University of Alberta

The Geochemical Evolution of Oil Sands Tailings Pond Seepage, Resulting from Diffusive Ingress Through Underlying Glacial Till Sediments

by

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Dedication

To the love of my life, Mariia

Abstract

Oil sands tailings are comprised of sands, silts, clays, and process-affected water (OSPW). The latter includes high concentrations of dissolved ions, as well as organic contaminants, making the water toxic to aquatic organisms. In Northern Alberta, tailings ponds are being constructed on glacial till, overlying sand channel aquifers, establishing a potential hydraulic connection between the pond and downstream water systems. However, to date, no targeted attempts have been made to characterize the biogeochemical evolution and end products as tailings pond OSPW infiltrates into glacial till prior to reaching these aquifers, thus overlooking a key component of the contaminant transport pathway. Addressing this knowledge gap is a critical step towards protecting aquatic resources. Cation exchange capacity, exchangeable cation, batch sorption and radial diffusion cell experiments and supporting geochemical simulations were conducted: a) to assess the potential for release (or attenuation) of trace elements and major ions from glacial tills when exposed to OSPW; and b) to identify the principal geochemical processes involved in controlling pore water and sediment chemistry. The experiments revealed that sediment-bound cations available for exchange, consisted of Ca>Mg>K>NH_4>Na; while the mean cation exchange capacity in the till (Methylene Blue method) was 4.7±2.7meq $100g^{-1}$. Results further indicate that the ingress and interaction of OSPW with the glacial till sediment-pore water system will result in: the mitigation of incoming sodium by ion exchange with sediment-bound calcium and magnesium, followed by limited precipitation of calcium and magnesium carbonates; sulfate reduction and subsequent sulfide

precipitation; and biodegradation of organic carbon. High concentrations of OSPW chloride (~375mg L^{-1}) are expected to persist. Ion exchange, oxidation-reduction, and mineral phase reactions including reductive dissolution of metal oxyhydroxides influenced trace metal mobility, which is similar to previous observations within sandy aquifer settings. Furthermore, though several trace elements showed the potential for release, large-scale mobilization is not supported. Understanding the environmental impact of tailings seepage is of great importance in managing water resources in Alberta. The present research offers a scientific basis to guide future remediation and reclamation strategies, seepage management schemes, and development of compliance legislation, and is therefore anticipated to have industry-wide benefit.

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List of Symbols, Nomenclature, or Abbreviations

BTEX	benzene, toluene, ethylbenzene and xylenes
^{12}C	an isotope of carbon with 6 protons and 6 neutrons
^{13}C	an isotope of carbon with 6 protons and 7 neutrons
CEC	cation exchange capacity
CSF	carbonate and sulfate field model
DI stage	deionized water stage (of radial diffusion experiments)
FOC	fraction of organic content
F1	fraction of trace elements in the solid phase, classified as “easily exchangeable” by sequential extraction procedures
F2	fraction of trace elements in the solid phase associated with poorly crystalline metal hydroxides, oxyhydroxides and hydrous oxides, by sequential extraction procedures
F3	fraction of trace elements in the solid phase associated with well-crystallized metal hydroxides, oxyhydroxides and hydrous oxides, by sequential extraction procedures
F4	fraction of trace elements in the solid phase associated with organic matter or sulfides, by sequential extraction procedures
F5	fraction of trace elements in the solid phase, associated with residual primary minerals, by sequential extraction procedures

GW stage	groundwater (desorption) stage (of radial diffusion experiments)
IC	ion chromatography
ICP-MS	inductively-coupled plasma mass spectrometry
K_d	linear sorption partitioning coefficients
K	partitioning coefficient (Freundlich model)
OSPW	oil sands process-affected water
OSPW stage	oil sands process-affected water stage (of radial diffusion experiments)
^{32}S	an isotope of sulfur with 16 protons and 16 neutrons
^{34}S	an isotope of sulfur with 16 protons and 18 neutrons
SEM-EDS	scanning electron microscopy – energy dispersive spectrometry
SEP	sequential extraction procedure
STP	(Suncor Energy Inc.'s) south tailings pond
TOC	total organic carbon
TIC	total inorganic carbon
WCSC	wood creek sand channel

