *et al*., 2012). The groundwater connectivity to the surrounding landscape is crucial for the resilience of fen peatlands as well as upland forests in the WBF eco-zone, and therefore both are essential to incorporate when attempting to reclaim the post-mine landscape (Price *et al.*, 2010; Daly *et al*., 2012). Currently, reclamation efforts are exploring fen peatland and upland re-construction to combat the disturbance to natural peatlands within the AOSR (Daly *et al*., 2012; Ketcheson *et al*., 2016; Pollard *et al*., 2012). Constructing these landscapes within the AOSR rely on the salvaged and post-mine waste materials that are a result of the bitumen recovery process. However, the salvaged and post-mine waste materials have residual elevated concentrations of contaminants that will threaten the health of newly reclaimed ecosystems.

The average bituminous oil sands ore (Figure 1 – 2) in the AOSR contains 10 to 12% bitumen by weight (Bott, 2010; Woynillowicz *et al*., 2005). The process of removing bitumen from the mineral soils (sand, silts and clays) is termed the Clark Hot Water Extraction (CHWE) process. CHWE processing of bituminous oil sands utilizes large amounts of caustic solvents (e.g. $NaOH$) that have many benefits in separating the bitumen. However, these additives may pose a threat to both aquatic and terrestrial ecosystems, as the waste products contain residual

Figure 1 – 1 Map of the AOSR and the associated disturbance from oil sands extraction. Taken from Government of Alberta (2015).

amounts of these solvents (Mackinnon *et al*., 2001; Scott, 2005). Once the bitumen is removed, the remaining solution of water and sediment (sand, silt and clay) is referred to as 'tailings'. Due to relatively low yields, approximately 2 tons (T) of oil sands must be excavated via surface mining to produce 1 barrel (159 L) of upgraded crude oil, and subsequently results in ~ 2 T of solid tailings materials (clay, silt and sands; Bott, 2010; Woynillowicz *et al*., 2005). The tailings are held within large settlement areas called tailings ponds. The addition of gypsum ($CaSO_4$) to tailings enhances flocculation and settlement of the fine sediments (Renault *et al*., 1998; BGC, 2010; Mackinnon *et al*., 2001). Once adequate settling has occurred tailings sand can be separated into coarse and mature tailings (CT and MT, respectively). CT, herein referred to as 'tailings sand', consisting of the silica sands and some silts, has the structural integrity required for landscape construction. Tailings sands are being used as construction materials for reclamation of the post-mine landscape within the AOSR (Daly *et al.* 2012; Ketcheson *et al*., 2016; Pollard *et al*., 2012). However, tailings sand contains elevated concentrations of salts derived from the additives used, as well as from natural constituents within the bitumen. Typical salts are $NaSO_4$, $CaSO_4$, $MgSO_4$ and naphthenic acid-sulfate ($NASO_4$; Bott, 2010; Leung *et al*., 2001; Mackinnon *et al*., 2001). Of these contaminants, Na^+ and NAs are of primary concern as they are relatively mobile within groundwater (Gervais and Barker, 2005) and have toxicological effects on aquatic and vegetation communities (Renault *et al*., 1998; Renault *et al*., 1999; Pouliot et al. 2012; Rezanezhad *et al*., 2012a). The term oil sands process-affected water (OSPW) has been coined to characterize the contaminated water that is generated by the interaction of groundwater and tailings sand. OSPW can be generated within all reclaimed landscapes that incorporate tailings sands materials, as in the case of this study (Daly *et al*., 2012). While current oil sands processing benefits from research and development that has reduced the number of additives and solutes required to remove bitumen, large volumes of tailings sands must be used to reconstruct the post-mined landscape within the AOSR. If tailings sands are to be used in the construction of upland-fen peatland systems, the understanding and managing water quality and the role of landscape design is crucial for large-scale reclamation.

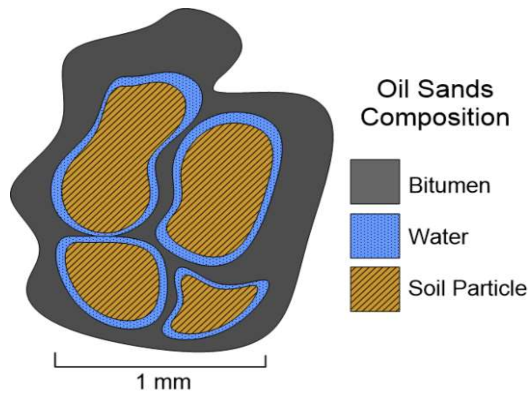

Figure 1 – 2 Oil sands composition of bitumen, water and mineral soils (sand, silt, and clays), adapted from the Government of Alberta (2015).

In addition to tailings sand and OSPW, there are other by-products from bitumen oil sands production. Bitumen contains heavy metals (e.g. vanadium, cadmium) and impurities (e.g. carbon and sulfur), which are removed before final production of synthetic crude oil (BGC, 2010; Bott, 2010; Zubot *et al*., 2012). These impurities are removed and produce a porous, carbon rich material called petroleum coke (also referred to as coke or slag). It has been hypothesized that because of favorable hydraulic characteristics, petroleum coke could be strategically used in landscape reclamation to provide more permeable layers that are common within the Quaternary deposits of the AOSR. Furthermore, petroleum coke has the potential to ameliorate OSPW contaminant concentrations, since the large surface area and carbon content result in a high adsorption capacity (Zubot *et al*., 2012).

Fen reclamation

To date, there are two pioneering projects with the primary objective of evaluating the feasibility of building a fen peatland and watershed from mine waste (tailings) and salvage materials (peat, peat-mineral mix prescriptions) within the AOSR. This includes the Sandhill Fen (Syncrude Canada Limited), a highly engineered landscape of coarse tailings overlying hypersaline composite tailings, which employs a network of underdrain pipes and pumps to distribute fresh water and manage saline groundwater generated from the tailings materials (Pollard *et al*., 2012; Biagi, 2015; Ketcheson *et al*., 2016). The other, the Nikanotee Fen (Figure 1 – 3.), which is the focus of this research, consists of a tailings sand upland designed to supply a lower-lying fen peatland (Price *et al.,* 2010), all of which is situated in a larger constructed landscape that aids in supplying water to the upland. Attempting to construct fen peatlands in a post-mine landscape from waste materials has many challenges and concerns, primarily with water quantity and quality (Daly et al., 2012; Pollard et al., 2012; Ketcheson *et al*., 2016). During climatic periods of water stress, typical of the AOSR, these constructed fens will rely on the supply of water from adjacent uplands, which will inevitably introduce OSPW and potentially harmful contaminants. It is anticipated that in the early years post-construction of the Nikanotee Fen, Na^+ (along with other solutes) will leach from the tailings sand materials and migrate towards the fen, where it will be attenuated by adsorption to the peat materials and diffusion into closed or dead-end pores of the peat matrix (Daly *et al*., 2012; Rezanezhad *et al*., 2012b). The intention is to delay the arrival time and minimize the peak concentrations of contaminants to the fen surface, allowing adequate time for newly planted or donor vegetation to establish a healthy population. The success of constructed fens as a reclamation technique will partly depend on both the arrival times of OSPW and the peak concentrations, since this can impact the newly planted and donor fen vegetation.

Figure 1 – 3 Photo (2014) of the Nikanotee Fen watershed. The constructed upland sloping towards the fen. Note that the wide-angled lens used exaggerates the true slope of the upland (2% grade).

Solute transport in peatlands

Fens are mineratrophic systems that receive water both from precipitation and groundwater (Ingram, 1983). This groundwater interaction can provide considerable base-ions and minerals (hence minerotrophic) to the fen, creating moderately-rich to extremely-rich geochemical conditions (Ingram, 1083). Fen geochemistry is well documented by surface or pore water surveys (e.g. Vitt and Chee, 1990; Reeve *et al.*,1996) yet there are very few studies with the specific aim of examining the transport and fate of solutes introduced into peatlands (e.g. Hoag and Price (1995), Baird and Gaffney (2000), and McCarter (2016)), all of which examined point source spill scenarios, unlike the slow-release non-point source generation from tailings sand materials anticipated in constructed fen peatlands. Due to decomposition and the compressibility of peat, which tends to increase with depth from the acrotelm to the catotelm (in undisturbed ecosystems), peatlands develop heterogeneous and anisotropic flow systems (Ingram, 1983; Beckwith *et al,* 2003). The degree of anisotropy and heterogeneity of hydraulic conductivity can greatly influence the flow rates and patterns of solutes in porous media (Sudicky, 1986). Since peatlands can have anisotropy ratios of 10:1 or even 100:1, it can strongly influence groundwater flow rates and patterns (Beckwith *et al.* 2003) and thus the migration of solutes.

The transport of solutes in peatlands is determined by the chemical characteristics of the solute (Hill and Siegel, 1991) and the physical properties of the peat matrix (Hoag and Price, 1997; Ours *et al.*, 1996). Peat is a dual-porosity medium, consisting of a complex network of pores with varying degrees of interconnectivity which results in mobile and immobile flow regions (Hoag and Price, 1995; Ours *et al.*, 1996; Rezanzehad *et al.*, 2010, Rezanzehad *et al.*, 2012b; Rezanzehad *et al.*, 2016). The hydraulic conductivity (K) of peat is proportional to the degree of decomposition and constrained by volume of the porous media that can actively contribute to flow, specifically the ratio of mobile and immobile regions, referred to as the effective porosity (Boelter, 1969). Mobile regions, where bulk solute movement occurs, consist of open or connected pores that allow for advective transport (Ours *et al.*, 1996). Concentration gradient driven diffusion into immobile regions, consisting of closed or dead-end pores, attenuate and slow (retard) the overall transport of solutes (Hoag and Price, 1995; Hoag and Price, 1997). Furthermore, significant retardation of solutes is caused by the sorption of the solutes to the peat surface material (Rezanzehad *et al.*, 2012b). Hoag and Price (1997) speculate that the retardation

(R) of a solute is velocity dependent, as slow groundwater flow velocities result in more time available for diffusion of solutes into the closed or dead-end pores. Hoag and Price (1995) and McCarter and Price (2016) both reported relatively high transport rates (2.3 m day^{-1} and 1.16 m day^{-1}, respectively) within the upper, most conductive layers of the peatland (acrotelm) which are subject to fluctuating water levels, yet diffusive processes dominated transport within the catotelm. Since natural peat structures of a discontinuous acrotelm-catotelm peat profile are not present in newly reclaimed peatlands (Ketcheson *et al*., 2016; Nwaishi *et al*., 2015) different transport processes are expected to dominate. The importance of by-passing or shortcutting due to preferential flow paths was identified by Baird and Gaffney (2000), where they observed transport rates much faster than those indicated by plot scale K data.

1.1 *Research Objectives*

Reclamation of the AOSR post-mined landscape requires the complete re-construction of fen peatlands. Unfortunately, the mine waste and salvage materials (i.e. tailings sand) available and partially relied on to construct such landscapes contain residual concentrations of Na^+ (and other contaminants) that are potentially hazardous to newly populated fen vegetation. The geochemical conditions generated and transport of solutes from mine waste materials is largely unknown. The design of constructed fen peatlands must account for the management of OSPW generated from mine-waste and salvage materials to be deemed a success. Therefore, the goal of this paper is to improve the understanding of geochemical conditions generated by tailings sand materials in a strictly constructed setting and the primary research objectives of this study are to:

1. Assess the initial spatial distribution and temporal variations of Na^+ concentrations throughout a constructed tailings sand upland aquifer - fen peatland system;

2. Characterize the processes controlling Na^+ transport dynamics from the tailings sand aquifer and the Na^+ attenuation within the fen peatland, and;

3. Comment on the system design with respect to the transport of Na^+ to the fen and recommend adaptions to minimize the generation and impact of OSPW.

1.2 Format and Project Role

This manuscript style thesis comprises of two complementary chapters that form the manuscripts intended for publication. The first manuscript evaluates the geochemical conditions generated by tailings sand upland, specifically investigating the transport of Na^+ to a lower lying constructed fen peatland. The second manuscript focuses on evaluating the success of recharge basins in recharging water into the tailings sand upland and discusses the associated implications on re-distributing Na^+ throughout the upland – fen system.

My role within the overall research project was to assist in the site-wide instrumentation of the hydrological monitoring network and collect the water chemistry samples for geochemical analysis. From this geochemical analysis, it was my responsibility to analyze the solutes generated (specifically Na^+) within the tailings sand upland and evaluate their transport towards, and attenuation within, the fen. I, with the help of others, collected and compiled the total three-year water chemistry data set (2013 – 2015, see appendix). I, Eric Kessel, wrote the first draft of each chapters of this thesis.

2.0 Manuscript Chapter 1. The distribution and transport of sodium from a tailings sand upland to a constructed fen peatland in the Athabasca Oil Sands Region

2.1 Context

As of December 2013, open pit mining to extract oil sands had disturbed over 767 km^2 of the Northern Boreal Forest within the Athabasca Oil Sands Region (AOSR; Government of Alberta, 2015). Given that wetlands comprise a significant portion (~ 50%) of this region, and that ~ 90% of these wetlands are fen peatlands (Vitt *et al.,* 1996), fen peatland construction has been incorporated into the mine closure planning, at least on a pilot scale, to reclaim the disturbed land to an equivalent land class (Daly *et al*., 2012). The construction of a fen peatland (named the Nikanotee Fen) is a pioneering attempt at post-mined AOSR landscape reclamation (Daly *et al*., 2012; Ketcheson *et al*., 2016). This particular constructed fen peatland relies on a constructed tailings sand upland aquifer to supply sufficient water to maintain water levels suitable for fen peatland development (Price *et al.,* 2010). Tailings sands are an abundant byproduct of oil sands production, but have high residual concentration of sodium (Na^+) salts (Mackinnon *et al*., 2001; Scott, 2005; Holden *et al*., 2011). Given that Na^+ rich leachate from tailings sands may be toxic to fen vegetation (Pouliot *et al.,* 2012, Rezanezhad *et al*., 2012a), the influence of process-affected materials on water quantity and quality must be considered (Daly *et al.,* 2012; Ketcheson *et al*., 2016). Post-construction, Na^+ will flush from the tailings sands upland aquifer, with additional inputs generated by surface runoff from previously reclaimed hillslopes. This will create pulses of elevated (above background) Na^+ concentrations that will enter the fen peat. Once in the fen, contaminant transport is anticipated to slow due to the dual-porosity nature of the peat (Price *et al*., 2010; Rezanezhad *et al*., 2012b). Retardation of solutes may occur due to diffusion of the Na^+ into closed or dead-end pores and sorption to the peat particulate surfaces, given its high cation exchange capacity (Rezanzehad *et al.,* 2012b). Thus, if tailings sands are to be used in the construction of upland-fen peatland systems, the mobility, distribution and transport of Na^+ generated from tailings sand materials must be understood.

Several collaborative projects have been conducted within the Nikanotee Fen watershed with specific objectives to understand the hydrological performance of the system (Nwaishi *et al*., 2015; Scarlett *et al*., submitted; Ketcheson and Price, 2016b; Ketcheson and Price, 2016c, Ketcheson *et al*., unpublished; Simhayov *et al*., unpublished). Thus far, in the constructed upland

– fen system the adjacent reclaimed hillslopes and upland have been shown to be capable of supplying sufficient water to maintain saturated conditions within the fen under moderate seasonal water deficit conditions (Ketcheson and Price, 2016b; Ketcheson *et al*., unpublished). However, emphasis has been placed on the importance of peat placement practices and management strategies that can minimize the disturbance to natural hydrological and biogeochemical functions (Nwaishi *et al*., 2015). High anisotropy ratios (K_h/K_v) typical of natural peatlands were not found at the Nikanotee fen, due to the peat structure being disturbed during placement, resulting in near isotropic conditions which can impact the vertical fluxes of water and solutes within the fen (Nwaishi *et al*., 2015). It is speculated that the dewatering during peat placement prior to construction resulted in increased concentrations of major ions within the peat (Nwaishi *et al.*, 2015), a phenomena reported before (e.g. Heathwaite, 1990). The geochemical interaction of anticipated solutes (i.e. Na^+) and mine waste and salvage materials used within the construction of the upland – fen system were evaluated in laboratory settings, concluding that Na^+ (among other ions) would be most mobile in groundwater flow from upland to fen (Simhayov *et al*., unpublished).

There is a potential for upward migration (diffusion) of salts within tailings sand units and salinization of soil covers within tailings sand units with relatively shallow water tables (Dobchuk *et al*., 2012; Price, 2005). However, upward diffusion can easily be counteracted by frequent downwards percolation of water (Dobchuk *et* al., 2012). Biagi (2015) documented the migration of Na^+ upwards from composite tailings into peat materials generating 'hotspots' of concentrated Na^+ within upland areas of the Syncrude Sandhill Fen and highlights the importance of underdrain engineering to manage salinity within the groundwater. Preliminary solute transport modeling (Suncor Energy Inc., personal communications) provides some important insight on the likely re-distribution of Na^+ migrating from the upland and into the fen using a variety of different material properties and water flux conditions. The most critical finding were the high peak concentrations and early arrival times of Na^+ within the deep peat layers but also the 'shortcutting' of Na^+ laterally into the peat profile along the toe of the upland. The highly permeable (order-of-magnitude higher than peat) petroleum coke underdrain (Ketcheson *et al*. unpublished) plays an important role in distributing Na^+ beneath the fen, resulting in a flowpath with high potential for attenuating Na^+ arrival at the fen surface due to its adsorption (Rezanezhad *et al*. 2012b) and retardation (Hoag and Price, 1997; Rezanezhad *et al*. 2012b).

Further understanding is needed on how system design and material properties influence the hydrology and water quality derived from tailings sands, and how they interact within the system. Therefore, the primary research objectives of this study are to: 1) characterize the distribution of Na^+ within all construction materials and 2) determine the hydrological processes that control the transport and fate of Na^+ from tailings sand upland to fen peat.

2.2 Study Site

Constructed upland – fen system

The study site, a constructed upland – fen peatland system, lies within the Nikanotee Fen Watershed (56°55.944'N, 111°25.035'W) ~ 30 km north of Fort McMurray, Alberta. The upland – fen system was designed to have the optimum geometry (upland to fen ratio of 3:1 and 3% water table gradient), layer thicknesses, and material soil hydraulic properties to support sufficient lateral groundwater flow from upland to fen that can maintain a water table at or near the surface of the fen under periods of water stress ($AET > P$) (Price *et al*., 2010; Daly *et al*., 2012). A combination of salvaged (peat and forest soil) and mine waste materials (tailings sand and petroleum coke) layers were incorporated into construction designs to convey water and manage the transport of solutes from the constructed upland to the constructed fen surface (Daly *et al*., 2012). The upland (7.7 ha) is a 3 m thick tailings sand aquifer on a 3% slope, underlain by an impermeable engineered geotextile clay liner and capped (overlain) by a relatively thin (0.3 – 0.5 m) LFH-mineral mix reclamation forest soil material (herein referred to as 'LFH') (Figure 2 – 1). The LFH is a sandy loam material that controls the infiltration and recharge of freshwater to the upland water table (Ketcheson and Price, 2016c) and provides a substrate for vegetation. The lower lying fen (2.9 ha), situated at the toe of the upland, is 2 m of moderately decomposed peat (average bulk density 0.2 g cm^3; anisotropy (K_h/K_v) of ~ 1.0; Nwaishi *et al*., 2015) overlying a 0.5 m thick petroleum coke layer (herein referred to as the 'petroleum coke underdrain') that extends ~ 100 m into the upland, beneath the tailings sand (Figure 2 – 1). The 2.2 ha zone where the petroleum coke underdrain underlies the upland is referred to as the 'transition zone' (Figure

2 – 1). The strong contrast in saturated hydraulic conductivities between the tailings sand and petroleum coke directs lateral flow into the petroleum coke underdrain, which transmits most of the flow towards and beneath the fen, then upwards through the peat profile (Figure 2 – 1; Ketcheson *et al*., unpublished). A spill box was installed at the north-east corner of the fen to allow for controlled outflow through a flume to an outflow pond. The maximum water level elevation within the fen was controlled manually by adjusting the height of outflow through the spill box (Figure 2 – 1). The surrounding hillslopes to the east, southeast, and west (8.1, 8.2, and 2.4 ha, respectively) generate and contribute surface runoff that recharges the upland aquifer, ultimately reaching the fen peatland (Ketcheson and Price, 2016b). A small depression in the south of the upland was lined with 0.5 m thick peat-mineral mix material (referred to as the 'peat-lined basin'; Figure 2 – 1) which acts as a recharge window due to its detention capability and high water storage capacity (Ketcheson, 2015). Approximately 5000 m^3 of water of unknown quality was used to aid in the compaction of the upland aquifer and to bring the tailings sand materials to residual water contents.