XRD	x-ray diffraction

Chapter 1: General Introduction

1.1 Introduction

1.1.1 Oil Sands Overview

Oil sands ore consists of approximately 80% sand, small amounts of clay and water, and 10% bitumen - a viscous mixture of hydrocarbons with cold molasses-like consistency at room temperature (Government of Canada, 2010). In Alberta, oil sands deposits cover an area greater than 140,000 km^2 (AGS, 2011), and contain an estimated 1.8 trillion barrels of crude bitumen, 169.3 billion barrels of which are recoverable economically given today's technology (Government of Alberta – Energy, 2012b). This rich endowment of presently recoverable reserves is the third largest in the world, trailing only Venezuela and Saudi Arabia (Government of Alberta – Energy, 2012b). The province's oil sands deposits are located in three different regions in Alberta. The largest and richest of these is the Athabasca Oil Sands region, which covers 40,000 square km. The other two are the Cold Lake region (22,000 square km) and the Peace River region (8,000 square km) (Oil Sands Discovery Centre, 2008). Not only is the Athabasca region the richest, but also the only one of the three to contain surface mineable reserves. The distinction is made based upon the depth of the oil sands deposits: those located 75m or less below ground surface can be recovered by surface mining, while those at greater depth, are recovered 'in-situ', or in place underground using steam, solvents or thermal techniques (Government of Alberta - Energy, 2012c). Only 20% of Alberta's deposits are surface mineable, while the remaining 80% require in-situ extraction (Government of Alberta, Department of Energy, 2012b). Nonetheless, historically emphasis has been placed on surface mining, and in 2010 recovery by surface mining still accounted for the majority (53%) of Alberta's crude bitumen production (Government of Alberta – Energy, 2012b).

There are four basic phases to surface mining operations: recovery, extraction, upgrading, and refining. Surface mining of oil sands is similar to that of any other mining industry: oil sands ore is excavated from the open-mine pit and transported by trucks to a plant where the bitumen is separated from the other components in the raw ore, such as sand, clay or water in the sediment pores (Government of Alberta, 2012). The second step, extraction, uses some variant of the Clark Hot Water process, in which warm or hot water, possibly supplemented with chemical additives, is used to separate the bitumen from the sediments and pore water. The extracted bitumen is collected for further processing (upgrading). Upgrading refers to a series of physical and chemical processes that transform bitumen into a lighter hydrocarbon (e.g. synthetic crude oil), which can then be easily refined. Lastly, refineries then further process the upgraded product into useful commodities including gasoline, diesel, jet fuel, lubricants, etc. (Government of Alberta - Energy, 2012c).

Tailings are a waste product of the extraction stage of surface mining operations, and consist of residual sand, silt, clay, water, and unrecovered bitumen (note: in-situ extraction does not generate tailings). From the extraction facility, tailings are pumped and discharged into nearby, vast settling basins – the oil sands tailings ponds. One of the simpler and historically common methods of disposal has been direct discharge from the transporting pipeline. The coarser sand particles in the tailings settle out quickly, closer to the point of discharge, while the remainder, a slurry of silts, clays, residual bitumen and water impacted by processing (hence process-affected water), migrates towards the centre of the pond, where it very slowly releases water and settles into a denser state. The sands may be used to construct (or expand) the tailings pond containment walls and the overlying layer of released water is recycled for re-use in the extraction process; the remaining material though, mature fine tailings (~70% water and 30% fine clay), can represent a legacy issue, as unaided, it may take decades or centuries to solidify into a soil-like deposit (Suncor, 2012).

1.1.2 Environmental Issues in the Oil Sands Industry

The oil sands industry is expanding rapidly, with production of 1.3 million barrel per day (bbl d^{-1}) in 2008, which is anticipated to reach 3 million bbl d^{-1} by 2018

(Government of Alberta – Energy, 2012). However, each barrel of synthetic crude oil produced generates 1.5 m^3 of tailings (Alberta Chamber of Resources, 2004). The resulting inventory of fluid tailings in Alberta was already a staggering 840 million m^3 in 2010 and the volume is growing (ERCB, 2010).

Oil sands process-affected water (OSPW) is a principal component of tailings. It includes not only trace elements, but high concentrations of dissolved ions which accumulate from ore extraction chemicals and oil sands ores. Moreover, naphthenic acids are released and concentrated during ore processing, making these waters toxic to aquatic life (Mackinnon and Boerger, 1986).Large amounts of water are required for oil sands processing, with estimates of 10-11 barrels of water per barrel of bitumen produced (Government of Canada, 2010).In an effort to mitigate the demands on the environment, much of this water is recycled from the tailings ponds; however, contaminant concentrations increase with each cycle. To protect the environment, oil sands tailings operations presently adhere to a policy of zero water discharge beyond their lease boundary and into the adjacent environment. Thus, storage and management of enormous volumes of tailings represents a major, long-term challenge for the industry.

One aspect to this challenge pertains to seepage. It is not possible to achieve perfect containment within these enormous man-made impoundments. Consequently, tailings ponds have the potential to act as long-term sources of OSPW leakage, or seepage, into the underlying and adjacent soils and water systems.

Nor is seepage into the subsurface a simple migratory process. As the OSPW migrates through the subsurface, it may be subject to a highly complicated series of interrelated biological and geochemical reactions. This could include dissolution of mineral phases in the pristine sediments, ion exchange reactions between incoming ions and those bound to the native sediments, microbially-mediated transformations such as biodegradation reactions, and more. A critical gap in research to date is detailed understanding of the complex biogeochemical processes taking place, and their end products, as seepage migrates through, and interacts with different sediments in the subsurface.

Over time, the Athabasca Oil Sands region has been influenced by the advance and retreat of glaciers in several directions, which has modified surficial soils and sediments into the present complex arrangement (Andriashek and Atkinson, 2007,King and Yetter, 2011). This includes widespread outwash sands in the east to north, regions of silts and clays from former glacial lakes to the south, and glacial ice-contact features, kames or kame moraines (silt and silty sand), near Fort Hills and to the north (Fox, 1980). Another sediment type commonly present is “till” - material deposited by a glacier that is unsorted, has no layering of sediment types, and may include clay, silt, sand, pebbles etc. Aside from this spatial variability, there may additionally exist a variable and complex arrangement of sediment types with depth. For example, this includes the presence of buried sand channel systems throughout the Athabasca Oil Sands region (Andriashek and Atkinson, 2007). With leases positioned throughout the region, tailings ponds have been, or are being, built atop a diversity of geological formations and sequences.

However, the fate of inorganic species (major ions and trace metals), as OSPW seepage infiltrates through the different sediments present in Northern Alberta, is not well understood. To date, the most relevant studies have focused exclusively on seepage into shallow groundwater-bearing sand formations (shallow aquifers) or surface waters (e.g. Gervais and Barker, 2004, MacKinnon et al., 2004, Oiffer et al., 2009, Yasuda et al., 2010). Additionally, emphasis of these works has been traditionally placed on naphthenic acids (organics), due to their toxicity, with arguably only one study offering detailed investigation of trace metal or salinity changes, though again, within a shallow aquifer (Oiffer et al., 2009). At an increasing number of locations in Northern Alberta, oil sands tailings ponds will be situated in glacial till or till overlying Pleistocene-era meltwater sand channels.