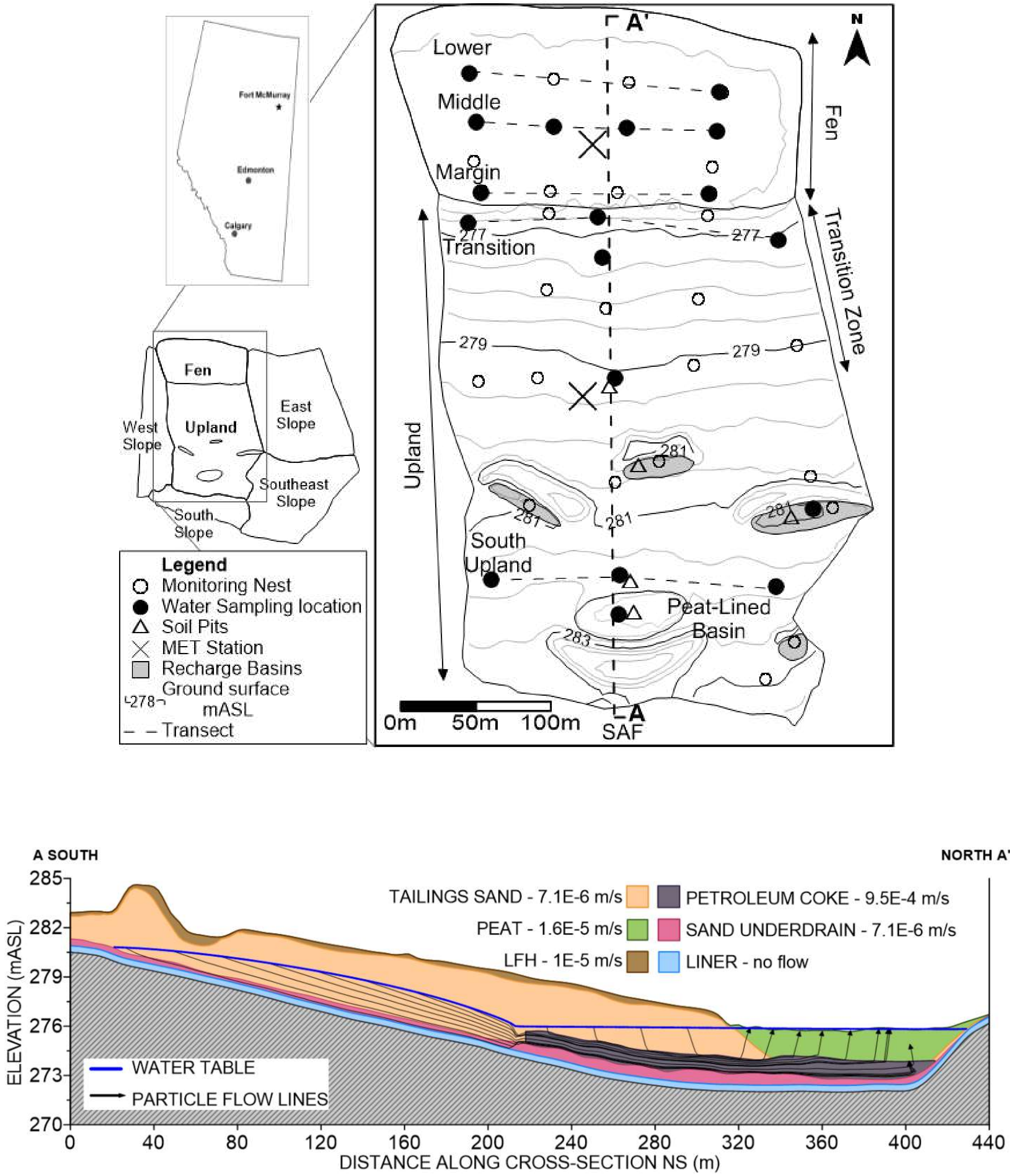

Figure 2 – 1 Map of the Nikanotee Fen with **s**ite instrumentation (top; plan view) and layer properties (bottom; A-A´ cross-section). Cross-section includes particle flow lines for particles dropped every 25 m within the upland tailings sand aquifer. Flow lines generated using MODFLOW display convergence of flow into the petroleum coke underdrain and then 'bottom up' flow within the fen peatland (Ketcheson *et al.,* unpublished).

In July, 2013, the fen was vegetated using a mosaic plot design consisting of control (bare peat), moss (*Tomenthypnum nitens, Aulacomnium palustre, Sphagnum warnstorfii)*, salt-tolerant (*Juncus balticus, Triglochin maritima, Calamagrostis inexpansa*) and fresh water (*Carex aquatilis, Betula pumila*) seedlings, seedling-moss and seeds with combinations of mulched plots (Scarlett *et al*., submitted; Borkenhagen *et al*., 2016). Evapotranspiration rates (*ET*) within the fen were highest over open water (4.4 mm day^{-1}) and lowest over moss-mulch plots (2.4 mm day^{-1}; Scarlett *et al*., submitted). Actual evapotranspiration (*AET*) from the fen was reported to be the dominant water flux within the entire upland – fen system, which typically created a water deficit for the fen (Ketcheson *et al*., unpublished; Scarlett *et al*., submitted). To promote more groundwater recharge, the LFH reclamation soil that caps the tailings sand upland was modified in Autumn 2013, using a dozer ripper shank (furrow dimension typically ~ 24 cm wide, ~ 10 cm deep, with ~ 85 cm spacing between furrows; Ketcheson and Price, 2016c) to create furrows across the surface to help detain overland flow and promote infiltration. To further assist in infiltration and freshwater recharge, four depressional features (herein referred to as `recharge basins`; Figure 2 - 1) were incorporated by excavating the LFH soil cap from behind upland landform with the intent of increasing the infiltration capacity and detention capacity of overland flow.

The soil hydraulic properties (bulk density, ρ_b; porosity, ϕ; saturated hydraulic conductivity, K_{sat}) of the primary construction materials originally reported by Ketcheson and Price (2016c) are summarized in Table 2 – 1.

Table 2 – 1 Soil hydraulic properties of construction materials, Adapted from Ketcheson and Price (2016c).

Properties		**Construction Materials**				
		LFH	**Tailings Sand**	**Petroleum Coke****	**Peat 0 – 50 cm**	**Peat 50 – 200 cm**
ρ_b (g cm^{-3})	**Average**	1.33	1.45	0.64	0.18	0.22
	± SD	0.19	0.14	-	0.04	0.03
	n	21	19	5	36	28
ϕ (fraction)	**Average**	.5	0.45	0.45	0.92	0.87
	± SD	0.07	0.05	0.07	0.02	0.02
	n	21	19	15	36	28
K_{sat} (m s^{-1})	**Average***	1×10^{-5}	4×10^{-6}	9.5×10^{-4}	8×10^{-5}	2×10^{-6}
	Min	5×10^{-7}	1×10^{-7}	-	5×10^{-5}	3×10^{-8}
	Max	2×10^{-4}	3×10^{-5}	-	2×10^{-4}	4×10^{-5}
	n	21	58	-	12	127

Average = arithmetic mean, Average* = geometric mean, SD = 1 standard deviation, n = sample size
**Values taken from Ketcheson *et al.* (unpublished) and Simhayov *et al*. (unpublished)

2.3 Methods

The study covered the first three-year period post-construction of the fen peatland and watershed. Each season was representative of the snow-free period from late May to early October for 2013, 2014, and 2015.

Instrumentation and monitoring

A grid network of monitoring locations (herein referred to as 'nests') of wells and piezometers was employed to target general water levels and pressure heads within distinct constructed material layers (Figure 2 – 1). Instrumentation began in late April 2013 and was generally completed by July 2013; hydrological and geochemical monitoring detail (i.e. sample sizes) increased as additional nests were installed. A maximum depth of 275 cm was targeted within the upland, transition zone and fen to ensure the basal liner was not punctured by deeper installation. Within the network, several series of nests have been used to visualize two-dimensional east-west and north-south transects (cross-sections). Primary transects used and referred to in this study are along the south end of the upland, along the transition, and four within the fen, all of which are oriented east-west. A north-south oriented transect was also used to illustrate data throughout the upland-fen peatland system (Figure 2 – 1).

All wells instrumented within the upland and transition zone were 2.54 cm inner diameter (I.D.) polyvinyl chloride (PVC) pipes installed in a pilot hole made using a portable earth auger (Stihl BT 121; 5.08 cm auger diameter). All wells were fully slotted and wrapped in filter sock. Soil cuttings during drilling were saved and used to backfill around the well casing. No PVC cement was used when joining two or more pipes together to ensure no contamination issues when water sampling throughout the study. All piezometers within the upland and transition zone were stainless steel drive points (Solinst Canada Ltd, Model 615; 20 cm slotted intake) installed using a portable rock percussion hammer (Pionjar 120) and lined with low density polyethylene (LDPE; 1.20 cm I.D.) tubing to prevent contamination of water samples by the galvanized steel casings.

Three locations along the south end of the upland were instrumented with wells and piezometers to targeted depths of 275 cm bgs (Figure 2 – 1). Initially, during the 2013 season, well/piezometer intakes in the central regions of the upland did not reach the water table, which exceeded 275 cm bgs. Until consistent water level measurements were recorded, the water levels in this region were noted as > 275 cm bgs and water chemistry samples were not retrieved. During May 2014, a deeper well (372 cm bgs) was installed, enabling the retrieval of water chemistry samples.

Three nests were installed along the transition zone ~ 10 m from the fen peatland (Figure 2 – 4). Each nest was instrumented with a well and two piezometers; one centered in the petroleum coke underdrain (275 cm bgs) and one in tailings sand immediately above the petroleum coke underdrain (225 cm bgs). The depths of wells varied at each nest and was noted if the well was installed with the slotted intake across two material types (i.e. tailings sand and petroleum coke).

A total of 13 nests, each consisting of a well and five piezometers, were installed within the fen peatland into pilot holes drilled with a 2.54 cm diameter auger (Figure 2 – 1). Fully slotted wells were installed to target depths of 150 cm bgs, intentionally confined to the peat profile. Piezometers were installed to targeted depths of 50, 90, and 150 cm bgs within peat and 225 and 275 cm bgs within the petroleum coke underdrain and tailings sand that underlies it, respectively. All wells and piezometers within the fen were constructed from PVC pipe (2.54 cm I.D.) and fen piezometers had a 20 cm slotted intake; both were wrapped with filter sock.

In May 2014, the east and southeast recharge basin were instrumented with wells to monitor the local water level response. A well downslope of the east recharge basin was installed to compare the ponding of water levels immediately below the recharge basin with the surrounding upland. In May 2015, monitoring wells were instrumented within the central and west recharge basins, similar to the east and southeast recharge basins.

All absolute positions and elevations (mASL; ± 0.5 cm vertical accuracy) of wells and piezometers were determined annually by a Topcon HiPER GL RTK GPS system (2013) and a Leica Geosystems Viva GS14 GNSS RTK GPS system (2014 and 2015). A topographic survey was conducted in 2015 with ~ 2 x 2 m and 5 x 5 m spatial resolution in the fen peatland and upland, respectively.

Metrological variables

Precipitation (*P*) was measured using a tipping bucket rain gauge (Texas Instruments Canada Ltd. TR-525M) located at the upland meteorological station (Figure 2 – 1) which recorded cumulative rainfall over 30 minute periods. *P* totals were also measured with 5 manual rain gauges distributed across the fen-upland system, which were measured after every rainfall. Actual evapotranspiration (*AET*) from the upland and fen was measured with eddy covariance systems at their respective meteorological stations. The specific details of meteorological instrumentation and protocols were reported by Ketcheson (2015).

Fen Outflow

Outflow from the system was initially intended to be measured by a Palmer-Bowlus flume (50.8 cm I.D.) but flow conditions were below the minimum discharge quantities needed for the engineered stage (height of water) versus discharge relationship. Outflow conditions remained under this minimum discharge for the entire duration of the study, so manual discharge measurements were conducted at the outfall with a bucket and stop watch. In 2013, manual discharge measurements were recorded at the outflow from the spill box and a nearby level logger was installed to build a stage – discharge relationship. In 2014, a v-notch weir was installed upstream of the spill-box, which captured all outflow leaving through the spill box (Figure 2 – 1). Manual discharge measurements over a range of flow conditions were used in conjunction with nearby water level loggers to build a stage – discharge relationship for the v-notch weir, in which the geometric mean of 6 manual measurements for each date of flow measurement was used.

Water Sampling and Analysis

Water samples were extracted from a sub-set of wells and piezometers from the hydrological monitoring network (Figure 2 – 4). Sampling locations and soil material layers were targeted to capture the anticipated geochemical variability. Primary transects along the south end of the upland and transition (Figure 2 – 4), along with 8 nests within the fen were sampled. Samples within the upland were taken from wells and within the transition zone from wells and 275 cm bgs piezometers (in petroleum coke). Samples within the fen were taken from piezometers at 50, 90, 150, 225 and 275 cm bgs on 28 May, 14 June, 18 August, and 18 October in 2013, on 20 June, 25 July, 14 August, and 4 October in 2014, and on 9 June, 16 July, 14 August and 4 October in 2015.

All wells and piezometers were completely purged (minimum 3 well volumes) within ~ 24 hours prior to water sample extraction. All water samples were extracted using a 12V peristaltic pump with designated vinyl tubing for each soil material type to avoid cross contamination between soil types. All devices and tubing were flushed thoroughly with de-ionized water between each sample to prevent cross contamination between sampling locations. Standard sampling protocols included evacuating a volume of water (~50 ml) into a clean reservoir for in-field measurements. An electrical conductivity (EC) and temperature (T) probe (YSI handheld multiparameter (2013), Thermo Scientific™ Orion™ Conductivity and Temperature probe (2014 and 2015)) and a pH probe were inserted into this extracted volume. Different models of pH electrode were used in each field season (YSI handheld multiparameter (2013), Orion Star A329 pH/Conductivity Portable Multiparameter meter with Thermo Scientific™ Orion™ 9156DJWP Double Junction pH Electrode (2014) and Thermo Scientific™ Orion™ Economy Series pH Combination Electrode (2015)). *EC* probes were calibrated to 1413 μS/cm monthly and pH probes were three-point calibrated before every use.

After the above procedure, another water sample was taken in a clean 60 or 120 ml high density polyethylene vial and stored in a cooler until they were returned that day to the lab, where they were stored at 4°C. Samples were filtered within 24 hours through 0.45 μm nitrocellulose filters, and then decanted into 60 ml vials for major ion and compound analysis.

Samples were then frozen and shipped in coolers for analysis at the Biotron Experimental Climate Change Research Facility at Western University, London, ON. Na^+ concentrations were determined in all samples by a Dionex ICS-1600 Method EPA 300.0 with AS-DV auto-sampler, with analytical precision to ± 1.0 mg L^{-1}. Field blanks, bottles filled with de-ionized water (<1µS), and sample duplicates were taken periodically through the sample campaigns for quality assurance/quality control.

Na^+ Mass calculations

To quantify the Na^+ migrating from the tailings sand upland through the petroleum coke underdrain and ultimately to the fen peat, a simplified numerical approach was taken to calculate the total Na^+ mass (M_{Na}) in the saturated regions (pore water) of the tailings sand (M_{TS}), petroleum coke (M_{PC}) and fen peat (M_{peat}). The upland – fen system was simplified into an array of cells, in which a single monitoring well or piezometer was the center, used to represent the entire cell. Each construction material was divided into the maximum number of cells as permitted by the monitoring network density. Each cell within the upland was one single layer of tailings sand. The transition zone was sub-divided into three layers; the tailings sand at the base with a deep piezometer (275 cm bgs), the petroleum coke by a piezometer in that layer (225 cm bgs), and the uppermost layer of tailings sand by a well penetrating only that layer. The fen peat was sub-divided into three distinct layers represented by the 50, 90, 150 cm bgs piezometers. The total number of cells used to represent tailings sand, petroleum coke and fen peat were thus 20, 11 and 24, respectively. For each cell, the Na^+ concentration observed at the monitoring well or piezometer was assumed to be a representative concentration of the entire cell. Cell thickness (height) was variable with respect to the water table or thickness of the saturated region at the time of calculations. If a cell did not have a water chemistry sample for a particular sampling event, an average of the values from adjacent cells, perpendicular to the flow direction, was used.

M for each respective construction material was calculated as:

$$M = A * b * \phi * C \qquad \text{(Equation 1)}$$

where A is cell area, b is the saturated cell thickness, ϕ is porosity and C is pore water concentration. The total mass of Na^+ (M_{total}; kg) for a single period in time was calculated as

$$M_{total} = M_{TS} + M_{PC} + M_{peat} - M_{out} \qquad \text{(Equation 2)}$$

where M_{out} is the mass of Na^+ flowing out of the system. The mass of Na^+ introduced to the system through P (at < 15 mg L^{-1} ; Table A – 1 Appendix) was deemed to be negligible and thus not included. M_{out} was calculated by the total discharge out (R_{out}) and the average Na^+ concentration of the outflow for the period of time between the current and previous time of mass balance calculation.

Data Analysis

Water table and geochemistry distributions in plan-view and cross-section were contoured using a kriging interpolation package (linear variogram model) within Surfer® 13 (Golden Software). Source of errors and uncertainties due to the use of a data interpolated contour plot is discussed in the appendix.

2.4 Results

Hydrological Context

All meteorological variables are reported for the periods from 17 May and 27 August (day of year (DOY) 137 to 238) in 2013, 2014 and 2015. P, fen AET, and R_{out} through the fen spill box totals are reported in Table 2 – 2.

Table 2 – 2 Hydrological components for 2013 – 2015.

Year	*P*	*AET*	R_{out}
2013*	254	268	131
2014*	193	381	148
2015	126	408	20

*Adapted from Ketcheson (2015). All values are expressed as depth (mm) with respect to the fen area (2.9 ha).

The Nikanotee Fen Watershed received infrequent but intense P events, with only a few (2 to 6) major (>10 mm day^{-1}) events each season (Figure 2 – 2). Large proportions of the seasonal P were received in the early half (May and June) for the 2013 and 2014 seasons and the latter half of these seasons were relatively dry, with events of similar frequency but lower intensity (< 10 mm day^{-1}). The 2015 season received very little rainfall in May and June, with most P received in July and August. The fen AET rates ranged from 1 to 6 mm day^{-1} throughout the 2013 season with no apparent systematic trend (Figure 2 – 2). In 2014 and 2015, when the fen vegetation was more established, the seasonal pattern of *AET* had a sinusoidal pattern, generally increasing in May, June and early July, peaking in late July (DOY 200), and decreasing through August to October (Figure 2 – 2). The average fen *AET* rates were 2, 4 and 4 mm day^{-1} in 2013, 2014 and 2015, respectively. R_{out} had a very fast response time to P in 2013 and 2014 (< 1 day; Figure 2 – 2). Most R_{out} occurred in the first half of the 2013 and 2014 seasons, similar to the trend of P (Figure 2 – 2). In 2015 R_{out} was low, with only two periods of flow occurring following the spring freshet and a single large P event in late July.

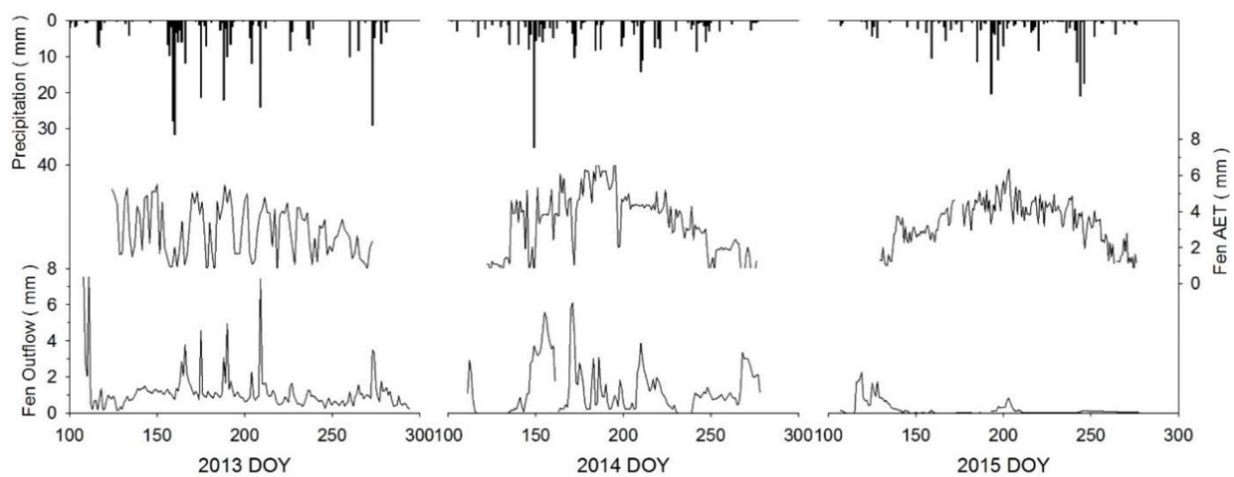

Figure 2 – 2 Hydrological components (P, *AET*, R_{out}) for 2013 – 2015. Fen *AET* and R_{out} are in depth (mm) with respect to the fen area (2.9 ha).

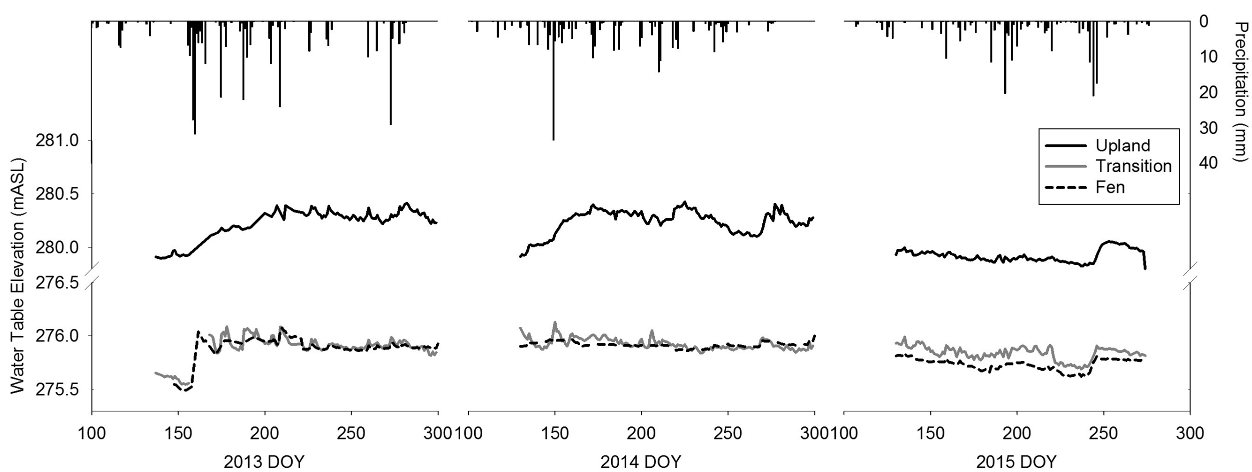

Figure 2 – 3 Average water table elevations in upland, transition zone and fen for 2013 – 2015.

The general groundwater flow direction was south to north; from upland to fen (Figure 2 – 3 and Figure 2 – 4). The water table was parallel to the slope of the basal liner within the southern (upper) part of the upland, forming a hydraulic gradient (i_{horz}) of ~ 0.028. Within the upland, the water table was ~ 1.5 to 2 m bgs; however, the water table within the center of the upland exceeded ~ 3 m bgs creating a relatively thick unsaturated zone within this region of the upland tailing sand aquifer (Figure 2 – 1). Following large *P* events, the upland water table increased (Figure 2 – 3), and mounding occurred in the south-east and east side of the upland proximal to the recharge basins, which increased the local hydraulic gradient (i_{horz} of ~ 0.05) along the east side of the upland for periods of up to 3 weeks following the recharge event (Figure 2 – 4). The upland water table flattened and i_{horz} diminished substantially at the beginning of the transition zone, projecting near horizontal (i_{horz} = ~ 0.0003) towards the fen. The water table within the transition zone was ~ 1 m bgs near the fen and remained somewhat stable (± 20 cm) throughout the duration of study. In the fen, the water table was shallow (± 10 cm bgs) and remained near the surface for the entire 2013 and 2014 seasons (Figure 2 – 3); however, during relatively dry conditions in 2015, the water table within the fen dropped to ~ 20 cm bgs (Figure 2 – 3). During this time, similar drops in water table elevation were observed within the upland (~ 30 to 40 cm) and the transition zone (~ 15 cm bgs). Overall, the water fluxes from upland to fen were strongest under relatively wet conditions in 2013 and 2014, and lowest during relatively dry conditions in 2015.

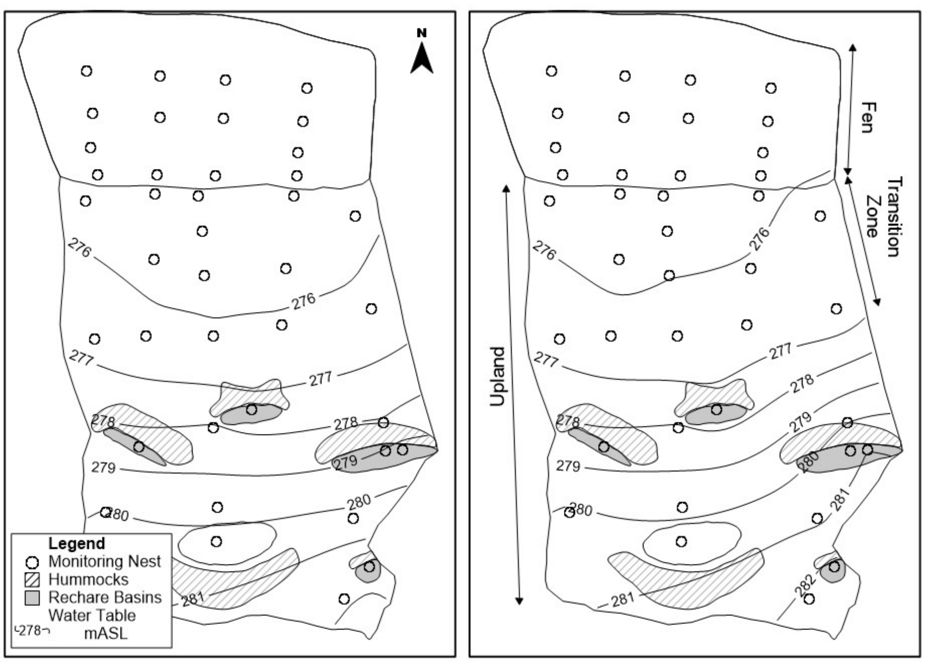

Figure 2 – 4 Average water table elevation contours (left), and during typical recharge scenarios (right) in 2014.

EC and pH distributions

In 2013, *EC* was generally highest in the tailings sand upland (mean of 2971 µS cm^{-1}) and lowest within the petroleum coke underdrain beneath the fen peatland (1492 µS cm^{-1}; Figure 2 – 5). *EC* in the fen was highly variable, ranging from 1144 to 3141 µS cm^{-1} with a mean of 2022 µS cm^{-1}. Between 2013 and 2014, *EC* within the tailings sand upland decreased to a mean of 2328 µS cm^{-1}. By 2014 the mean *EC* within the petroleum coke underdrain increased to 3025 µS cm^{-1}, the highest in all construction materials. During the same period the mean *EC* within the fen also increased to 2577 µS cm^{-1}, with the highest average values in the deep peat layer (150 cm bgs). The highest *EC* temporal variability was in shallow peat layers (50 cm bgs). The *EC* in fen peat increased (to mean of 2706 µS cm^{-1}) in 2015, with the highest averages in deep peat and highest variations in shallow peat. There were no substantial changes in *EC* in the tailings sand or petroleum coke underdrain between 2014 and 2015. Over the duration of the study, the petroleum coke underdrain was slightly basic (mean pH of 7.5) and the tailings sand upland was slightly acidic (mean pH of 6.5) in all seasons. The pH of fen peat was generally neutral (mean pH of ~7) throughout the study (Figure 2 – 5).

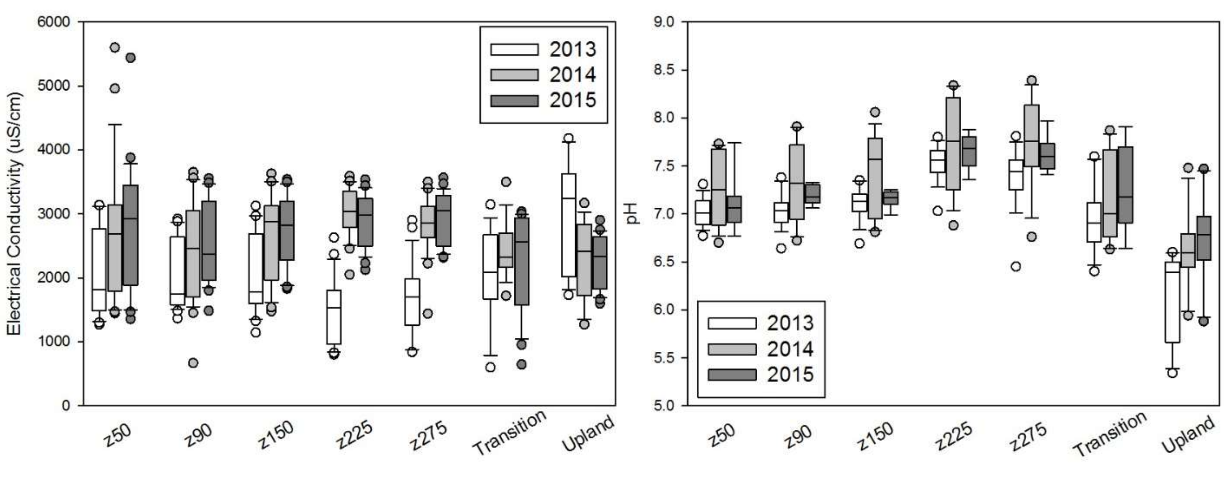

Figure 2 – 5 Boxplots of electrical conductivity (µS cm^{-1}; left) and pH (right) of all construction materials and materials regions within the upland - fen system for the 2013 – 2015 study period. 'z' corresponds to piezometer depth within the fen; z50 to z150 are in peat, z225 is in petroleum coke and z275 is in the basal sand. Upland and Transition are monitoring well observations for tailings sand and a combination of tailings sand and petroleum coke, respectively. For boxplots, error bars are the 5th and 95th percentiles and black line is the median value.

Na^+ Distribution

Yearly average (mean) Na^+ concentrations within all the construction materials are summarized in Table 2 – 3. Generally, Na^+ concentrations were highest within the tailing sand upland and petroleum coke underdrain, and lowest within the fen peat (Table 2 – 3). Similar trends were observed in Na^+ concentrations within the tailings sand upland and petroleum coke underdrain throughout the duration of the study, despite tailing sands initially (early 2013; Figure 2 – 6) having the highest Na^+ concentrations, on average. Decreases in Na^+ concentration immediately following the substantial rainfall received in early 2013 and 2014; yet both maintained relatively high Na^+ concentrations throughout the dry (low rainfall relative to 2013 and 2014) 2015 season (Figure 2 – 6). Na^+ concentrations were generally low within the fen peat throughout 2013 and 2014; however, increased considerably by 2015 (Table 2 – 3 and Figure 2 – 6).

Table 2 – 3 Mean groundwater Na^+ concentrations (± Standard Deviation) within all construction materials 2013 – 2015. Bolded values denote the highest average of that season.

Ion	Year	Fen Peat				Petroleum Coke	Tailings Sand
		Well (150cm)	50 cm	90 cm	150 cm		
Na^+	2013	119 ± 38.9*	87.3 ± 35.5	78.5 ± 35.4	121 ± 66.3	200 ± 119	**232 ± 140**
($mg\ L^{-1}$)	2014	90.3 ± 64.9	79.7 ± 64.1	66.3 ± 42.9	97.4 ± 71.2	**182 ± 103**	138 ± 111 [a]
	2015	207 ± 110 [a]	153 ± 105 [a]	129 ± 73.8 [a]	188 ± 79.4 [a]	**303 ± 78.7** [a]	238 ± 146 [a]

[a] denotes a significant change ($P < 0.05$) in concentration from the previous year for each respective construction material. A two-sample T-test assuming unequal variance was done using P-value of 0.05.
* inconsistent sampling locations with following years, and therefore removed from statistical significance testing.

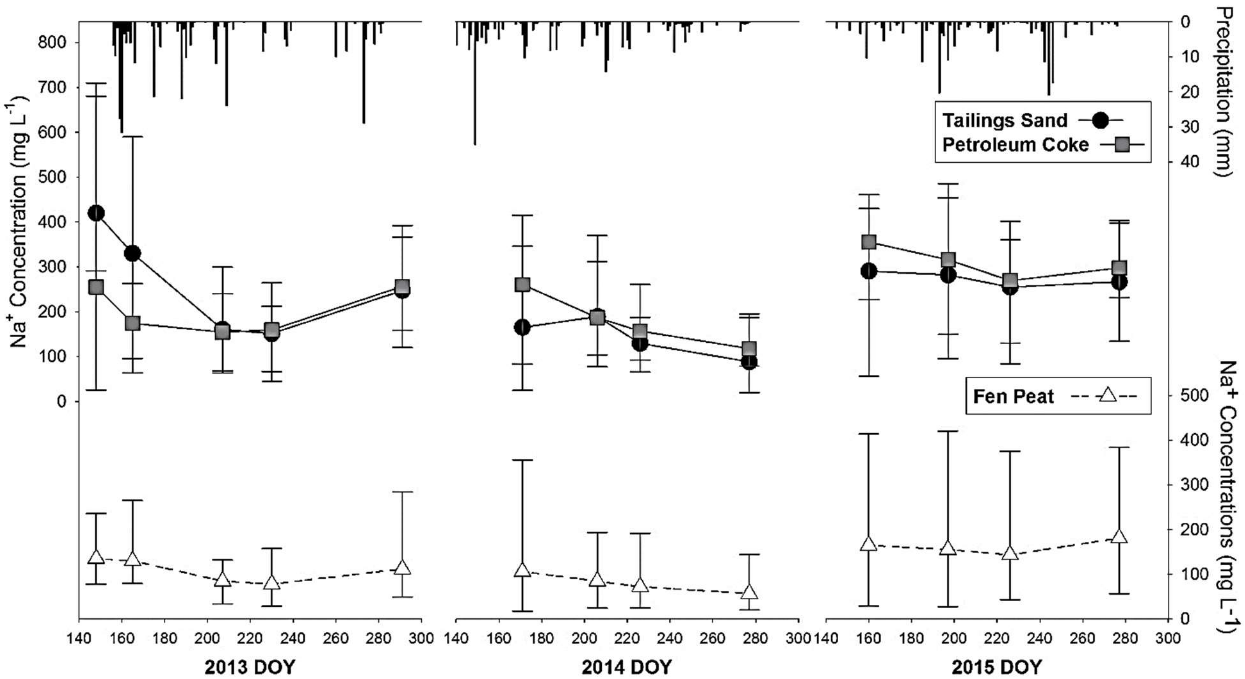

Figure 2 – 6 Average (mean) Na^+ concentrations (symbols) in construction materials over the duration of the three-year study period. The fen peat values are an average and range of all peat layers. Bars are the minimum and maximum observed concentrations.

The spatial patterns of average Na^+ concentrations show that it was relatively high throughout the tailings sand upland and petroleum coke underdrain beneath the transition zone in 2013 (Figure 2 – 7 and Figure 2 – 8), with highest concentrations within the southwest portion of the upland (mean of 428 mg L^{-1}) and lowest immediately downslope (~ 5 m) of the peat-lined basin (mean of 202 mg L^{-1}). Average Na^+ concentrations within the petroleum coke underdrain beneath the fen were highest adjacent to the upland (Margin Transect Figure 2 – 1) in 2013, which decreased with increasing distance from the upland (i.e. towards Middle and Lower Fen Transects; Figure 2 – 7 and Figure 2 – 8). The aforementioned decreases in Na^+ concentrations in 2014 were most pronounced within the southeast region of the tailings sand upland and along the east side of the petroleum coke underdrain in 2014 (Figure 2 – 7), following the addition of recharge basins and tillage of LFH. Similar decreases in Na^+ concentrations were observed the southeast region of the upland in 2015; however, there was no decrease along the east side of the petroleum coke underdrain and concentrations were relatively high throughout the remaining areas of the upland and transition zone (Figure 2 – 7), similar to 2013. Na^+ concentrations increased throughout the entire petroleum coke underdrain beneath the fen by 2015 (Figure 2 – 7 and Figure 2 – 8). Substantial increases in Na^+ concentrations within the deep fen peat layers (nearly doubling, average 97.4 mg L^{-1} to 188 mg L^{-1}) and within the fen margin adjacent the toe of the upland were observed in 2015 (Figure 2 – 8).

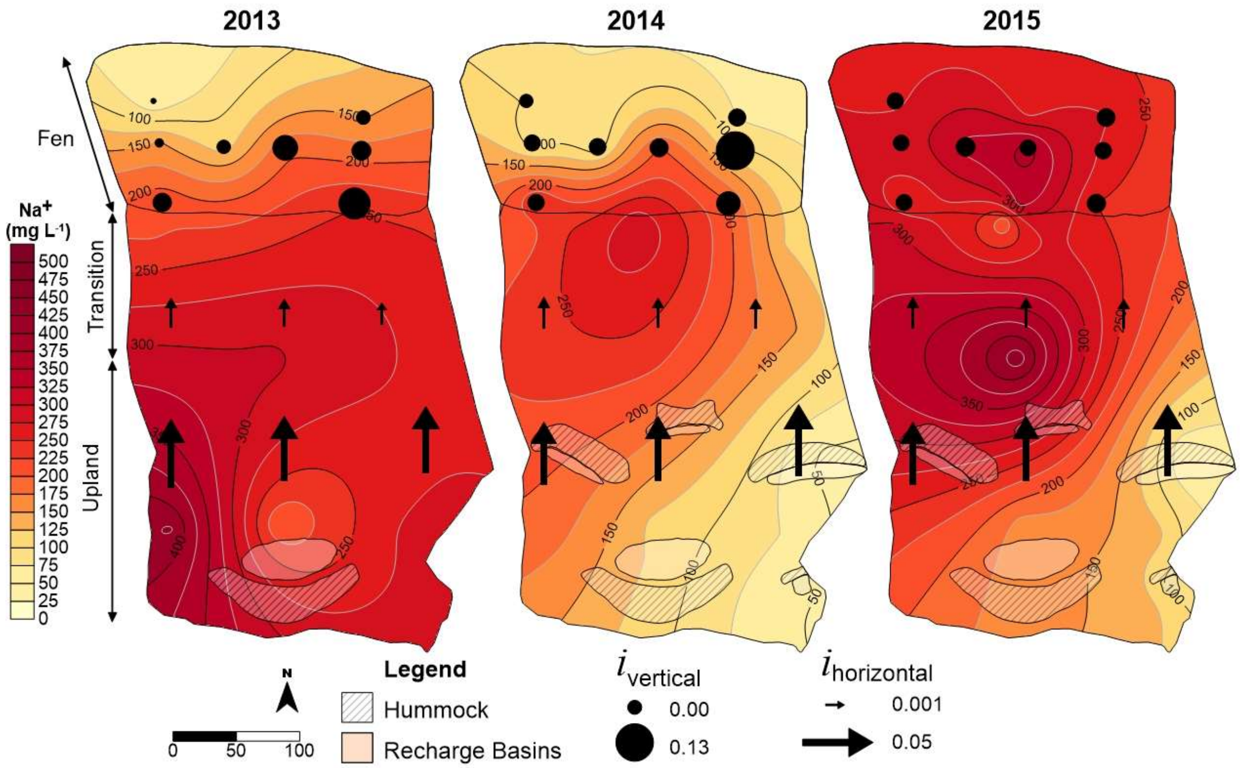

Figure 2 – 7 Spatial distribution of the seasonal average Na^+ concentrations (colour scale; mg L^{-1}) within the tailings sand upland and petroleum coke underdrain (beneath peat) for 2013 – 2015. Included are seasonal average $i_{horizontal}$ (upland and transition zone) and $i_{vertical}$ (fen) represented by arrows and black dots, respectively.