However, no known research has attempted to characterize the attenuation capacity, or biogeochemical evolution and inorganic end products, as OSPW seepage infiltrates through glacial till prior to reaching these aquifers, thus overlooking a key component of the contaminant transport pathway. Addressing this knowledge gap is a critical step towards protecting aquatic resources.

1.2 Objectives

The overall objectives of the present research therefore are to:

1) Assess the potential for release (or attenuation) of major ions and trace elements of environmental interest; and to
2) Identify the principal biogeochemical processes involved;

as oil sands tailings pond fluids seep through glacial till sediments, en route to underlying and downstream water resources.

Objectives will be achieved through a series of increasingly complex and representative (of field conditions) laboratory experiments, with each stage building upon the understanding gained from its predecessor.

Despite recent improvements to tailings de-watering treatment, vast oil sands tailings ponds will be a legacy of the industry for years to come. Clarifying the evolution and persisting contaminants resulting from tailings pond seepage is critical in guiding appropriate remediation, groundwater monitoring and seepage management strategies. This research is anticipated to be of interest to the entire oil sands industry.

1.3 Hypothesis

The following hypothesis was established at the outset of the research project:

The trace element and major ion composition of ingressing OSPW seepage will be modified during migration through a surficial clay-rich aquitard, through the processes of competitive exchange and sorption, and by redox and mineral phase precipitation-dissolution reactions.
As part of this overall hypothesis, specific hypotheses to be tested include:

- Competitive cation exchange between ingressing OSPW and clay till sediments will alter the major ion composition of infiltrating waters;
- Sorption by clay till sediments will mitigate concentrations of abundant cations;
- The influx of a dissolved carbon source in OSPW will stimulate redox reactions in the clay till; and
- The ingress of a moderately high ionic strength solution, featuring high concentrations of select cations and anions, will stimulate both dissolution (e.g. salting in) and conversely precipitation of different mineral phases.

1.4 Outline of Thesis

Chapter 2 provides an overview of the research conducted in this field to date, supplemented by background information necessary for understanding work presented in the later chapters. Chapter 3 provides an overview of the materials and methods used in the progression of experiments constituting this thesis. Chapter 4 characterizes the basic properties of the pristine (non-impacted) sediments on site, including the cation exchange capacity and exchangeable cations. Initial experiments of these types revealed the presence of carbonate mineral phases in these glacial tills, which confound many cation exchange tests.

As a result, this chapter includes an important aside – the evaluation of a suitable cation exchange method for use with these sediments. Chapter 5 begins to directly explore objectives 1 and 2, using batch sorption experiments to gain a preliminary understanding of the ion exchange and adsorptive tendencies, when OSPW is mixed with sediments. Chapter 6 uses a much more representative laboratory test to further investigate objectives 1 and 2: radial diffusion cells which utilize long-term reactions, oxygen-free conditions, diffusive influx of OSPW, etc. Reactive transport modeling of the diffusion cells is conducted to gain further insight into the processes governing system behavior. Lastly, the conclusions and engineering significance of the work are addressed in Chapter 7.

1.5 Summary of Accomplishments

A number of publications and presentations have resulted from the work outlined in this doctoral thesis. These accomplishments are summarized below, while the conclusions and engineering significance of the work are presented in detail in Chapter 7.

Table 1-1
Dissemination of thesis results

Publications and Presentations	**Published / Completed**	**In Review**	**In Progress**
Refereed publications	1	2	2
Refereed conference papers	1		
Other conference presentations	9	1	
Invited talks	1		
Non-refereed articles/internal Reports	4		

Supervisory Experience:

B.Sc. Environmental Engineering Student (May, 2010 - March, 2012)

1.6 Chapter 1 References

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Chapter 2: Theoretical Background and Literature Review

Chapter 2 is organized as follows: sections 2.1 to 2.4 introduce background theory intended to help the reader better understand concepts discussed later in the thesis. Sections 2.5 to 2.8 transition from theory into a literature summary of relevant research conducted to date: beginning with an overview of environmental challenges facing the oil sands industry, through to previous investigations concerning tailings ponds seepage. Having thus established context for the present work, the section culminates with a discussion of the thesis-wide objectives, hypotheses, and an overview of the proposed experiments.