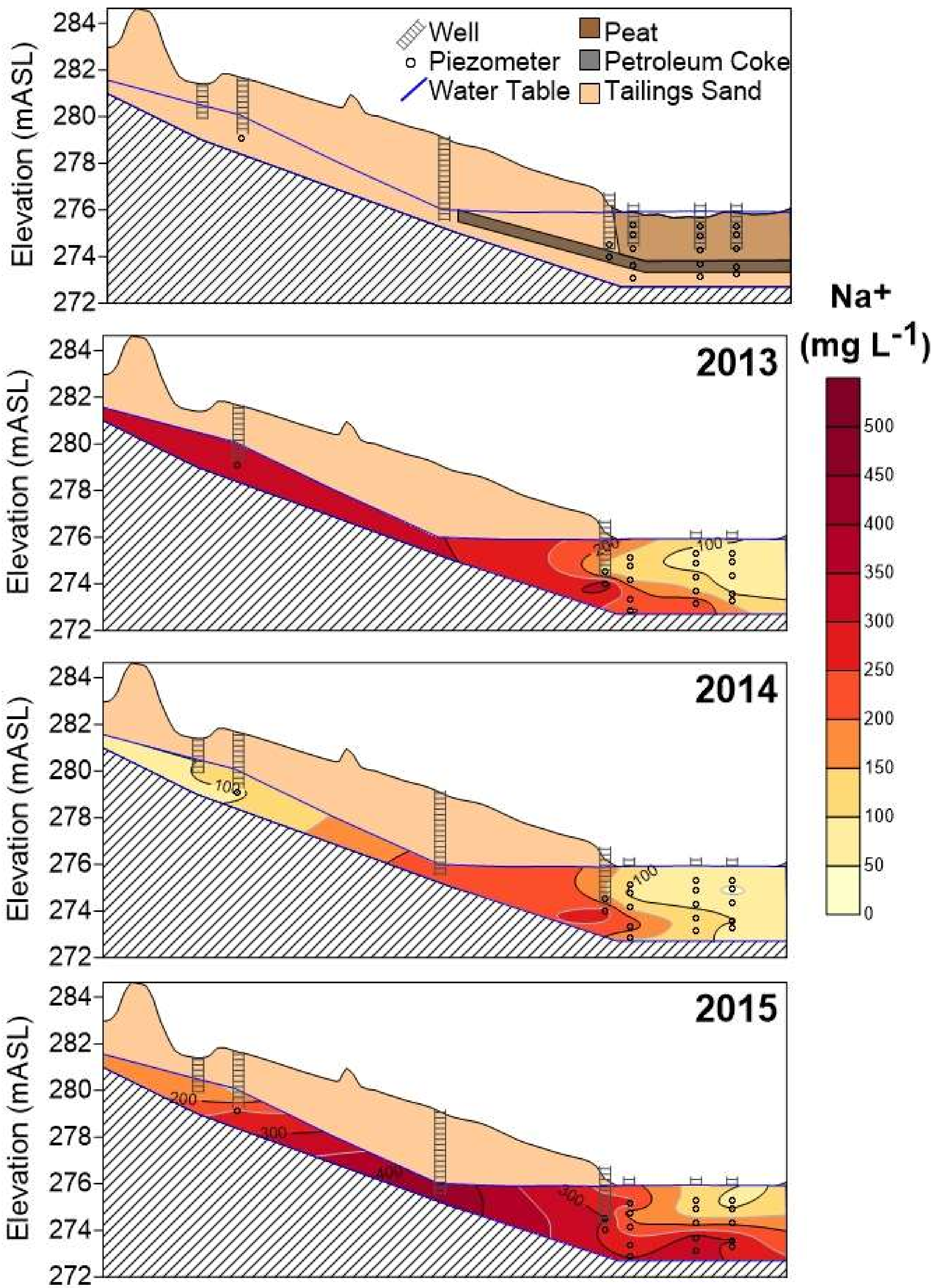

Figure 2 – 8 Cross-sectional visualization of average (mean) Na^{+} concentration distributions in groundwater (colour scale; mg L^{-1}) along the primary A – A′ transect (Figure 2 – 1) for 2013 – 2015.

Geochemical Stratification

In 2013 and 2014, upland groundwater was somewhat homogenous in *EC* with low vertical concentration gradients between the upper and deeper layers of the saturated regions (Central Upland Figure 2 – 9), resulting in little geochemical stratification within the tailings sand aquifer. In-field comparisons (not shown) of the monitoring well and deep piezometer showed negligible variations in *EC* (< 100 µS cm^{-1}) and therefore only the monitoring well was used to represent such locations within the upland, assuming there was no vertical variability within the tailings sand aquifer. However, in 2015 there was a considerable increase in *EC* (2000 to 3000 µS cm^{-1}; Figure 2 – 9) in deeper layers of the tailings sand aquifer (represented by piezometers; z260 or z275), compared to samples drawn from the adjacent well (that sampled typically from 190 cm to 246 cm below the surface, depending on water table elevations). Following the observed increases in *EC* with depth, all other monitoring locations along the South Upland Transect (Figure 2 – 1) were incorporated into routine sampling and showed similar trends of geochemical stratification (East and West Upland Figure 2 – 9).

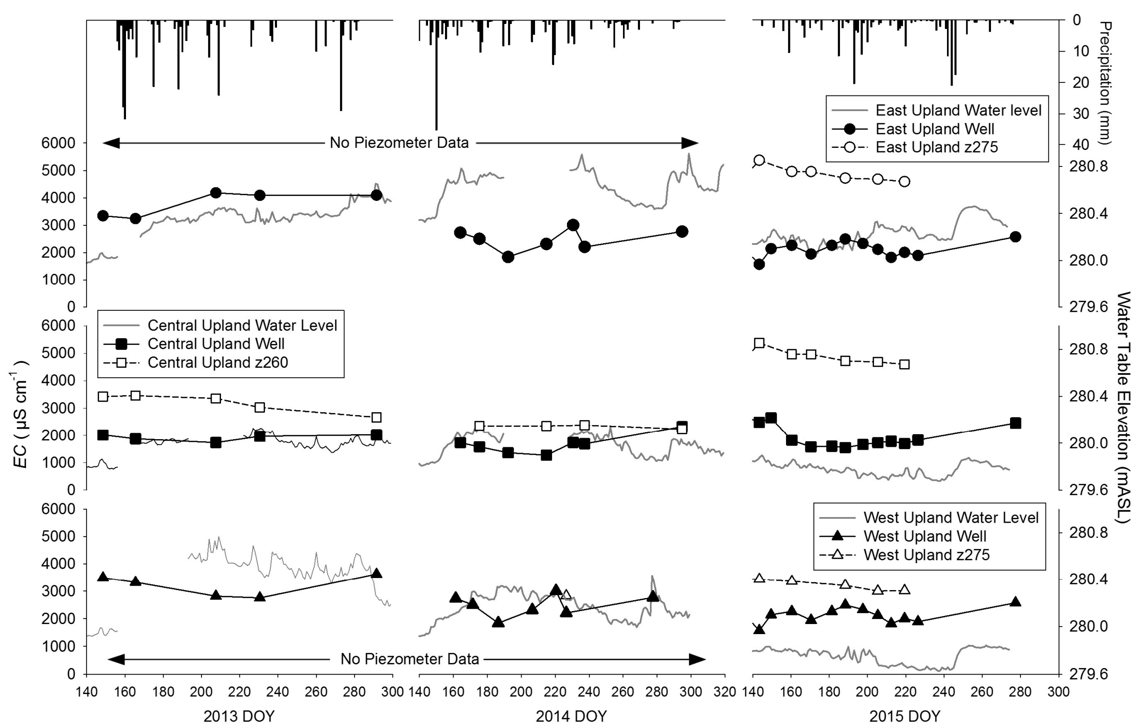

Figure 2 – 9 Time series of *EC* within the South Upland Transect (Figure 2 – 1). Monitoring wells (infilled symbols) and deep piezometers (z260 or z275, unfilled symbols) illustrate the vertical concentration gradient within the tailings sand aquifer. Note the evolution of geochemical stratification in 2015.

Na^+ Mass Totals

The mass totals for Na^+ calculated for each construction material on 26 July, 2013, 25 July, 2014, and 16 July, 2015, are reported in Table 2 – 4.

Table 2 – 4 Saturated zone Na^+ Mass Totals in construction materials for July 2013 – 2015.

Material	Sat. Vol. (x10^3 m^3)	26 July 2013	25 July 2014	16 July 2015
Upland TS		6,342	8,786	9,920
Transition TS		1,445	1,837	2,202
Fen TS		3,080	2,562	4,936
TS total	**142.8**	**10,868**	**13,185**	**17,059**
Transition PC		1,287	1,550	1,134
Fen PC		808	1,213	2,006
PC total	**30.0**	**2,095**	**2,763**	**3,140**
Peat (120 – 200cm)		1,734	1,826	3,353
Peat (70 – 120 cm)		1,230	1,127	2,035
Peat (0 – 70 cm)		1,711	1,573	2,980
Peat total	**58.0**	**4,674**	**4,526**	**8,368**
Discharge*	**-**	**848**	**870**	**590**
Grand Total	**230.8**	**17,637 kg**	**20,474 kg**	**28,567 kg**

TS = Tailings sand, PC = Petroleum coke, Sat. Vol. = saturated volume of material. All values are mass of Na^+ in kg, unless otherwise stated.
*Discharge not included in the total mass of Na^+ within the upland-fen system.

A total of 17.6, 20.5, and 28.6 T of Na^+ were estimated to be mobile within the pore water of the saturated regions of the entire upland – fen system for July of 2013, 2014, and 2015 sample periods, respectively. The largest Na^+ mass was within the tailings sand materials, which increased in July 2013 to July 2014 to July 2015 (Table 2 – 4). Similarly, the mass in the petroleum coke increased throughout the duration of the study; however, mass totals were relatively low compared to other construction materials (i.e. tailings sand and peat). The fen peat contained a considerable mass of Na^+ in July, 2013 (4.7 T) and 2014 (4.5 T), and nearly doubled to 8.4 T by July, 2015 (Table 2 – 4). The largest increase in Na^+ mass (per kg peat) was within the deepest peat layer (120 to 200 cm bgs; Table 2 – 4). The total mass of Na^+ lost (outflow from the system) were relatively small compared to the mass totals remaining within the upland – fen system (Table 2 – 4).

2.5 Discussion

Characterization of peatland type

Based on the relatively high *EC* (Figure 2 – 5), somewhat neutral pH (Figure 2 – 5), and abundance of base ions (see Table A – 2 Appendix) the Nikanotee Fen can be characterized as an extremely rich fen peatland system (according to Chee and Vitt (1989)). Simhayov *et al*. (unpublished) has reported the donor peat used in construction originated from a rich fen, as intended (Daly *et al*., 2012); however, the introduction of ion rich water from the constructed upland has likely transitioned the fen from rich to extreme-rich conditions. It is speculated that the mineralization of ions may have occurred during drainage of the peat in the salvage processes, increasing the available ions which further contributed to a transition to extremely-rich conditions; however, this is yet to be proven. Several natural wetlands surrounding the AOSR serve as a reference to compare with the geochemical characteristics, of the Nikanotee Fen, including a poor fen (Pauciflora Fen; ~ 90 km to the south; Wells *et al*., in-review), a moderately-rich fen (Poplar Fen; ~ 10 km west; Elmes and Price, personal communications), and a saline-spring fen (Saline Fen; ~ 60 km south; Wells and Price, 2015a; Wells and Price, 2015b) (Table 2 – 5). The range in Na^+ concentrations (~ 100 to 700 mg L^{-1}) are 1 to 2 orders of magnitude greater than observed within most fens within the AOSR (Chee and Vitt, 1989; Price *et al*., unpublished; Elmes and Price, unpublished), yet are well below (1 to 2 orders of magnitude) the hyper-saline (> 3,500 mg L^{-1}) conditions found within saline-spring fens (Wells and Price, 2015). While the Na^+ concentrations in the Nikanotee Fen are not currently hyper-saline, accumulation of Na^+ and other salts within the near surface peat may begin to increase concentrations from evapo-concentration due to the high evaporative demands (Rezanezhad *et al*., 2012a; Simhayov *et al*., unpublished). It is likely that the vegetation cover will transition to species tolerant to the extremely rich conditions and relatively high salinity being received by the fen (Trites and Bayley, 2009).

Table 2 – 5 Comparison of EC and Na^+ between the constructed fen and local reference fens

Study Site	Year	Peat		Mineral*	
		EC (μS cm^{-1})	Na^+ (mg L^{-1})	*EC* (μS cm^{-1})	Na^+ (mg L^{-1})
Constructed Fen (Nikanotee)	2013	2,250 ± 514	119 ± 39.0	3,020 ± 770	304 ± 165
	2014	2,280 ± 545	90.7 ± 65.8	2,280 ± 793	156 ± 117
	2015	2,770 ± 725	207 ± 110	2,540 ± 1,090	272 ± 115
Poor Fen (Pauciflora)	2011	61.8 ± 26.7	-	245 ± 124	-
	2012	49.4 ± 20.0	-	262 ± 169	-
	2013	-	-	-	-
	2014	53.2 ± 28.0	4.0 ± 2.6	132 ± 111	-
Moderately-Rich Fen (Poplar)	2013	456 ± 199	-	513 ± 136	-
	2014	470 ± 152	6.9 ± 2.19	618 ± 134	14.4 ± 10.9
Saline-Spring Fen (Saline)	2011	29,800	-	49,600	-
	2012	34,600	13,000	48,700	9,090

*Mineral is representative of the underlying substrate and/or uplands.

Transport of Na^+

Precipitation-driven recharge to the upland (Ketcheson *et al*., unpublished), along with the sloping topography, was the driving force for water flow and thus the re-distribution of Na^+ within the system. Generally, groundwater flow was from tailings sand upland to petroleum coke underdrain (transition zone), and upwards into the fen peat (Figure 2 – 1 cross-section); however, water fluxes and thus the transport rates of Na^+ varied from wet to dry periods throughout the study.

The initial Na^+ concentrations measured within the tailings sand upland in May, 2013, were the highest observed over the duration of the study (Figure 2 – 6). Prolonged periods without recharge, as in the winter seasons, likely allowed for increased concentrations of Na^+ within the tailings sand aquifer ($C_0 \approx 421$ mg L^{-1}). Elevated concentrations may have also been influenced by the water used during construction (5000 m^3, ~ 65 mm across the upland area) to wet and compact the tailings sand materials, which may have introduced solutes. Rainfall directly resulted in freshwater recharge and dilution, which in turn caused a decrease, in Na^+ concentrations site wide. Following the first substantial rainfall in early June (DOY 156), 2013, Na^+ concentrations decreased (from 421 to 332 mg L^{-1}) within the tailings sand upland. Frequent and intense rainfall through June and July, 2013, further decreased the Na^+ concentrations (to 195 mg L^{-1}; Figure 2 – 6). The decreases in Na^+ concentrations were attributed to dilution as a result of the pulse of relatively fresh rainwater, which also resulted in a large change in water storage, as reflected by the increasing water table (Figure 2 – 3). However, following a relatively dry second half of the 2013 season (August to September) Na^+ concentrations increased within the tailings sand upland (256 mg L^{-1}), generating a Na^+ plume (> 200 mg L^{-1} or ~ ½ C_0) that migrated into the petroleum coke underdrain, extending ~ 60 m from the toe of the upland to beneath the fen (Figure 2 – 7 and Figure 2 - 8). The introduction of the Na^+ plume at the base of the fen peat profile increased the Na^+ concentrations within the deep fen peat (150 cm bgs; Table 2 – 3 and Figure 2 – 6) that lies immediately above the petroleum coke interface. Na^+ concentrations within the peat likely remained below the plume concentrations due to removal of Na^+ by adsorption to the peat (Rezanezhad et al. 2012b). In 2013, the deep peat (150 cm bgs) with highest Na^+ corresponded to the highest concentrations within the petroleum coke underdrain (nearest the toe of the transition zone) and the strongest i_{vert} (i.e. highest mass flux; Figure 2 – 7 and Figure 2 – 8). There was no evidence that Na^+ plume had reached the middle layers or near surface of the peat profile (Table 2 – 3 and Figure 2 – 8) by the end of the 2013 study period.

The installation of upland recharge basins, along with the tillage of the LFH, detained a greater proportion of the early 2014 spring freshet and rainfall, promoting freshwater recharge that diluted Na^+ within the tailings sand aquifer (Figure 2 – 6). The most pronounced decreases were within the south-east regions of the upland (Figure 2 – 7) near the south-east and east recharge basins, into which there were large contributions of snowmelt and rainfall from the adjacent hillslopes. As in 2013, the high P received within the first half of the 2014 season diluted the Na^+ concentrations within the tailings sand and petroleum coke underdrain (Figure 2 – 6). The diluted water flowed along the east side of the upland towards the fen, reducing Na^+ concentrations in this region (Figure 2 – 7). Na^+ concentrations within the west and central regions of the tailings sand upland remained relatively high due to the comparatively small quantity of freshwater recharge through the LFH (Ketcheson and Price, 2016c) and comparatively thick unsaturated tailing sand layers. The Na^+ plume within the petroleum coke underdrain was present in June, 2014, with comparable concentrations and extent as at the end of the 2013 season. The advance of the Na^+ plume beneath the fen in 2014 was likely slowed by the pulse of diluted water caused by the enhanced recharge through the recharge basins. As in 2013, there was no evidence that the Na^+ plume had reached the middle layer of the fen peat as Na^+ concentrations remained relatively low (~ 66 mg L^{-1} at 90 cm bgs; Table 2 – 4 and Figure 2 – 8).

The 2015 season had the least *P* of all three years and, unlike 2013 and 2014, there was no substantial rainfall early in the season. As such, the upland did not receive the early season freshwater recharge to dilute the Na^+ concentrations within the tailings sand. During the winter months (not studied), it is speculated that drainage of the tailings sand released Na^+ to the groundwater; without substantial freshwater recharge early in the spring, Na^+ concentrations remained relatively high (averaged 238 mg L^{-1}). Also, *EC* trends (Figure 2 – 9) indicate that Na^+ concentrations increased considerably in the deeper layers of the tailings sand, creating a pronounced geochemical stratification of the aquifer. Freshwater recharge that did occur settled on the upper layers of the saturated zone, diluting Na^+ concentrations. Throughout the 2015 season, low *P* and high *AET* (126 and 408 mm, respectively Table 2 – 2) generated the highest water demand for the fen (as reflected by the decline in fen water table levels throughout the 2015 study period; Figure 2 – 3) in which the groundwater fluxes from the upland helped to slow the drying of the fen. Consequently, in 2015, the concentration of Na^+ within the groundwater flowing from the upland to the fen was high, and the Na^+ plume expanded to fully encompass the petroleum coke underdrain beneath the transition zone and fen (Figure 2 – 7 and Figure 2 – 8). High *AET* demands in the summer season caused the Na^+ plume to migrate upwards into the fen peat, as Na^+ concentration (Table 2 – 3) and mass (addition of ~ 1.5 T since 2014; Table 2 – 4) increased substantially by July, 2015, within the deep fen peat layers (120 to 200 cm bgs).

Overall, the greatest loads of Na^+ from upland to fen were in 2015, which is counterintuitive as 2015 had the lowest *P* and thus lowest water fluxes from upland to fen. Na^+ loading in 2013 and 2014 was comparatively less under stronger hydraulic gradients as freshwater recharge was ensured relatively low Na^+ concentrations in groundwater within the tailings sand aquifer. It was hypothesized that because there was no apparent geochemical stratification within the tailings sand aquifer in 2013 and 2014, the petroleum coke underdrain drew from relatively diluted groundwater, low in Na^+. However, in 2015, the lack of freshwater recharge resulted in geochemical stratification (elevated Na^+ within deep tailings sand) within the tailings sand aquifer, in which the deep Na^+ rich water converged into the petroleum coke underdrain within the transition zone (cross-section Figure 2 – 1). This resulted in elevated loads of Na^+ being received by the fen, as evidenced by the advance of the Na^+ plume. The geochemical stratification in 2015 could be a result of slow drainage of water over the winter season, coupled with the relatively low amount of freshwater recharge to the water table. The slow percolation would allow for maximized desorption or dissolution of available Na^+ within the tailings sand, resulting in elevated concentrations within the saturated zone.

Attenuation of Na^+ in peat

Peat has been shown to have the ability to remove Na^+ from mobile water in active pores by diffusing into closed or dead-end pores and by adsorbing to the peat material surfaces (Hoag and Price, 1995; Hoag and Price, 1997; Rezanzehad *et al*., 2012b; Rezanzehad *et al*., 2016). Na^+ concentrations (Table 2 – 3, Figure 2 – 6 and Figure 2 – 7) and mass (Table 2 – 4) within the fen peat remained relatively low in 2013 and 2014. The peat was capable of removing Na^+ from the groundwater relatively low in Na^+ concentrations. However, as Na^+-rich groundwater was received at the fen, the proportion of Na^+ adsorbed to the peat also increased (Goldberg *et al*., 2007; Rezanzehad *et al*., 2012b). As sorption sites began to fill with respect to Na^+, the Na^+ plume was able to migrate further into the peat deposit. By the end of the 2015 season, increasing Na^+ concentrations and mass within the middle layers indicate that the front of the Na^+ plume was present; however, average concentrations remained below breakthrough concentrations (½ C_0). It is likely that the total Na^+ attenuation capacity of the peat is less than reported by Rezanezhad *et al*. (2012b) due to the influence and competition of other cations or more complex adsorption behaviors not considered in single cation laboratory experiments (Goldberg *et al*., 2007). High fen *AET* demands (~ 300 to 400 mm) during the study periods resulted in solutes being left behind, thus increasing its concentration in pore-water near the surface (evapo-concentration). The low net fluxes (*AET* – *P*) and high R_{out} in 2013 resulted in a relatively small degree of evapo-concentration of Na^+, which was reflected in stable Na^+ concentrations (Table 2 – 3 and Figure 2 – 6). Comparatively larger water loss (21 cm of storage) in 2014 likely resulted in slightly elevated concentrations of Na^+ within the near surface peat but was not evident in the 50 cm bgs piezometers. In 2015, the high *AET*, low R_{out}, and drop in fen water levels resulted in the greatest water loss (31 cm of storage) and considerable evapo-concentration of Na^+, which nearly doubled since 2013 and 2014 (Table 2 – 3, Table 2 – 4 and Figure 2 – 6).

2.6 Conclusions

This study is the initial assessment of the distribution and transport of Na^+ within the Nikanotee Fen within the first three years post-construction. In general, the tailings sand upland generated considerable Na^+ concentrations (average of 244 mg L^{-1}, upwards of 400 mg L^{-1}), which migrated into the petroleum coke underdrain and into the fen peat deposit, as anticipated. Na^+ concentrations within the petroleum coke underdrain were largely reflective of the concentrations within the tailings sand upland, experiencing very similar increases and decreases due to the strong hydrological connection between the two units. Initially the Na^+ concentrations were low within the peat deposit, as expected. The first two years (2013 and 2014) indicated that the tailings sand upland was capable of transmitting relatively low Na^+ water following periods of rainfall. Freshwater recharge within the eastern regions of the upland diluted Na^+ within the tailings sand groundwater and relatively lower Na^+ concentrations migrating to the fen along the east side system. However, comparatively less freshwater recharge throughout the central and western regions of the upland resulted in groundwater with higher Na^+ concentrations flowing down-gradient to the fen. During the 2013 and 2014 seasons, a Na^+ plume was observed within the petroleum coke underdrain, beneath the fen along the toe of the upland. Little upward migration of Na^+ into the peat occurred and concentrations remained relatively low within the near surface peat layers and rooting zone of the fen in 2013 and 2014. However, during dry periods, there was insufficient rainfall and freshwater recharge within the upland to maintain low Na^+ concentrations within the groundwater. In 2015, despite lower water fluxes from upland to fen, elevated Na^+ concentrations within the upland resulted in a considerable amount of Na^+ migrating from the tailings sand upland, into the petroleum coke underdrain and vertically through the fen peat deposit. Na^+ concentrations within the fen peat increased considerably over the study. Concentrations averaged 153 mg L^{-1} within the near surface peat by 2015, which was greater than that immediately after construction, due to migration through the peat and evapo-concentration by high *AET* demand.

The petroleum coke underdrain was successful in receiving Na^+ enriched groundwater from the tailings sand upland and dispersing it beneath the fen. Without this, contrasts in the hydraulic properties of the tailings sand and peat may have resulted in water discharge at the hinge-line between upland and fen (Ketcheson *et al.*, unpublished), creating hotspots of elevated Na^+

concentrations. By directing the flow of Na^+ beneath the fen, the arrival time of Na^+ to the fen surface was delayed significantly, because of the longer flowpath and the high cation adsorption capacity of peat (Rezanezhad *et al*., 2012b). Effective dispersion within the petroleum coke underdrain also allowed for lower peak concentrations entering the base of the peat deposit until the Na^+ plume fully encompassed the petroleum coke underdrain. Na^+ concentrations began to increase by the 2015 season, with the greatest increase within the deep peat layer immediately above the petroleum coke underdrain as the Na^+ plume began to migrate upwards. The higher Na^+ concentrations within the near surface peat compared to the middle peat layer was likely due to the evapo-concentration of Na^+. Substantial increases in Na^+ within the peat between 2014 and 2015 suggest that the number of adsorption sites in the fen peat may be approaching a maximum, and therefore the potential for Na^+ attenuation may be limited. Na^+ may be out-competed for sorption sites by other abundant ions within the OSPW that could decrease the available sink for Na^+. In general, there was little evidence for complete shortcutting or bypass flow from the bottom of the peat to the surface that could potentially accelerate contaminant transport. Thus, it is recommended that similar designs of sub-surface hydrological connections are used in future constructed fen peatland designs to direct the flow of contaminants beneath the fen to allow for the longest delayed arrival time to the fen surface possible.

The amount of Na^+ transmitted from upland to fen in each season was sensitive to the total concentrations within the tailings sand upland. Upland recharge basins were important for freshwater recharge to the upland aquifer, evident by a transient water table and subsequent decreases in Na^+ concentrations within the groundwater beneath effective recharge basins immediately following rain events. The promotion of freshwater recharge within the southern regions of the upland was capable of diluting the Na^+ within the tailings sand aquifer which led to relatively lower Na^+ concentrations in water being received downslope by the fen. Thus it is recommended that recharge features are incorporated in future reclamation designs, not just to promote sub-surface storage but to manage Na^+ concentrations within the system. However, the size, geometry and positioning of recharge basins needs to be assessed to optimize the success of freshwater recharge and also their implications on the flushing of Na^+ (and other solutes) in underlying tailings sand.

3.0 Manuscript Chapter 2. Use of recharge basins to modify the hydrology and solute transport in a constructed tailings sand aquifer for oil sands reclamation

3.1 Context

Over 767 km^2 of the Western Boreal Plain in the Athabasca Oil Sands Region (AOSR) has been disturbed from activities related to oil sands extraction (Government of Alberta, 2015), which the oil companies responsible are required to reclaim the land to an equivalent land class prior to disturbance (OSWWG, 2000). Due to the natural abundance of wetlands prior to disturbance, specifically fen peatlands (Vitt *et al*., 1996), fen peatland construction has been incorporated into post-mine landscape reclamation plans (Daly *et al.,* 2012; Pollard *et al.,* 2012; Ketcheson *et al*., 2016). A pilot upland – fen system, the Nikanotee Fen, was constructed on Suncor Energy Inc. mine lease from mine-waste and salvageable materials to assess the feasibility of AOSR reclamation (Price *et al*., 2010; Daly *et al.,* 2012; Ketcheson *et al*., 2016). The Nikanotee Fen design relies on a tailings sand upland, supplemented with runoff from the surrounding hillslopes, to supply sufficient quantities of water to the adjacent fen (Price *et al*., 2010; Ketcheson *et al*., 2016). Thus far, the system design has been successful in maintaining a water table near the surface of the fen (Ketcheson *et al*., unpublished). However, the tailings sands materials used to construct the upland aquifer, an abundant bi-product of oil sands production, contains high residual concentrations of salts ($NaSO_4^{2-}$, $MgSO_4^2$, $CaSO_4^2$ and naphthenic acid salts; Scott, 2005; Mackinnon *et al*., 2001) that are mobile in groundwater and can be toxic to aquatic vegetation (Gervais and Barker, 2005; Daly et al., 2012; Rezanezhad *et al*., 2012a; Trites and Bayley, 2009). Given that the region has a sub-humid climate, where potential evapotranspiration is typically greater than precipitation (Devito *et al*., 2012) and the tailings sand materials have elevated residual sodium (Na^+), there is concern for both water quantity and quality when designing building a fen peatland as a reclamation project (Daly *et al.,* 2012; Pouliot *et al.* 2012; Ketcheson *et al*., 2016). Ketcheson (2015), among others (BGC, 2010; Pollard *et al*., 2012; Wytrykush *et al*., 2012), suggest depressional features can be incorporated into landscape designs to optimize the infiltration of precipitation and increase the detention of surface runoff. However, promoting infiltration and sub-surface storage of freshwater into tailings sands units increases the mobility of Na^+ (along with other salts), which are anticipated to migrate from the tailings sand upland to the fen over relatively short time frames. If transport rates are too great, salts will accumulate within the rooting zone of the fen peat elevating concentrations to levels that are hazardous to fen vegetation species (Rezanezhad *et al*., 2012a; Pouliot *et al*., 2012). This may be offset by dilution of salts resulting from enhanced recharge in such features (Chapter 2).

Groundwater recharge

Sub-surface storage of water within reclaimed landscapes in the AOSR is desired to ensure sufficient quantities of water are available for ecosystem demands (wetlands, forests) during periods of water stress or drought (Devito *et al*., 2012; Daly *et al*., 2012; Ketcheson *et al*., 2016). Therefore, constructed landscape designs should incorporate depressional features that serve as recharge windows to the local water tables (Ketcheson *et al*., 2016; Pollard *et al*., 2012). By detaining and capturing overland flow generated by rainfall, periods of ponding allow for larger volumes of water to infiltrate. By encouraging and increasing the sub-surface storage of water, the total evaporative loss of water within the system is minimized (Schwartz and Zhang, 2003; Dingman, 2002).

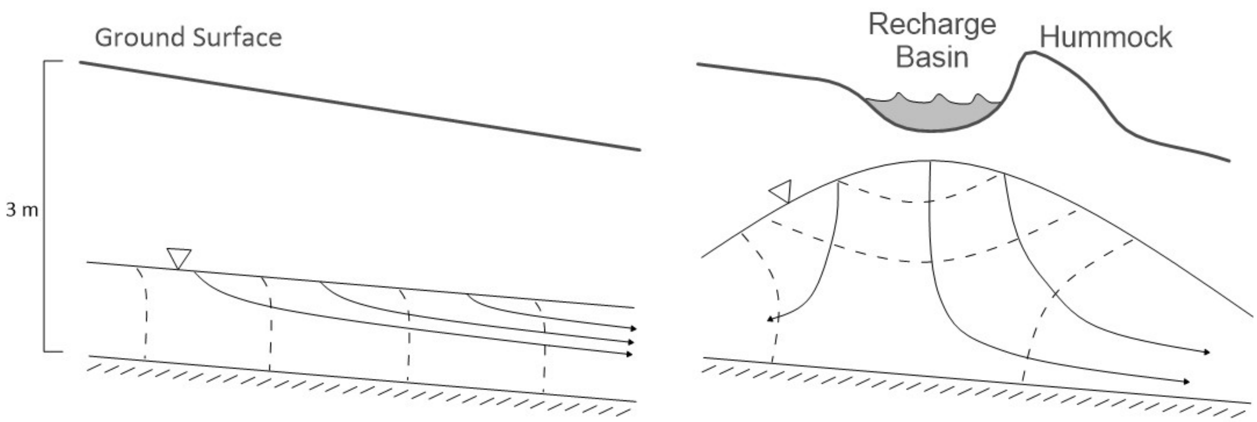

Figure 3 – 1 Conceptual flow with the tailings sand upland under uniform recharge (left) and enhanced recharge or recharge-controlled water table (right). The recharge-controlled water tables are anticipated if recharge basins are incorporated in landscape designs.

Under uniform recharge conditions (Figure 3 – 1, left) the water table remains more-or-less parallel to the topographic surface throughout the aquifer, as all areas receive similar quantities of recharge. However, under focused recharge, as in the case with depressional features, there is more recharge than in the surrounding areas, resulting in a locally elevated or mounded water table (Figure 3 – 1, right; Freeze and Cherry, 1979; Hendriks, 2010). Increasing the recharge of relatively fresh water through the unsaturated layer of constructed tailings sand materials will cause desorption and dissolution of adsorped solutes, which will be leached to the water table. Simhayov *et al*. (unpublished) have determined that among the available ions (Na^+, Ca^{2+}, Mg^{2+}, S^{6+}) within the tailings sand used to construct upland portions of the Nikanotee Fen, Na^+ was the most available due to its abundance. Once mobile, these dissolved solutes will be transported downgradient to the fen (Chapter 2). Therefore, the implications of enhanced flushing rates and transport of Na^+ within the tailings sand aquifer must be considered. Pulses of Na^+ transported to the fen peatland could exceed the naturally high adsorption capacity of the peat (Rezanzehad *et al*., 2012b), resulting in elevated concentrations of salts in the fen rooting zone or surface, to levels unsuitable to some plant species (Daly *et al*., 2012; Pouliot *et al*., 2012, Rezanezhad *et al*., 2012a). Optimizing subsurface recharge while simultaneously mitigating OSPW will be the key to success of AOSR reclamation with tailings sand materials

Since subsurface storage is necessary for maintaining the ecological functioning of the constructed fen peatland (Ketcheson *et al*., 2016), the efficacy of depressional features to enhance recharge must be evaluated, as well as how it impacts the redistribution of salts. Initial investigations into the geochemical conditions generated by tailings sand materials have been reported in Biagi (2015) and in this thesis (Chapter 2); however, the processes responsible for the re-distribution of Na^+ within such constructed upland-fen peatland systems are not fully understood. Therefore, the primary research objectives of this study are to 1) evaluate the function of the recharge basins on groundwater recharge, 2) assess the geometry (size and shape) and positioning of the recharge basins to maximize recharge, and 3) determine the implications for enhanced recharge on preferential flushing of Na^+ within the tailings sand upland.

3.2 Study Site

Constructed tailings sand upland

The study site was the Nikanotee Fen, a constructed upland – fen system, (56°55.944'N, 111°25.035'W) ~ 30 km north of Fort McMurray, Alberta. The Nikanotee Fen was designed with the requisite dimensions and geometry to generate the hydrological conditions that maintain an adequate water supply to the fen under the periods of water stress that occur frequently in the

AOSR (Price *et al*., 2010; Daly *et al*., 2012). The upland consists of a thick (3 m) tailings sand aquifer overlain by a thin (0.3 to 0.5 m LFH-mineral mix (over-stripped forest soil; herein referred to as 'LFH'), commonly used in oil sands reclamation (Naeth *et al*., 2013). The entire constructed portion of the fen-upland system overlies an impermeable geosynthetic clay liner which is on a 3% grade establishing a hydraulic gradient towards the fen. The southern end of the upland is 2 m, increasing to ~ 3 m towards the fen. The fen peat is underlain by a highly permeable petroleum coke underdrain layer (~ 0.5 m thick, ~ 2 m bgs) which extends ~ 100 m upslope beneath the tailings sand upland, a sub-region of the upland herein referred to as the 'transition zone' (shaded area in Figure 3 – 2). The entire upland – fen system (10.6 ha; Figure 3 – 2) is situated in a much larger reclaimed watershed (32.1 ha) composed of four primary hillslopes. The west (2.4 ha) and southeast (8.4 ha) hillslopes were constructed in 2011 and had immature and relatively sparse vegetation communities at the time of this study. The east (8.1 ha) hillslope was reclaimed and planted in 2007, and had developed significant vegetation growth. Of these slopes, the southeast and west were found to generate considerable runoff during rainfall events that flowed over the tailings sand upland, some of which infiltrates and contributes to the groundwater that sustains the fen water table (Ketcheson and Price, 2016b). The south hillslope is an undisturbed hillslope, which due to its small size, dense vegetation and position with respect to the geosynthetic clay liner, has no or negligible contribution to upland recharge (Ketcheson and Price, 2016b). A depressed basin (0.5 m bgs) with a 0.5 m thick peat-mineral mix substrate overlying the tailings sand aquifer (herein referred at as the 'peat-lined basin'; Figure 3 – 2) is situated in the south region of the upland. The peat-lined basin has been shown to act as a recharge window (Ketcheson *et al*., unpublished).

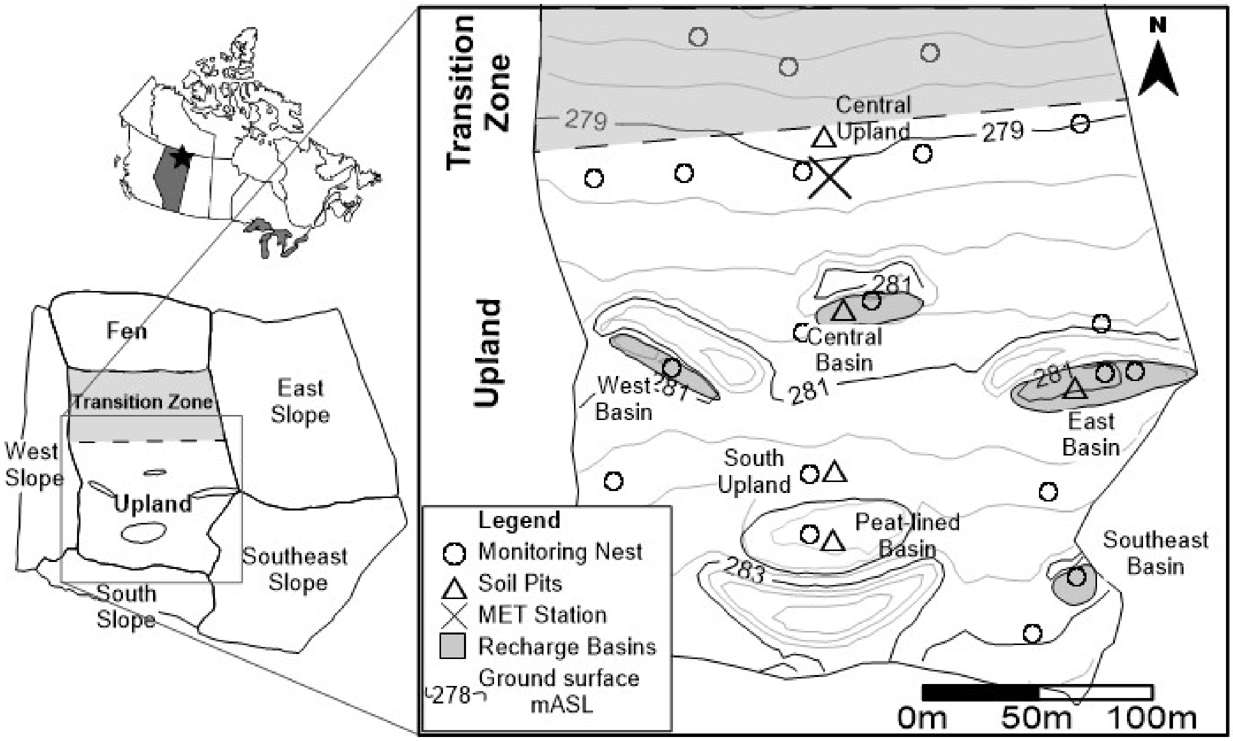

Figure 3 – 2 Map of the Nikanotee Fen upland in plan view with hummock and recharge basin features illustrated. The east and southeast recharge basins were instrumented (monitoring nest) in 2014. The central and west recharge basins were instrumented in 2015. All other instrumentation was pre-existing as mentioned in Chapter 1.

Several meso-scale, raised landforms (10 to 100 m width by 1 m height) were incorporated within the upland in which tailings sand was piled and capped (~ 20 cm) with LFH reclamation soil, similar to the surrounding upland. Over the 2013 season, these raised landforms (herein referred to as 'hummocks') detained and trapped a small amount of overland flow on their upslope side; however, they did not contribute considerable preferential recharge compared to the surrounding upland because the LFH that covered all upland areas had a relatively low infiltration capacity (Ketcheson and Price, 2016c). Thus, in late August, 2013, several modifications were made within the upland to promote groundwater recharge. Firstly, a dozer ripper shank was used to till furrows (furrow dimension typically approximately 24 cm wide, 10 cm deep, with ~ 85 cm spacing between; Ketcheson and Price, 2016c) to retain overland flow, increase water detention and thus infiltration. The furrows were perpendicular to the slope, but the irregular heights created a complex and unpredictable, dendritic like flow path for surface runoff, making it difficult to quantify runoff volumes. Second, the LFH reclamation material directly behind (up gradient) of the hummocks was excavated, with exception of the south hummock. The excavated soil material was placed at each end of the respective hummock to strategically extend the hummocks, to further increase their detention capacity. The resulting depressional features (~ 30 to 50 cm deep; herein referred to as 'recharge basins'; Figure 3 – 3) were capable of detaining much larger volumes of overland flow, and effectively increased the infiltration to the tailings sand aquifer by removing the LFH reclamation soil. A total of four recharge basins were added; the east (area = 700 m^2), central (450 m^2), west (400 m^2) and southeast (100 m^2) recharge basins (Figure 3 – 2). A peat-lined basin situated in the south end of the upland, that was part of the original construction design, has a minor recharge function, due to the location and high storage capacity of peat (Ketcheson, 2015), because it has a negligible contributing area. Hillslope runoff from the southeast slope during heavy rainfall resulted in substantial fine grained materials out-washing into the east and southeast recharge basins, forming a ~ 20 to 30 cm cap across both basins.

Figure 3 – 3 East recharge basin empty (left) and full shortly after a large rain event (right).

3.3 Methods

The study was conducted during the snow-free periods of May to October for 2013, 2014 and 2015. The 2013 season was representative of conditions prior to the furrowing of the upland LFH. Investigation of the recharge basins was conducted throughout the 2014 and 2015 seasons. Preliminary field observations showed that the east recharge basin received the most surface runoff and therefore was chosen for the most detailed monitoring and instrumentation.

Instrumentation and hydrological monitoring

The same network of wells and piezometers described in Chapter 1 was used to monitor water levels in the pond and hydraulic head within the tailings sand upland aquifer. Monitoring wells and deep piezometers (225 to 275 cm bgs) were instrumented within the east and southeast recharge basin in May, 2014. In addition, monitoring wells and deep piezometers (275 cm bgs) were instrumented in the central and west recharge basins in May, 2015. All water tables were automatically recorded with water level loggers or pressure transducers (Dataflow systems environmental monitoring Odyssey Capacitance Water Level Logger; Schlumberger Limited Mini Diver). Manual measurements of hydraulic head were performed every ~ 5 to 7 days. Initially, in May and June 2014, an incremented rod was installed to monitor pond height (stage) within the east recharge basin but was replaced by a fully slotted stand pipe with water level logger (Odyssey Capacitance) in July, 2014, which recorded stage at 15 minute intervals. The stage accurately monitored ponded water within the recharge basin only when it was above a threshold capacity of 10 cm, due to the minimum height required for the water level logger. Detailed stage measurements were quality assured by field observations and manual measurements of pond depth.