2.1 Oxidation-Reduction (Redox) Reactions (Langmuir, 1997)

Before addressing redox reactions in detail, it is important to first define some basic terminology. The oxidation state of an element reflects the number of electrons that have been added to, or removed from, an element to achieve its present condition. In terms of reactions, oxidation reactions release electrons, while reduction reactions consume them. Or, put a different way, oxidation increases the oxidation state of a reactant, while reduction decreases it. (Clark, 2002)

2.1.1 What are Oxidation States?

A large number of elements exist in 2 or more oxidation states in natural waters or mineral systems. Of these ‘redox’ elements, under the definition that major species are present at aqueous concentrations > 1mg L^{-1}, and minor at < 1mg L^{-1}, in oil sands tailings, major redox elements consist of H, O, C, S, N, Fe while minor redox elements typically include (but are not limited to): As, Cr, Fe, Mn, Mo, Pb, and V (Allen, 2008, Kasperski, 1992, and in-house analysis of Suncor South Tailings Pond process-affected water) (summarized in Table 2-1). Under this definition, note that iron may be either a major or minor element for a particular oil sands operation. From a practical perspective, redox states are important because they influence an element's biological or chemical properties, such as toxicity or mobility in the system. For example, among Cr oxidation states: Cr(III) and Cr (VI), the latter is both the more mobile and toxic form, and thus of greater environmental concern (CCME, 1999).

Table 2-1
Elements possessing more than one oxidation state, relevant to the oil sands industry

Element	**Oxidation States**[a]	**Of Potential Importance to OSPW Seepage Reactions**[b]
Hydrogen (H)	1+, 0	
Oxygen (O)	2-, 0	
Carbon (C)	4+, (0), 4-, 2-	Yes
Sulfur (S)	6+, 4+, 0, (1-), 2-	Yes
Nitrogen (N)	5+, 3+, 0, 3-	Yes
Fluorine (F)	1-, 0	
Iron (Fe)	3+, 2+	Yes
Manganese (Mn)	2+, (3+), (4+)	Yes[d]
Arsenic (As)	3+, 5+, (0)	Yes
Chromium (Cr)	6+, 3+	Yes
Copper (Cu)	2+, 1+, (0)	Yes
Mercury (Hg)	2+, 1+, (0)	
Molybdenum (Mo)[c]	2-, 1-, 0, 1+, 2+, 3+, 4+, 5+, 6+	Yes
Nickel (Ni)	5+, 3+, 0, 3-	
Lead (Pb)	2+, (4+), (0)	Yes
Antimony (Sb)	3+, 5+	
Selenium (Se)	6+, 4+, (0), 2-	
Vanadium (V)	5+, 4+, 3+	Yes
Uranium (U)	6+, 4+	

Modified from Langmuir, 1997.

[a] Oxidation states in parentheses exist in solid phase only

[b] Present in tailings pond water (from several operators) (Allen, 2008), with anticipated potential involvement in seepage reactions

[c] IMOA, 2008 – solubility information not included for Mo

[d] Kasperski, 1992

2.1.2 Introducing Redox Reactions and Oxidation Potentials

By convention, redox half-reactions are expressed as reduction reactions, that is, with the transferred electrons appearing on the left hand side of the equation. A generic reduction reaction may therefore be expressed as:

$$aA + bB + ne^- = cC + dD \qquad (2.1)$$

where the left hand side represents the oxidized state and the right hand side, the reduced state. The letters a, b, c, d are the stoichiometric coefficients of the reactant species A, B, C, D, e- are electrons, and n, the number of electrons.