In May, 2013, two vertical soil moisture profiles were instrumented within the variably saturated layer of the tailings sand aquifer; one in the south end of the upland, downslope of the peat-lined basin, and the other in the center of the upland, ~ 15 m downslope of the central recharge basin. These are herein referred to as the south and central upland *VWC* stations, respectively (Figure 3 – 2). Soil moisture profiles consisted of 8 time domain reflectometry sensors (TDR; Stevens Water Monitoring Systems Inc. Hydra II); 4 within the LFH soil cap and 4 within the underlying tailings sand, typically at depths of 5, 10, 35, 40 cm and 45, 60, 100, 150 cm, respectively. Sensor depths varied slightly depending on LFH layer thicknesses. In May, 2015, the east and central recharge basin were instrumented with similar vertical soil moisture profiles within the variably saturated tailings sand (Figure 3 – 2). Two soil moisture profiles were instrumented in the east recharge basin ~ 10 m apart and consisted of 5 and 3 sensors at 5, 25, 40, 60, and 100 cm bgs and 5, 25, 60 cm bgs, respectively. One soil moisture profile consisting of 5 sensors at 5, 25, 40, 60, and 100 cm bgs was placed within the central recharge basin. All TDR sensors recorded in-situ volumetric water content (*VWC*) every 30 – 240 minutes, with CR1000 data loggers (Campbell Scientific Canada Corp.).

Precipitation (*P*) was measured by a tipping bucket rain gauge (Texas Instruments Canada Ltd. TR-525M) located at the upland meteorological station (Figure 3 – 2). Potential evaporation rates (*PET*) were taken from the fen meteorological station, which was assumed to be most representative of open water evaporation, to simulate the evaporative loss of the open water ponded within the recharge basins (discussed further below). *P* and *PET* values measured were cumulative rates for 30-minute intervals. Specific methods of calculating *PET* are reported in Scarlett *et al.* (submitted).

Groundwater samples were taken periodically from monitoring wells and piezometers within the recharge basins and surrounding upland throughout the duration of the study. Several grab samples were also taken from the water ponded within the recharge basins following contributing rain events (> 10 mm day^{-1}). All samples were stored at 4°C until being passed through a 0.45μm cellulose nitrate filter within 24 hours of being retrieved. Samples were frozen then sent to the Biotron Experimental Climate Change Research Facility at Western University, London, ON and Na^+ concentrations were determined by a Dionex ICS-1600 Method EPA 300.0 with AS-DV auto-sampler to an analytical precision of ± 1.0 mg L^{-1}.

Soil Hydraulic Properties

Soil hydraulic properties including particle size distribution, porosity, and infiltration capacity for upland LFH and tailings sands are reported in Ketcheson and Price (2016c). Single ring, constant head infiltration tests were conducted for tailings sands within all four recharge basins. Infiltration tests within the east and southeast recharge basins included ones in which the fine-material over-wash sediments were excavated to expose the tailings sand. As there were little to no fine sediments introduced to the central and west recharge basins, no excavation was necessary and infiltration tests were simply conducted on the bare tailings sand 'as is'. Additional single ring infiltration tests were conducted on the fine grained over-wash material within the east recharge basin.

Recharge basin capacity and infiltration volumes

Recharge volumes were calculated for the east recharge basin only. Due to difficulty in quantifying hillslope and overland flow directly into the east recharge basins, an alternative approach was taken to quantify the total recharge volumes. The east recharge basin's geometry can be approximated by an ellipsoidal cap (Figure 3 – 4). Using the dimensions of the east recharge basins the area of infiltration (A) and volume of the ponded water (V) were calculated using Equation 1 and 2, respectively), where h and c (z-axis) are the ponded water height (stage) and maximum water height (corresponding to the lip of the basin) within the recharge basin, respectively.

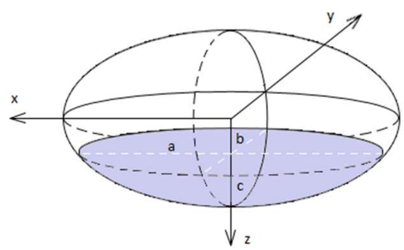

Figure 3 – 4 Ellipsoidal cap volume used to conceptualize the recharge basin geometry.

$$A = \frac{\pi ab}{c^2} h(2c - h) \qquad \text{(Equation 1)}$$

$$V = \frac{\pi ab}{3c^2} h^2(3c - h) \qquad \text{(Equation 2)}$$

where a is the length radius of the recharge basin (m) and b is the width radius of the recharge basin (m). The rate of the change in volume of the pond (dV/dt) was derived from the volume of the ellipsoidal cap as

$$\frac{dV}{dt} = \frac{\pi ab}{3c^2}(6ch - 3h^2)\frac{dh}{dt} \quad . \qquad \text{(Equation 3)}$$

Change in volume (dV/dt) was determined by a water balance approach as

$$\frac{dV}{dt} = (P + R)_{in} - (ET + f)_{out} \qquad \text{(Equation 4)}$$

where P is precipitation (mm hr^{-1}), R is runoff into the basin (m^3 hr^{-1}), ET is evaporation of open water (mm hr^{-1}) and f is the infiltration rate (mm hr^{-1}).

The base infiltration rate (*f*) for the recharge basin can be calculated by back calculating Equation 4. If high intensity rainfall ($\geq$ 10mm hr^{-1}) results in near instantaneous filling of the recharge basin, as observed, then immediately after the basin is full *P* and *R* =can be assumed to equal zero, and

$$f = -(ET + \frac{dV}{dt}) \quad . \qquad \text{(Equation 5)}$$

Finally, the cumulative infiltrated volume of water through a recharge basin is the summation of the product of *f* and the period of ponding for each time step (Δt = 15 minutes), such that

$$Volume\ Infiltrated = \sum_{i=1} f_i * (t_{i+1} - t_i) \quad . \qquad \text{(Equation 6)}$$

3.4 Results

Hydrological Context

A total of 254, 193 and 126 mm of *P* were received between 17 May and 24 August in the 2013, 2014 and 2015 study periods, respectively. *P* in both seasons was dominated by infrequent but high intensity (>10 mm per 24 hours) events (Figure 3 – 5). Following these substantial P events, the recharge basins were observed to fill nearly instantaneously (within 15 minutes of peak rainfall) with subsequent surface and overland flow. Once full, the ponded water would spill out around the edges of the raised hummock, continuing as overland flow towards the fen. However, intense *P* events were not received in a single period of continuous rainfall but could span over 24 to 28 hour periods, resulting in partial re-filling of the recharge basins capacity, illustrating the saw-tooth pattern in ponded water level (stage) hydrograph (e.g. Figure 3 – 6).

Recharge Basins

Recharge basins experienced stronger increases in *VWC* in the underlying tailings sand compared to that in tailings sands of the surrounding upland that are covered by LFH (Figure 3 – 5). *VWC* within the tailings sand layers (5 and 60 cm bgs) in the east and central recharge basins responded to the rainfall events above 10 and 15 mm day^{-1} for each respective basin. The water table in the east recharge basin was shallower (~ 90 and 190 cm bgs in 2014 and 2015, respectively) and responded to these events. The water table beneath the central recharge basin was deeper (~ 2.60 m in both 2014 and 2015) and did not respond to early season recharge. No clear water table responses were recorded in the LFH-covered south and central upland sites (Figure 3 – 5 c and d). Period of ponding within the recharge basins resulted in prolonged elevated *VWC* in the tailings sand, persisting above residual *VWC* for ~ 20 days following large rainfall events. Relatively dry periods between large rainfall events (~ 2 to 3 weeks) resulted in *VWC* returning to residual values (~ 0.06) at all locations, and for the mounded water tables beneath the recharge basins to dissipate.

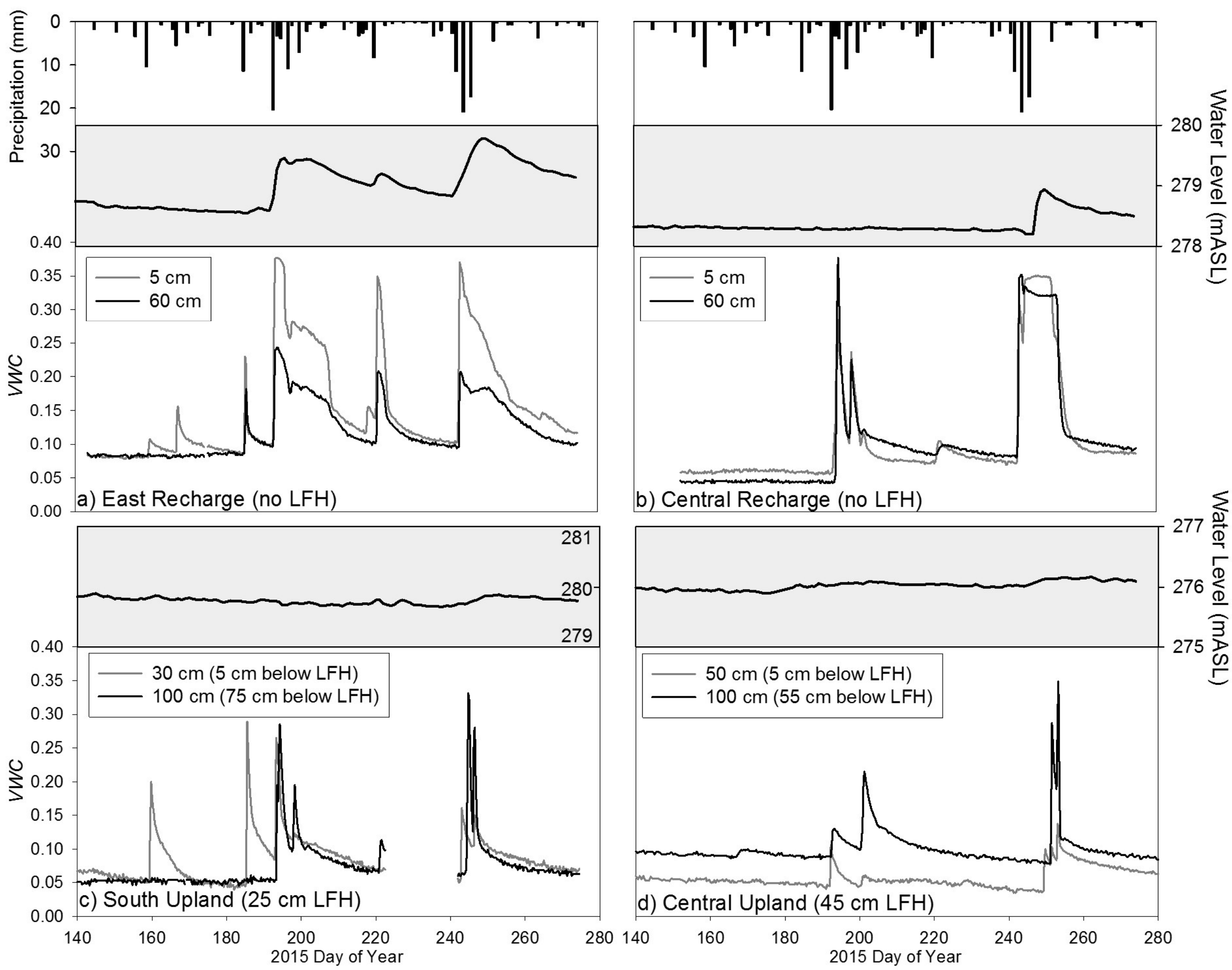

Figure 3 – 5 *VWC* within tailings sand 5 and 60 cm bgs in the east (a) and central (b) recharge basins (LFH removed) compared to similar depths in tailings sand below the LFH soil cap within the south (c) and central upland (d) stations over the 2015 study period.

The east recharge basin was observed to receive the most overland flow (not measured) of all the recharge basins within the upland, having ponded water for 27 and 23 % of the 2014 and 2015 seasons, respectively (Figure 3 – 6), compared to the central recharge basin which was ponded for less than 5% of both seasons. Periods of ponding typically persisted for ~ 9 to 14 days, with the exception of multiple rain events resulting re-filling and prolonged ponding for a period of 19 days in 2015 (Figure 3 – 6). Cumulative infiltrated volumes through the east recharge basin were 1308 and 928 m^3 (45 and 32 mm with respect to the fen area), in 2014 and 2015, respectively. The rate of increase of infiltrated volumes corresponded with the maximum depth of ponded water, which decreased proportionally with A (given Equation 1; Figure 3 – 6). High overland flow rates from the southeast slope, which fed the east recharge basin, resulted in a fine grained material outwash that covered the entire basin. The value of f estimated by the measured drop of ponded water levels within the east recharge basin ranged from 2 – 4 mm hr^{-1} (mean of 2.4 mm hr^{-1}), which was reasonably close to the value determined with single ring infiltration tests (mean of 4.6 mm hr^{-1})

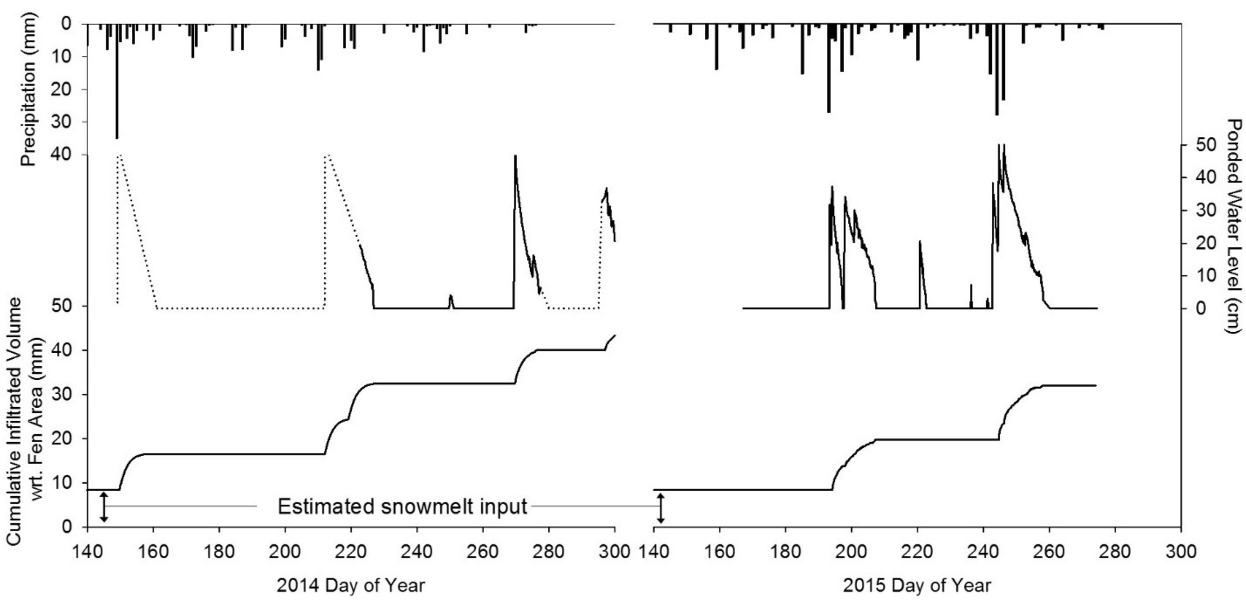

Figure 3 – 6 East recharge basin ponded water levels and infiltration volumes with respect to the fen area (2.9 ha) for the 2014 and 2015 study periods. Dashed lines are interpolated stage measurements based on manual measurements.

Na^+ distribution

Na^+ concentrations in the tailings sand aquifer immediately beneath the east recharge basin decreased throughout the 2014 and 2015 seasons (Figure 3 – 7). Concentrations were high before any ponding or response at the water table occurred, with mean concentrations of 78 and 140 mg L^{-1} in the early portions of 2014 and 2015, respectively. Immediately following ponding and percolation in the east recharge basin, Na^+ concentrations decreased considerably to below 46 mg

L^{-1} for the remaining portions of the 2014 and 2015 seasons (Figure 3 – 7). Electrical conductivity (not shown) within the tailings sand aquifer below the central and west recharge basins did not show similar decreases, remaining relatively high throughout the 2015 season.

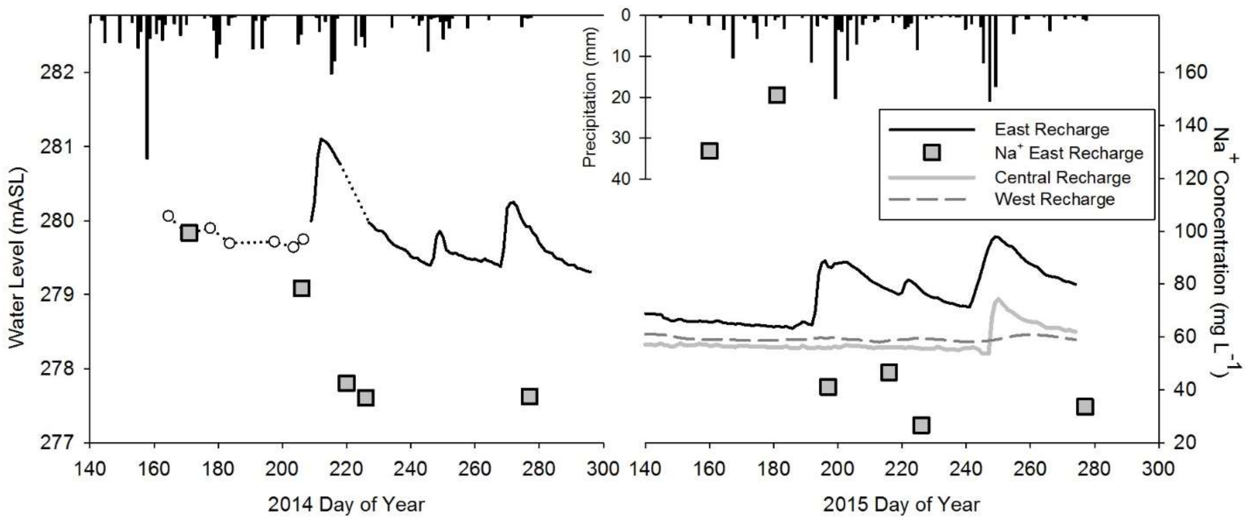

Figure 3 – 7 Water tables under the east, central, and west recharge basins for 2014 and 2015. Na^+ concentrations are shown for the groundwater beneath the east recharge basin.

Following construction (completed January 2013) and prior to the addition of recharge basins and development of furrows within the upland, Na^+ concentrations within the tailings sand aquifer were uniformly high across the southern portion of the upland (east to west) in May, 2013 (day of year (DOY) 148; Figure 3 – 8), decreasing throughout the 2013 season (Figure 3 – 9). Decreases were strongest following substantial rainfall in early June (DOY 165; Figure 3 – 9), which continued through to July, 2013. Na^+ concentrations within the transition zone were relatively uniform from east to west (Figure 3 – 8). As in the upland, Na^+ concentrations in the transition zone generally decreased following rainfall, in June, 2013 (Figure 3 – 9). During relatively dry conditions in August (DOY 230), 2013, which had no rain events exceeding 10 mm hr^{-1}, Na^+ concentrations increased in both the tailings sand upland and transition zone (Figure 3 – 9).

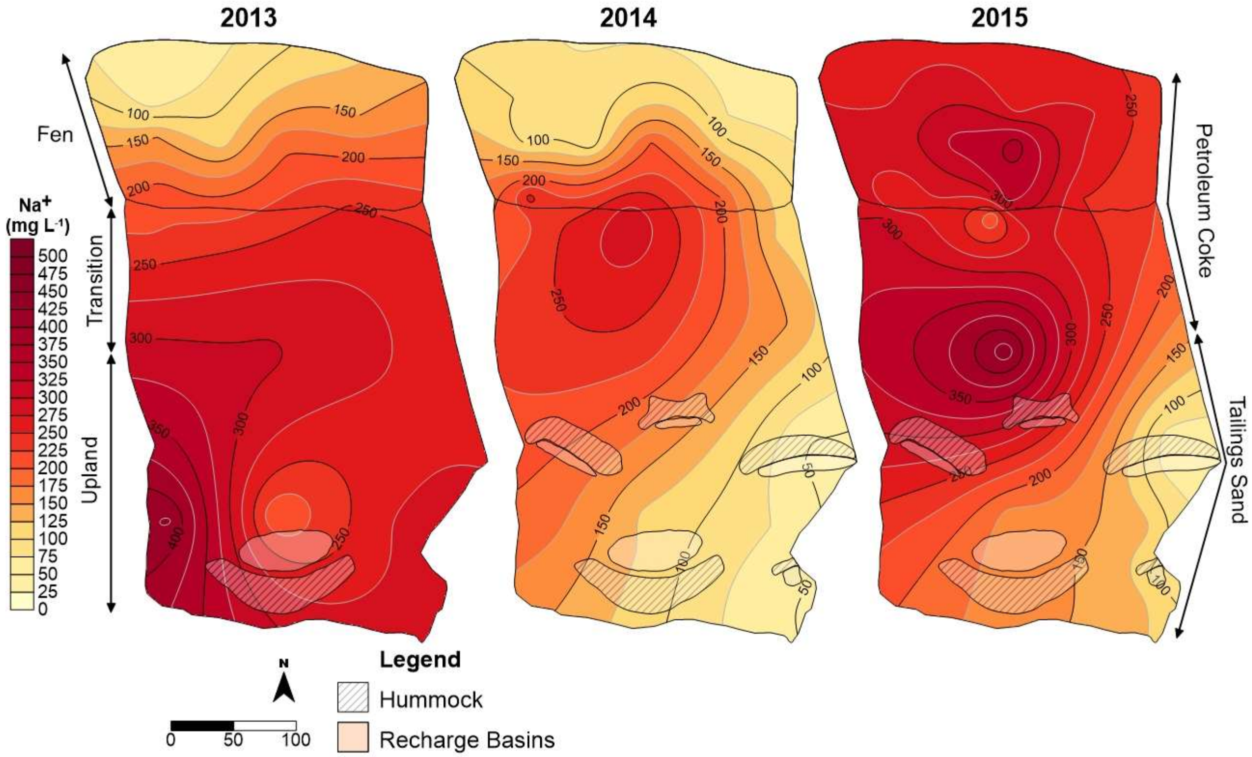

Figure 3 – 8 Average spatial distribution of Na^+ concentrations for May to October in 2013 and June to October in 2014 and 2015. Note the addition of recharge basins in 2014 and 2015.

In 2014, following tillage of the LFH surface and addition of recharge basins within the upland, Na^+ concentrations within the tailings sand aquifer decreased from northwest in the transition to the southeast in the upland (Figure 3 – 8). Prior to substantial infiltration through the east recharge basin, Na^+ concentrations were comparable to the rest of the east side of the upland (see Figure 3 – 8, 2013); however, following recharge through the basin, Na^+ concentrations were mostly lower beneath the basin (Figure 3 – 9; 2014 and 2015). Distinct peaks with maximum concentrations were observed within the west side of the upland and west and central regions of the transition zone in early July, 2014 (day of year 186; Figure 3 – 9). In 2015, Na^+ concentrations were highest in the west and lowest, on average, in the east (Figure 3 – 8). Similar to 2014, Na^+ concentrations were lowest along the east side of the transition zone and highest within the central and west regions (Figure 3 – 9). Na^+ concentrations did not vary considerably at each location within the transition zone throughout 2015.

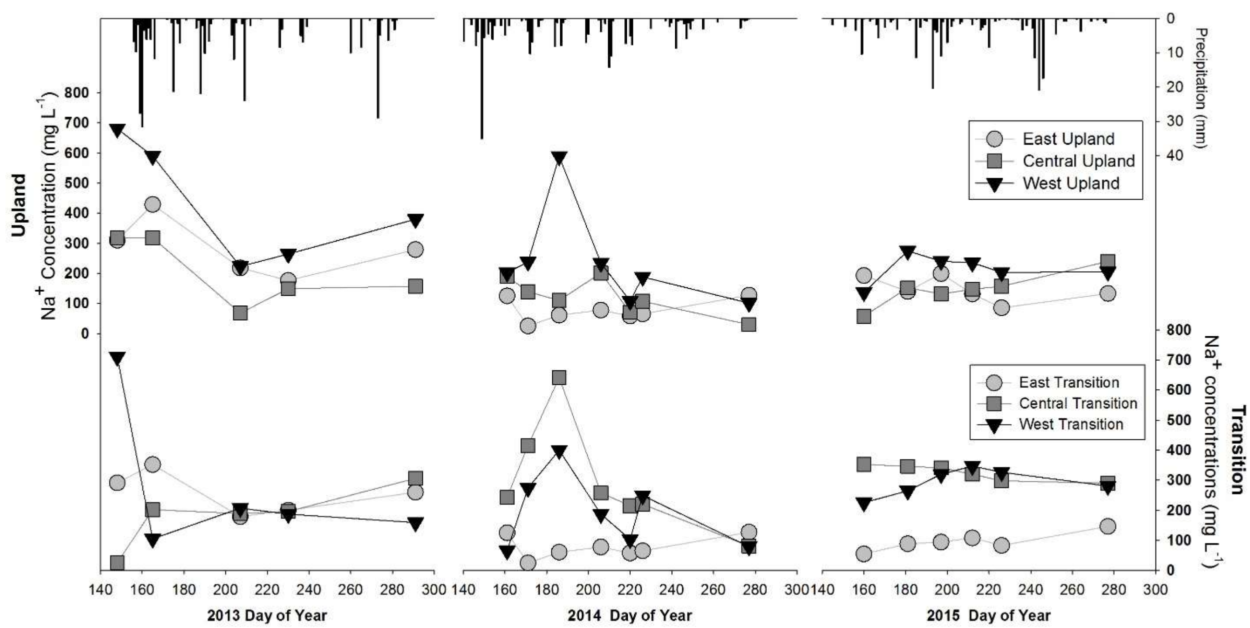

Figure 3 – 9 Na^+ concentrations within upland and transition zone over the entire 2013, 2014, and 2015 study period. Each data point is one extracted pore water sample.

3.5 Discussion

Recharge basins as recharge windows

The east recharge basin, as evident by frequent and persistent ponding (~ 23 to 27% of the season) compared to others (Figure 3 – 3 and Figure 3 – 5), was deemed the most successful of all basins in terms of detaining overland flow and promoting positive groundwater recharge to the tailings sand aquifer. Based on basin size (700 m^2 or 0.9% of the upland area) and contributions to recharge over the 2014 growing season (~ 15% of lateral groundwater flow towards fen; Ketcheson *et al*., unpublished), recharge was 16 times more effective (based on fraction area) at promoting recharge than the surrounding upland. The strongest contributing factor to the success of the east recharge basins was its ideal positioning at the toe of the confluence between the east and south-east slopes. The large contributing hillslope areas (8.1 and 8.4 ha) generated substantial runoff (Ketcheson and Price, 2016b), of which a large portion was received by the east recharge basin, resulting in the basin filling with each large rain event (Figure 3 – 6). Partial filling of the east and central recharge basins were observed following smaller rain events (< 10 mm hr^{-1}; Figure 3 – 6); however, these minor recharge events did not contribute substantial recharge volumes as there were only responses in *VWC* at 5 cm bgs and not 60 cm bgs (Figure 3 – 5). The east recharge basin was the largest of the four recharge basins; however, consistent filling of the basin to its capacity (Figure 3 – 6) suggests that the basin could have further increased aquifer recharge had it been larger than the current design (75 x 12 m, capacity of 240 m^3). Notwithstanding its size and storage capacity, the estimated *f* of the east recharge basin (2 to 4 mm hr^{-1}) was much lower than infiltration through the surrounding LFH (4 to 400 mm hr^{-1}, mean of 91 mm hr^{-1} in 2014) reported by Ketcheson and Price (2016c). The low *f* of the east recharge basin is attributed to the accumulation of a thin (~ 15 to 20 cm) organic-rich, fine-grained sediment that washed down from the east and southeast hillslopes during extreme rain events. However, in spite of the low *f*, the prolonged periods of time in which the basin detained water, resulted in substantial volumes of water percolating downwards to the water table. While LFH outside the recharge basin had higher *f*, the duration of surface flow/ponding was much less (observed ~ 1 to 2 days), thus the opportunity for recharge was less. The southeast basin, despite being much smaller (0.02 ha), likely contributed recharge, proportional to its size and capacity, as the east recharge basin. It was positioned at the toe of the southeast slope, which generated considerable runoff during large rain events (not shown; Ketcheson and Price, 2016b).

The central recharge basin was less successful in detaining overland flow and promoting recharge than the east recharge basin (Figure 3 – 5). Positioning the basin in the center of the upland (Figure 3 – 2), isolated it from the adjacent hillslopes, thus limiting sources of runoff that were essential to the east and southeast recharge basins' success. The relatively small upland contributing to the central research basin consisted of tilled LFH, which detained much of the surface flow that would otherwise have entered the basin. The west recharge basin elicited no response in the water table below it (Figure 3 - 7), since the contributing area of the west slope was too small to generate much runoff (Ketcheson and Price, 2016b) or simply did not converge to focus runoff into a single discharge point, as it did on the east and southeast slopes. Strategic placement of recharge basins in areas that can generate high flow volumes, such as confluences or gullies, is needed. Erosion control or sediment fences around recharge basins could improve their performance.

In current Nikanotee Fen design, there remains a significant portion of overland flow generated within the upland that runs directly to the fen surface (not shown; Ketcheson and

Price, 2016a). This bypassing of the tailings sand upland aquifer system resulted in a flashy water table response at the fen and low residence times, in which considerable volumes of water flowed out of the fen across the weir (Ketcheson and Price, 2016a). By detaining larger volumes of overland flow with recharge basins, and thus promoting more recharge, groundwater storage could increase the residence time of freshwater, regulating its release to the fen.

Implication for Na^+ transport

Infiltration through the LFH was much less effective than through the east and southeast recharge basins (Figure 3 – 5), resulting in persistently higher Na^+ concentrations in the groundwater below (Figure 3 – 8). The percolation through the LFH and underlying tailing sand was likely much slower than through the eastern recharge basins, desorbing and leaching Na^+ to the water table. The water table responses beneath upland regions covered by LFH were muted by the relatively large unsaturated zone (Figure 3 – 5), thus the Na^+ rich groundwater is not effectively flushed away under enhanced hydraulic gradients. As such, tailings sand aquifer areas covered by LFH (i.e. without recharge basins) will likely be long-term sources of salinity that migrate relatively slowly to the fen.

The enhanced recharge through the east and southeast recharge basins resulted in preferential 'flushing' of Na^+ from the tailings sands materials. The large volumes of freshwater recharge diluted Na^+ concentrations within the groundwater (Figure 3 – 7), and caused localized groundwater mounding following large recharge events (> 10 – 15 mm). This increased the hydraulic gradient from ~ 0.03 to 0.05 (Figure 2 – 4), which mobilized Na^+ beneath the recharge basins, flushing it downslope towards the fen. The rapid removal of Na^+ beneath the east and southeast recharge basins created localized zones of lower Na^+ concentrations within the east side of the tailings sand aquifer (Figure 3 – 8 and Figure 3 – 9). Within the first year of installing the recharge basins, Na^+ concentrations beneath the east and southeast recharge basins decreased from ~ 200 to < 100 mg L^{-1} (Figure 3 – 7 and Figure 3 – 8). Persistently high *EC* and Na^+ concentrations within the tailings sand aquifer beneath the central and west recharge basins reflect the poor recharge capabilities of these basins (Figure 3 – 5), which had little to no influence on Na^+ re-distribution within the tailings sand aquifer (Figure 3 – 8).

3.6 Conclusions

This study has evaluated the success and importance of recharge basins on detaining overland flow and promoting groundwater recharge, which is desired in the sub-humid climate of the AOSR. Excavating the LFH behind hummocks allowed for greater detention volume within the recharge basins, further allowing for an increase in infiltration time and thus an increase in total recharge. The size and positioning of recharge basins was critical to their hydrologic function. The east and southeast recharge basins were found to consistently detain overland flow derived from upslope, thus focused groundwater recharge following large rainfall events. Neither the central and west recharge basins with their relatively small contributing area, nor the upland LFH soil cap outside of the recharge basins, had a sufficient duration of ponding to be as effective as the east and southeast basins in recharging water. The east recharge basin was the largest of all the recharge basins and was ideally placed with respect to contributing slopes; it contributed 15% of the lateral groundwater flow to the fen in the 2014 season. The effectiveness of recharge basins is therefore sensitive strategic placement along the toes of slopes or where flow otherwise converges. However, with time, as the reclaimed hillslopes transition from water conveyance to water storage features (Ketcheson and Price, 2016b) and the infiltration capacity of the LFH upland cover increases (Ketcheson and Price, 2016c; Loch and Orange, 1997; Meiers *et al*., 2011), the importance of the basins will diminish. Yet, in early years post-construction, it is essential to ensure saturated conditions within the fen peatland as vegetation establishes; recharge basins that promote water storage will modulate the effect of short-term meteorological conditions and stabilize water levels in the fen peatland (BGC, 2010; Wytrykush *et al*., 2012).

Considerable sediment outwash occurred from the contributing slopes and collected in the east and southeast recharge basins. These fine sediments capped the bare tailings sand and reduced the infiltration capacity of the basins. However, the longer duration of ponding in the basins, compared to the general surface of the LFH-covered upland, more than compensated for the low infiltration capacity by providing more time for infiltration. Improved erosion control on slopes (e.g. furrows) and sediment fences around recharge basins could reduce the introduction of fine material and improve the effectiveness of the recharge basins. It is likely that ‘spontaneous wetlands’ will develop in the recharge basins if persistent ponding occurs, although this is unlikely to affect the performance of the upland – fen system.

While the east and south-east recharge basins increased local recharge, this enhanced desorption and dissolution of adsorbed Na^+ resulted in more Na^+ being mobile within the groundwater. Yet, Na^+ concentrations in the tailings sand upland affected by this recharge were diluted to < 100 mg L^{-1} (lowest within the tailings sand upland) due to the consistent influx of freshwater. In contrast, on the west side of the tailings sand upland, where there was little enhancement of recharge, Na^+ concentrations remained relatively high. The recharge basins cover a relatively small proportion of the system, so there remains a considerable amount surface runoff that inundates the fen. Recharge and flushing could be enhanced basin-wade if future designs employ larger and more recharge basins. It is suggested that sub-surface storage is encouraged in upslope regions of the upland to allow for maximized residence time; however, this would also maximize the potential for Na^+ mobilization towards the fen. Yet, sufficient freshwater recharge should ensure low Na^+ concentrations within the groundwater.

4.0 Conclusions and recommendations

Given the large volumes of solid tailings materials produced as a consequence of oil sands extractions, it is necessary to incorporate them as a construction material within reclaimed landscapes. This evaluation of the hydrogeochemistry and transport of Na^+ within a constructed fen peatland, which utilizes a tailings sand aquifer to supply a fen with adequate water supply, indicates that when receiving sufficient freshwater recharge, the upland is capable of supplying groundwater of necessary quality (relatively low Na^+) – to allow for delayed arrival times of Na^+ to the fen surface – and quantity to sustain fen hydrologic functioning. However, under insufficient fresh recharge, as in the case of prolonged periods of drought and below-average annual precipitation, the upland tailings sands generate and transmits a considerable amount of Na^+ to the fen, despite lower water fluxes. It is unclear if enhanced loading of Na^+ in 2015 due to increased concentrations with depth (geochemical stratification) in the tailings sand aquifer was an artifact of lack of freshwater recharge or an evolutional characteristic that is to be expect in all constructed tailings sand units. Hillslopes and upland recharge features were important in providing relatively fresh recharge to the tailings sands and ultimately diluting the groundwater, effectively managing the Na^+ concentrations and, despite increased gradients, reducing the overall migration of Na^+. Landscape reclamation designs must ensure adequate seasonal volumes of freshwater recharge, preferably in the early portion of the seasons, to maintain relatively low Na^+ concentrations within the tailings sands aquifers, allowing for the peatland to receive predominately diluted, low Na^+ water. It is recommended that landscape designs incorporate upland landforms and recharge basins to maximize the detention of the spring freshet and periodic recharge events, to ensure that precipitation that falls as snow is used effectively, and minimize the amount of overland flow that is received downslope.

The *EC* and Na^+ concentrations within the OSPW generated by the tailings sand upland aquifer remained well below some saline-spring fens and above typical rich to extremely-rich fen peatlands representative of those in the AOSR. Consequently, it is expected that the fen vegetation will transition to saline tolerant species, as opposed to fresh-water or hyper-saline. The duration of this three-year study is not sufficient time post-construction to fully understand the total potential elevation of salt. However, under a warmer climate that is predicted within the AOSR (IPCC, 2013), and therefore greater water loss from evapotranspiration (Devito *et al.*, 2012), it is expected that Na^+ concentrations will increase to levels greater than observed within these first several years. Elevated concentrations are expected within the upper layers of fen peat as the Na^+ continues to migrate upwards to the fen surface, where evapo-concentration will eventually result in elevated solute concentrations. Na^+ levels at the fen surface will partly depend on how much is exported by surface outflow from the fen. As long as this increase in Na^+ occurs relatively gradually the fen should have the ability to self-design to support a transition towards saline tolerant vegetation. As the sorption capacity of fen peat begins to saturate with respect to Na^+, the Na^+ concentrations within the outflow will begin to increase.

The Nikanotee Fen is relatively young compared to its anticipated flushing time of decades to hundreds of years (Daly *et al*., 2012; Wytrykush *et al*., 2012); as such, continued hydrogeochemical monitoring is essential for a stronger understanding of the trajectory this constructed upland – fen system will take. It is evident that the current salinity of the system is sensitive to climatic conditions as there was considerable seasonal variation in Na^+ concentrations throughout the study and therefore must be considered when attempting to characterize these constructed systems in the future. In the hotter and drier climate projected for the AOSR (IPCC, 2013), with increased evapotranspiration, the landscape design should incorporate landforms that detain and promote freshwater recharge to ensure not just water quantity but also water quality is adequate for fen construction and re-vegetation. It is unclear how prolonged periods of drought will impact the hydrogeochemistry of these constructed upland – fen systems; however, it is likely that drought conditions will result in more elevated solute concentrations migrating from the tailings sand upland to fen, giving rise to elevated concentrations throughout the peat deposit. Given the young age of the system and relatively short study period of the first three years post-construction, prolonged monitoring and hydrogeochemical modeling that encompass variable climatic conditions, will offer insight into long-term system performance.

Up-scaling the design of the Nikanotee Fen to industrial reclamation scales (100's of km^2) will necessitate the increase in tailings sand to peat material ratios due to material availability, which will magnify the potential for elevated solute concentrations within the fen portions of the landscape. Elevated concentrations and an increased loading of Na^+ can be expected if the design ratios of upland to fen, and tailings sand to fen peat, are increased. The thick (2 m) peat substrate was deemed necessary to delay and attenuate Na^+ migration to the fen surface and therefore it is recommended that future fen construction designs include a similar thickness of peat to delay and moderate the arrival of peak solute concentrations to allow for appropriate vegetation to establish. Thinner (0.5 to 1 m) peat deposits would likely not be sufficient to delay arrival times of OSPW to the surface as considerable upward migration of Na^+ was observed by the end of the third year post-construction within the Nikanotee Fen.

Up-scaling design geometry while maintaining the 3:1 upland to fen ratio will result in overall more available Na^+ within the system; however, not with respect to the fen attenuation capability. As such, it is likely that a larger system of similar proportions should generate hydrogeochemical conditions similar to that seen in the Nikanotee Fen. However, increasing the width or length would increase the proximity from the reclaimed hillslopes which are important for conveying freshwater runoff (Ketcheson and Price, 2016b), resulting in less uniform recharge throughout the upland. Therefore, when enlarging designs, it is suggested that hummock landforms and recharge basins are strategically used to detain and direct overland flow inwards across the upland to encourage recharge and ensure low OSPW concentrations within selected zone of the upland, not just along the toe of hillslopes. Perhaps of more concern is increasing the tailings sand to fen peat material ratios (i.e. increasing upland to fen area ratios greater than 3:1 or increasing layer thicknesses), because it will increase the total available Na^+ with respect to peat materials and likely result in elevated Na^+ concentrations within the fen peat, compared to what was observed within the Nikanotee Fen over the study period. This could result in earlier arrival times and higher peak concentrations of OSPW to the shallow peat layers, and therefore the rooting zone of fen vegetation. Increasing the thickness of tailings sand aquifer could affect freshwater recharge, which was shown to be important on ensuring low Na^+ concentrations within the saturated zones of Nikanotee Fen watershed. Regardless of the modifications to design geometry it is recommended that future designs incorporate highly conductive underdrains which were important in the Nikanotee Fen, because they transmitted and dispersed most of the OSPW beneath the peat deposit, allowing for delayed arrival times at the fen surface.

It is speculated that subtle variations in hydraulic gradients (i.e. slope of the upland water table) would not have considerable implications for the loading of Na^+ from tailings sand to fen, as mass transport in the Nikanotee Fen was dominated by the variations in concentrations and not water fluxes. Water levels were in part controlled by the impermeable geosynthetic liner; this approach may or may not be used in future constructed fens. The alternative is to use relatively low permeability saline-sodic or composite tailings; however, both of these are comparatively more permeable than a geosynthetic liner. Deep water seepage loss and diffusion of salts from saline-sodic and composite tailings are both primary concerns if they are used instead of a geosynthetic liner. Water loss due to deep seepage has the obvious implications for the loss of water crucial for maintaining saturated conditions within the fen (Ketcheson *et al*., 2016). Biagi (2015) reported the upward diffusion of Na^+ from composite tailings into peat materials within another constructed fen (Sandhill Fen); however, in a design where deep seepage occurs this is unlikely to be a problem.

There are many potential design modifications to the Nikanotee Fen Watershed that could improve subsurface storage while simultaneously minimizing the potential for elevated contaminant concentrations within the fen portions of the landscape. In general, increasing the ratios of tailings sand to peat will result in elevated concentrations of contaminants within the fen, which will influence the fen vegetation community composition. It is probable that future system designs will use less peat, based on its more limited availability compared to tailings materials. Consequently, hydrogeochemical models will be needed to better predict how variations geometry and hydraulic properties will affect these constructed systems.