The theoretical voltage associated with this reaction, is:

$$Eh = E^o + (RT / nF) * \ln([A]^a[B]^b / [C]^c[D]^d) \qquad (2.2)$$

Where Eh is the potential (in volts), n is the number of electrons, T is temperature (K), R (gas constant) = 0.001987 kcalmol^{-1}K, F (Faraday constant) = 23.061 kcal $(\text{volt g eq})^{-1}$, and,

$$E^o = -\Delta G_r^o / nF \qquad (2.3)$$

where E^o is the standard potential of the half reaction (volts), n, F are as defined in equation (2.2), and ΔG_r^o is the standard-state Gibbs free energy of a reaction (kcalmol^{-1}).

Thus for example, the Eh potential for the reduction of iron, would be expressed as follows: the reaction is given by,

$$Fe^{3+} + e^- = Fe^{2+} \qquad (2.4)$$

For which Eh is given by,

$$Eh = E^o + (RT / F) * \ln([Fe^{3+}] / [Fe^{2+}]) \qquad \text{(note, here n = 1)} \qquad (2.5)$$

Though it is possible to measure system-wide Eh (redox) potentials using appropriate probes, its accuracy can be questionable. Meaningful Eh measurements are possible in systems where the redox species are both abundant, and readily oxidized or reduced at the electrode surface (for example in water containing ample concentrations of dissolved Fe, Mn or sulfides). On the other hand, many redox couples (i.e. a redox half reaction that is paired with another to yield an overall redox reaction) react either irreversibly or sluggishly, leading to disequilibrium among different couples within the overall system. As a result, measured Eh potentials may not be stable, or meaningful representations of the system. This is particularly true for redox systems dominated by C, N, O, H and oxidized S. Chemical analysis of specific redox couples may offer a useful alternative, particularly in applications such as “groundwaters contaminated by waste disposal, where redox gradients are often steep, and the fate of redox-sensitive contaminants may be rate dependent or otherwise unpredictable” (p415, Langmuir, 1997). Using water composition to assess redox state, though useful, requires careful interpretation; for example, the presence of a reaction product such as CH_4 is not conclusive proof of active methanogenesis at the sampling location, but instead it may have been produced upgradient, and transported by the groundwater to the present location (Appelo and Postma, 2005).

2.1.3 Establishing a link between Oxidation Potentials and Redox Behavior in Environmental Systems

In theory, when pH is constant, oxidized species belonging to a redox couple that possesses a higher relative Eh potential (more positive), can oxidize reduced species belonging to a couple with lower Eh. Thus couples maybe ranked according to Eh. This diagrammatical representation, termed a redox ladder, helps one to predict an element’s oxidation state or chemical speciation, under the system conditions at hand, or more broadly, allows one to hypothesize reaction sequences and products in contaminated systems.

The redox ladder in Figure 2-1 includes several reactions suspected to be relevant to seepage of oil sands process-affected water (OSPW) into the subsurface. (Note: OSPW contains high concentrations of sulfate, bicarbonate, and organic carbon (Allen, 2008), and a previous study has identified iron and manganese oxyhydroxides presence in sandy aquifer sediments near Fort McMurray (Haque, 2009)). As the ladder further suggests, redox-driven changes in water chemistry may be manifested in some cases by the disappearance of the electron acceptor reactant (e.g. NO_3^- or SO_4^{2-}), or in other instances by emerging concentrations of a reaction product (e.g. Fe^{2+}).