References

Alberta Government. (2015). Alberta's Oil Sands: Reclamation. http://oilsands.alberta.ca/reclamation.html

Baird, a J., & Gaffney, S. W. (2000). Solute movement in drained fen peat: a field tracer study in a Somerset (UK) wetland. Hydrological Processes, 14(14), 2489–2503. http://doi.org/10.1002/1099-1085(20001015)14:14<2489:AID-HYP110>3.0.CO;2-Q

Beckwith, C. W., Baird, A. J., & Heathwaite, A. L. (2003). Anisotropy and depth-related heterogeneity of hydraulic conductivity in a bog peat, I: laboratory measurements, 101(March 2002), 89–101. http://doi.org/10.1002/hyp.1116

BGC Engineering Inc. (2010). Review of Reclamation Options for Oil Sands Tailings Substrates. OSRIN Report No. TR-2., (July), 59 pp.

Biagi, K. (2015). Understanding flow pathways, major chemical transformations and water sources using hydrochemical data in a constructed fen, Alberta, Canada. McMaster University.

Boelter, D. H. (1969). Physical Properties of Peats as Related to Degree of Decomposition. Soil Science Society of America Journal, 33(4), 606. http://doi.org/10.2136/sssaj1969.03615995003300040033x

Borkenhagen, A., & Cooper, D. J. (2015). Creating fen initiation conditions: A new approach for peatland reclamation in the oil sands region of Alberta. Journal of Applied Ecology. http://doi.org/10.1111/1365-2664.12555

Bott, R. D. (2010). Canada's Oil Sands, (September).

Chee, W.-L., & Vitt, D. H. (1989). The vegetation, surface water chemistry and pear chemistry of moderate-rich fens in Central Alberta, Canada. Wetlands, 9(2), 227–261.

Daly, C., Price, J., Rezanezhad, F., Pouliot, R., Rochefort, L., & Graf, M. D. (2012). Initiatives in oil sand reclamation: Considerations for building a fen peatland in a post-mined oil sands landscape. Restoration and Reclamation of Boreal Ecosystems, 179–201.

Devito, K., Mendoza, C., & Qualizza, C. (2012). Conceptualizing water movement in the Boreal Plains. Implications for watershed reconstruction, 164.

Dingman, S.L. (2002). Physical Hydrology Second Edition. Waveland Press Inc.

Dobchuk, B. S., Shurniak, R. E., Barbour, S. L., O'Kane, M. A., & Song, Q. (2012). Long-term monitoring and modelling of a reclaimed watershed cover on oil sands tailings. International Journal of Mining, Reclamation and Environment, 2013. Vol. 27, No. 3, 180-201, doi 10.1080/17480930.2012.679477

Freeze, R. A., & Cherry, J. A. (1979). Groundwater. Prentice-Hall.

Gervais, F. M., & Barker, J. F. (2005). Fate and transport of naphthenic acids in groundwater. In: Bringing groundwater quality research to the watershed scale - the 4th international groundwater quality conference, IAHS, pp: 305-310.

Goldberg, S., Criscenti, L. J., Turner, D. R., Davis, J. a., & Cantrell, K. J. (2007). Adsorption–Desorption Processes in Subsurface Reactive Transport Modeling. Vadose Zone Journal, 6(3), 407. http://doi.org/10.2136/vzj2006.0085

Government of Alberta. (2015). Alberta's Oil Sands: Reclamation. Government of Alberta. http://oilsands.alberta.ca/FactSheets/FactSheet-Reclamation-2015.pdf.

Heathwaite, A. L., (1990). The effect of drainage on nutrient release from fen peat and its implications for water quality–a laboratory simulation. Water Air Soil Pollut. 49 (1-2), 159-173.

Hendriks, M. R. (2010). Introduction to Physical Hydrology. Oxford.

Hill, B. M., & Siegel, D. I. (1991). Groundwater flow and the metal content of peat. Journal of Hydrology (Amsterdam, Netherlands), 123(3), 211–224. http://doi.org/10.1016/0022-1694(91)90091-U

Hoag, R. S., & Price, J. S. (1995). A field-scale, natural gradient solute transport experiment in peat at a Newfoundland blanket bog. Journal of Hydrology, 172(1-4), 171–184. http://doi.org/10.1016/0022-1694(95)02696-M

Hoag, R. S., & Price, J. S. (1997). The effects of matrix diffusion on solute transport and retardation in undisturbed peat in laboratory columns. Contaminant Hydrology, 28, 193–205.

Holden, A. A., Donahue, R. B., & Ulrich, A. C. (2011). Geochemical interactions between process-affected water from oil sands tailings ponds and North Alberta surficial sediments. Journal of Contaminant Hydrology, 119(1-4), 55–68. http://doi.org/10.1016/j.jconhyd.2010.09.008

Ingram, P. (1983). Hydrology.

IPCC. (2013). Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, pp. 1535.

Ketcheson, S. J. (2015). Hydrology of a Constructed Fen Watershed in a Post-Mined Landscape in the Athabasca Oil Sands Region, 180.

Ketcheson, S. J., & Price, J. S. (2016a). Snow hydrology of a constructed watershed in the Athabasca oil sands region, Alberta, Canada. Hydrological Processes.

Ketcheson, S. J., & Price, J. S. (2016b). A comparison of the hydrological role of two reclaimed slopes of different age in the Athabasca Oil Sands Region, Alberta, Canada. Canadian Geotechnical Journal, (ja).

Ketcheson, S. J., & Price, J. S. (2016c). Hydrophyscial properties of mine reclamation materials (LFH, tailings sand, petroleum coke and organic peat soils) in a constructed watershed. International Journal of Mining, Reclamation and Environment.

Ketcheson, S. J., Price, J. S., Carey, S. K., Petrone, R. M., Mendoza, C. A., & Devito, K. J. (2016). Constructing fen peatlands in post-mining oil sands landscapes: challenges and opportunities from a hydrological perspective. Earth Science Reviews. http://doi.org/10.1016/j.earscirev.2016.08.007

Ketcheson, S.J., Price, J.S., Petrone, R.M., Sutton, O. and Sutherland, G. (in prep, draft complete) An initial assessment of the hydrological functioning of a constructed fen wetland watershed in the Athabasca Oil Sands Region, Alberta, Canada. Targeted submission: Water Resources Research

Loch, R. J., & Orange, D. N. (1997). Changes in some properties of topsoil at Tarong Coal-Meandu Mine coalmine with time since rehabilitation. Australian Journal of Soil Research, 35: 777-784.

Mackinnon, M. D., Matthews, J. G., Shaw, W. H., Cuddy, R. G., Matthews, J. G., Shaw, W. H., & Water, R. G. C. (2001). Water Quality Issues Associated with Composite Tailings (CT) Technology for Managing Oil Sands Tailings, 5265(June). http://doi.org/10.1076/ijsm.15.4.235.7416

McCarter, C. P. R. (2016). The hydrochemical fate and transport of treated domestic wastewater contaminants during a wastewater polishing experiment in a sub-arctic ladder fen peatland, 121.

Meiers, G. P., Barbour, S. L., Qualizza, C. V., & Dobchuk, B. S. (2011). Evolution of the hydraulic conductivity of reclamation covers over sodic/saline mining overburden. Journal of Geotechnical and Geoenvironmental Engineering, 137: 968-976. DOI: 10.1061/(asce)gt.1943-5606.0000523

Naeth, M. A., Wilkinson, S. R., Mackenzie, D. D., Archibald, H. A., & Powter, C. B. (2013). Potential of LFH mineral soil mixes for reclamation of forested lands in Alberta. Oil Sands Research and Information Network Report No. TR-35.

Nwaishi, F., Petrone, R. M., Price, J. S., Ketcheson, S. J., Slawson, R., & Andersen, R. (2015). Impacts of donor-peat management practices on the functional characteristics of a constructed fen. Ecological Engineering, 81, 471–480. http://doi.org/10.1016/j.ecoleng.2015.04.038

Oil Sands Wetlands Working Group. (2000). Guideline for Wetland Establishment on Reclaimed Oil Sands Leases. Neil Chymko (Editor) Report # ESD/LM/00-1, Alberta Environment, Environmental Service. ISBN 0-7785-1042-5, Publication No. T/517.

Ours, D. P., Siegel, D. I., & Glaser, P. H. (1997). Chemical dilation and the dual porosity of humified bog peat. Journal of Hydrology, 196(1-4), 348–360. http://doi.org/10.1016/S0022-1694(96)03247-7

Pollard, J., McKenna, G. T., Fair, J., Daly, C., Wytrykush, C., & Clark, J. (2012). Design aspects of two fen wetlands constructed for reclamation research in the Athabasca oil sands. Mine Closure 2012, 815–829.

Price, A. C. R., (2005). Evaluation of groundwater flow and salt transport within an undrained tailings sand dam. MSc. Thesis, University of Alberta, Edmonton, Alberta.

Price, J. S., McLaren, R. G., & Rudolph, D. L. (2010). Landscape restoration after oil sands mining: conceptual design and hydrological modelling for fen reconstruction. International Journal of Mining, Reclamation and Environment, 24(2), 109–123. http://doi.org/10.1080/17480930902955724

Reeve, A. S., Siegel, D. I., & Glaser, P. H. (1996). Geochemical controls on peatland pore water from the Hudson Bay Lowland: a multivariate statistical approach. Journal of Hydrology, 181(1-4), 285–304. http://doi.org/10.1016/0022-1694(95)02900-1

Renault, S., Lait, C., Zwiazek, J. & MacKinnon, M. (1998). Effect of high salinity tailings waters produced from gypsum treatment of oil sands tailings on plants of the boreal forest. Environmental Pollution, 102(2-3), 177–184. http://doi.org/10.1016/S0269-7491(98)00099-2

Renault, S., Paton, E., Nilsson, G., Zwiazek, J. J., & MacKinnon, M. D., (1999). Responses of Boreal Plants to High Salinity Oil Sands Tailings Water. Journal of Environmental Quality, 28(6): 1957-1962.

Rezanezhad, F., Andersen, R., Pouliot, R., Price, J. S., Rochefort, L., & Graf, M, D. (2012a). How Fen Vegetation Structure Affects the Transport of Oil Sands Process-affected Waters. Wetlands, 32: 557-570. DOI: 10.1007/s13157-012-0290-z.

Rezanezhad, F., Price, J. S., & Craig, J. R. (2012b). The effects of dual porosity on transport and retardation in peat: A laboratory experiment. Canadian Journal of Soil Science, 92(5), 723–732. http://doi.org/10.4141/cjss2011-050

Rezanezhad, F., Quinton, W. L., Price, J. S., Elliot, T. R., Elrick, D., & Shook, K. R. (2010). Influence of pore size and geometry on peat unsaturated hydraulic conductivity computed from 3D computed tomography image analysis. Hydrological Processes, 24(21), 2983–2994. http://doi.org/10.1002/hyp.7709

Rooney, R. C., Bayley, S. E., & Schindler, D. W. (2012). Oil sands mining and reclamation cause massive loss of peatland and stored carbon. Proceedings of the National Academy of Sciences, 109(13), 4933–4937.

Scarlett, S. (2015). Characterizing controls on plot-scale evapotranspiration and soil water dynamics of a constructed fen in the AOSR. 59.

Scarlett, S., Price, J. S., & Petrone, R. (submitted). Controls on plot-scale evapotranspiration from a constructed fen in the Athabasca Oil Sands Region. submitted to Ecological Engineering (2016)

Schwartz, F. W., & Zhang, H. (2003). Fundamentals of Groundwater. John Wiley & Sons Inc.

Scott, A. C., MacKinnon, M. D., & Fedorak, P. M. (2005). Naphthenic acids in Athabasca oil sands tailings waters are less biodegradable than commercial naphthenic acids. Environmental Science and Technology, 39(21), 8388–8394. http://doi.org/10.1021/es051003k

Simhayov, R. B., Price, J. S., Smeaton, C. M., Parsons, C., Rezanezhad, F., & Van Chappellen, P. (in review, unpublished). Solute pools in the Nikanotee constructed watershed in the Athabasca oil sands region of Alberta, Canada.

Sudicky, E. A. (1986). A natural gradient experiment on solute transport in a sand aquifer: Spatial variability of hydraulic conductivity and its role in the dispersion process. Water Resources Research, 22(13), 2069–2082. http://doi.org/10.1029/WR022i013p02069

Trites, M., & Bayley, S. E. (2009). Vegetation communities in continental boreal wetlands along a salinity gradient: Implications for oil sands mining reclamation. Aquatic Botany, 91(1), 27–39. http://doi.org/10.1016/j.aquabot.2009.01.003

Vitt, D. H., & Chee, W. L. (1990). The relationships of vegetation to surface-water chemistry and peat chemistry in fens of Alberta, Canada. Vegetation, 89(2), 87–106.

Vitt, D., Halsey, L., Thormann, M., & Martin, T. (1996.) Peatland inventory of Alberta. Phase 1: Overview of peatland resources in the natural regions and subregions of the province., Centre PR (ed.) University of Alberta.

Wells, C. M., & Price, J. S. (2015a.) A hydrologic assessment of a saline-spring fen in the Athabasca oil sands region, Alberta, Canada – a potential analogue for oil sands reclamation. Hydrol. Process., 29: 4533–4548. doi: 10.1002/hyp.10518.

Wells, C. M., & Price, J. S. (2015b.) The hydrogeologic connectivity of a lowflow saline spring fen peatland within the Athabasca oil sands region, Canada. Hydrogeol J (2015) 23:1799–1816. DOI 10.1007/s10040-015-1301-y

Wells, C.M., Ketcheson, S.J. & Price, J.S. (in review) Hydrology of a wetland-dominated headwater basin in the Boreal Plain, Alberta, Canada. Submitted to: Journal of Hydrology. MS# HYDROL-22572. Submitted: 30-June-2016.

Woynillowicz, B., Raynold, M., & Severson-Baker, C. (2005). Oil Sands Fever; The environmental implications of Canada's oil sands rush. The Pembina Institute.

Wytrykush, C., Vitt, D., McKenna, G., & Vassov, R., (2012). Designing landscapes to support peatland development on soft tailings deposits. In: Restoration and reclamation of boreal ecosystems. Vitt D, Bhatti JS (eds.), pp: 161-178.

Zubot, W., MacKinnon, M. D., Chelme-Ayala, P., Smith, D. W., & Gamal El-Din, M. (2012). Petroleum coke adsorption as a water management option for oil sands process-affected water. Science of the Total Environment, 427-428, 364–372. http://doi.org/10.1016/j.scitotenv.2012.04.024

Appendix

Geochemical Analysis

All water samples collected in the field were stored at 4°C and filtered through 0.45 μm nitrocellulose filters. Once filtered the samples were decanted into 60 ml and 30 ml vials for major ion and isotope analysis, respectively. Major ion samples were given adequate headspace within the vial and frozen until analysis. Isotope samples had no headspace and were stored at 4°C until analysis. All samples were shipped in coolers for analysis to the Biotron Experimental Climate Change Research Facility at Western University, London, ON. Major cations were analyzed by the Dionex ICS-1600 Method EPA 300.0 with AS-DV auto-sampler for Na^+, K^+, Ca^{2+}, Mg^{2+}, Li^+, and NH_4^+, with analytical precision to ± 1.0, 1.0, 0.1, 0.01, 0.01, 0.1 mg L^{-1}, respectively. Major anions were analyzed by a Dionex IC Method A-102 for Cl^-, Br^-, F^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}, with analytical precision to ± 0.05, 0.1, 0.05, 0.1, 0.1, 0.05, and 0.05 mg L^{-1}, respectively. Isotopic samples were analyses for δ18O and δD using a Picarro L2120-i Cavity Ring-Down Spectroscopy analyzer with an analytical precision of ±0.5‰ for δD and ±0.1‰ for δ18O.

The chemical composition of rainfall for the Nikanotee Fen Watershed is reported in Table A – 1. Yearly average concentrations of the dominant ions and compounds within the constructed upland – fen system for 2013, 2014, and 2015 are reported in Table A – 2.

Table A – 1 Chemical composition of rainfall within the Nikanotee Fen Watershed.

Year	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	δ18O	δD
2013	14.7	12.0	55.9	1.2	167.0	-15.3	-117
2014	10.4	0.0	6.0	1.1	83.8	-18.4	-140
2015	12.6	7.8	47.9	8.9	101.8	-18.4	-152

All values are in mg L^{-1}.

Table A – 2 Major ions and compounds within all construction materials 2013 – 2015.

Ion	Year	Fen Peat				Petroleum Coke	Tailings Sand
		Well	50 cm	90 cm	150 cm		
Na^+ (mg L^{-1})	**2013**	119±38.9	87.3±35.5	78.5±35.4	121±66.3	200±119	**232±140**
	2014	90.3±64.9	79.7±64.1	66.3±42.9	97.4±71.2	**182±103**	138±111
	2015	207±110	153±105	129±73.8	188±79.4	**303±78.7**	238±146
Ca^{2+} (mg L^{-1})	**2013**	411±117	268±144	**278±123**	284±151	161±67.8	184±134
	2014	135±76.1	**117±69.8**	112±49.5	99.6±49.3	84.4±32.4	69.7±32
	2015	345±133	285±152	250±87.5	**303±84.6**	251±48.5	225±88.5
Mg^{2+} (mg L^{-1})	**2013**	59.6±44.3	**52.3±38.2**	48.8±20.1	50.1±32	33.2±16.9	39.2±30.6
	2014	54.9±51.1	**45.8±35.2**	39.2±29.7	36.2±23.1	35.5±29.3	26.3±19.3
	2015	98.8±32.7	**91.3±42.7**	68.8±31.9	78.2±29.5	74.8±20.6	65.1±28
Cl^- (mg L^{-1})	**2013**	16.3±7.3	14.2±7.2	15.1±7.5	28.1±19.2	43.6±34.9	**52.6±48.1**
	2014	23.2±18.8	21±19.4	22.2±17.2	28.4±21	**41.3±29.1**	30.2±35
	2015	48.5±31.4	31.2±17.9	28.8±18.2	46.6±20.2	**59.7±21.1**	43.9±40.1
SO_4^{2-} (mg L^{-1})	**2013**	1230±544	657.8±369	670.6±397	797.6±471	758.8±349	**882.1±716**
	2014	560±314	569.9±367	490.3±252	595.3±297	**722.9±310**	510.5±253
	2015	961.3±505	778.5±566	596.4±301	934.2±271	**1190±257**	963.6±437

Annual mean (arithmetic) and ± Standard deviation (SD) of ion concentrations within all materials over the duration of the study period (2013-2015). Locations of samples were kept identical to ensure unbiased interpretation. Bolded values are the highest average that year (excluding wells).

Potential sources of error

To ensure minimal errors within this study, great care was taken when conducting all in-field manual measurements, such as water level and pressure head elevations and discharge from the fen outflow. Errors associated with auto-logging measurements of precipitation, evapotranspiration, volumetric water content, water level and pressure head loggers or geochemical analysis were confined to the precision of the instruments, all of which are common practice and generally accepted throughout the scientific community. All above-mentioned potential errors were relatively minimal and therefor deemed negligible in comparison to the uncertainties associated with site-scale instrumentation and investigation into the hydrogeochemistry of the Nikanotee Fen Watershed. Site-scale dependent heterogeneity within the constructed upland-fen system was likely the largest source of error within this research.

Uncertainties arise due to a somewhat sparse monitoring network (Chapter 2. Figure 2 – 1) within the tailings sand upland due to the extreme difficulty of instrumentation within the central portions of the upland, where the water table remained relatively deep (~ 2.6 to 3.0 m bgs). This lack of monitoring points within the central regions of the tailings sand aquifer biased yearly averages and seasonal trends of Na^+ concentrations within the tailings sand as monitoring points that were in within relatively close proximity to recharge basins experienced enhanced freshwater recharge, diluting groundwater samples. This is a phenomenon which was speculated to not have occurred to the same degree in other regions of the upland somewhat isolated from hillslopes and recharge basins. The use of data interpolation contouring tools to illustrate the spatial distribution of Na^+ magnifies this uncertainty due to a sparse monitoring network. As such, interpolated contours are not to be used to yield exact concentrations between points, but as a tool to illustrate the overall change in distribution from season to season. Given the uncertainties discussed, it is highly recommended that ample time and effort is invested into the instrumentation of such tailings sand uplands to ensure adequate characterization of the hydrogeochemistry.

The use of and reliance on fully slotted monitoring wells to extract groundwater samples within the tailings sand aquifer is also a concern for uncertainties and misinterpretation of temporal variations of Na^+ concentrations (Figure 2 – 6) as there was geochemical stratification present (Chapter 2). The slotted intake of a monitoring well across the entire saturated region of the tailings sand will be influenced by the somewhat fresh water recharge introduced to the water table, resulting in lower Na^+ concentrations than what may be representative of the aquifer. The general decrease in Na^+ concentrations within the tailings sand aquifer in 2013 and 2014 is artifact of incoming freshwater recharge resulting in dilution of the upper portions of the aquifer. Therefore, when using fully slotted monitoring wells across a considerable saturated zone, this uncertainty must be considered when discussing dilution versus flushing of solutes from tailings sands. It is recommended that a combination of monitoring wells and deep piezometers are used to characterize tailings sand units to capture the effects of geochemical stratification, as it is unclear if geochemical stratification was due to the design of the system or an evolutionary trait that these constructed systems will inherit with time.