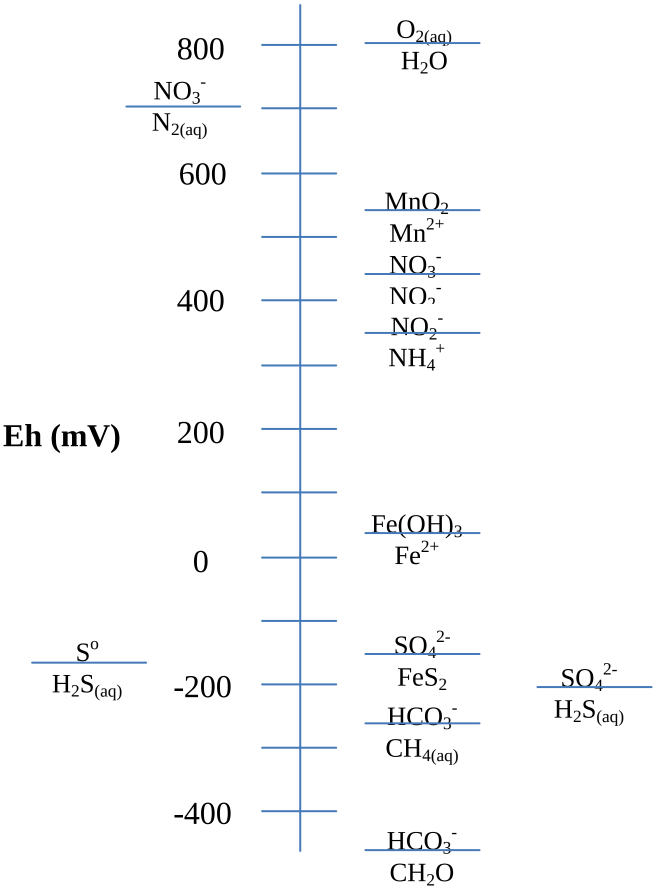

Figure 2-1 Theoretical redox ladder (Langmuir, 1997) (Conditions used in derivation include: pH=7; Temperature = 25^{o}C; equal molar ion concentrations (unless specified in the following); $NO_3^-/N_2(aq)$ at $N_2(aq) = 14mgL^{-1}$ and $NO_3^- = 62mgL^{-1}$; MnO_2/Mn^{2+} at $Mn^{2+} = 1mgL^{-1}$; $Fe(OH)_3/Fe^{2+}$ at $Fe^{2+} = 1mgL^{-1}$ assuming K_{sp} for $Fe(OH)_3 = 10^{-38.5}$; SO_4^{2-}/FeS_2 at $Fe^{2+} = 1mgL^{-1}$ and $SO_4^{2-} = 96mgL^{-1}$, and $S^o/H_2S(aq)$ at $H_2S(aq) = 108mgL^{-1}$)

2.1.4 Redox Reactions and Metal Mobility (Appelo and Postma, 2005)

A final class of redox reactions, reductive dissolution of metal oxyhydroxides, deserves special mention due to its anticipated relevance on-site. This class of minerals generally refers to iron oxides, hydroxides or oxyhydroxides (hereafter termed simply oxyhydroxides), but also includes Mn. And though discussion will focus on Fe, it should be noted that Mn behaves similarly to Fe, though it tends to be present at lower concentrations than Fe, and as seen in Figure 2-1, iron oxide reduction requires stronger reducing conditions than Mn oxide reduction.

Iron oxyhydroxide minerals often present in sediments include: ferrihydrite ($5Fe_2O_3$-$9H_2O$), lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and hematite (α-Fe_2O_3) (ordered in increasing stability).The reduction of iron oxyhydroxides by organic carbon, can be an important determinant of water quality in groundwaters. The reaction may be summarized by:

$$CH_2O + 4FeOOH + 7H^+ = 4Fe^{2+} + HCO_3^- + 6H_2O \tag{2.6}$$

In the subsurface, distribution and mobility of trace elements is controlled by changing pH values and redox conditions. The dissolution of metal oxyhydroxides can occur under acidic conditions ($pH < 3$; Bowers and Higgs, 1987); however this mechanism is not anticipated in the present system, where at the tailings pond site, native pore waters are circumneutral pH and the intruding OSPW has pH ~8.3. Alternately, release could be facilitated by reductive dissolution. Previous research within sandy aquifer sediments from the Athabasca Oil Sands region revealed that a large fraction of trace element content in the solid phase, was associated with poorly crystalline and well-crystallized Mn and Fe oxyhydroxides (e.g. Haque, 2009). This was true for the elements: Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Sr and V. Thus, ingress of carbon-rich OSPW has the potential to induce both reductive dissolution of native metal oxyhydroxides and the consequent mobilization of associated trace elements.

It should also be noted that microbial mediation can be extremely important in redox reactions. Detailed assessment of how native microbiological communities change, or are changed, by seepage is beyond the scope of this thesis (and is being conducted by complementary research). Nonetheless, it is important to acknowledge their potential importance to the geochemical changes taking place. For example, in a review, Lovely (1991) noted that evidence indicates only a "trivial" amount of Fe(III) is reduced by organic compounds abiotically (or nonenzymatically), versus that through microbial metabolism. This is particularly true for systems at circumneutral pH. And even among the few compounds seemingly capable of such nonezymatic reduction, the quantity of organics oxidized, or iron reduced, is much smaller than when biologically mediated. Similar findings pertain to Mn reduction by organic carbon, though abiological reactions at circumneutral pH were more common than for Fe. Since from work such as Tompkins 2009, Mn, Fe and organic carbon are all anticipated in the seepage system under study (Mn, Fe in sediments (or as colloids) and organic carbon in both sediments and seepage), microbial participation in these biogeochemical reactions is strongly expected, though again, it will not be the focus of this thesis, but of later work.

2.2 Mineral Phase Reactions (Langmuir, 1997)

The progress of chemical reactions dictates the composition and fate of species in an aqueous system. Therefore, knowledge of kinetics and also the equilibrium state of the system - in particular, whether or not equilibrium has been reached and the present direction of change - are critical in predicting species' concentrations and system behavior.

Two useful concepts are Gibbs Free Energy, which allows one to predict the direction a reaction will spontaneously proceed (if not limited by kinetics), and saturation indices, which typically define the saturation state of minerals, including whether dissolution or instead precipitation is favoured. Saturation states are important to the discussion of mineral reactions in this thesis, therefore, the next few paragraphs will introduce Gibbs Free Energy, culminating in how it relates to saturation indices and what these values mean.

Absolute values in free energy are not known; instead differences in free energy among substances in a reaction are considered. This parameter, the difference in

Gibbs Free Energy or ΔG represents the maximal change in energy as useful work. In order to relate Gibbs Free Energy to the concept of equilibrium, let us begin with a general reaction similar to 1) above.

$$aA + bB = cC + dD \tag{2.7}$$

where a,b,c,d are the stoichiometric coefficients of the reaction, belonging to species A,B,C,D.

The Gibbs Free Energy of one mole of the first reactant, (G_A), at a constant temperature and pressure, is

$$G_A = \Delta G_A^o + RT \ln[A] \tag{2.8}$$

where R is the gas constant, [A] the activity (akin to concentration) of reactant A, T is temperature and ΔG_A^o is simply the Gibbs Free Energy of A, when the activity of A = 1 (unity).

From this, a similar reaction-wide expression may be developed, taking the sum of reaction products minus the sum of the reactants. In this manner, considering all reaction terms in (2.7), and expanding them as in (2.8), leads to

$$\Delta G_r = cG_C + dG_D - aG_A - bG_B \tag{2.9}$$

and

$$\Delta G_r = c\Delta G_C^o + RT \ln[C]^c + d\Delta G_D^o + RT \ln[D]^d - a\Delta G_A^o + RT \ln[A]^a - b\Delta G_B^o + RT \ln[B]^b$$

$$= (c\Delta G_C^o + d\Delta G_D^o - a\Delta G_A^o - b\Delta G_B^o) + RT(\ln[C]^c + \ln[D]^d - \ln[A]^a - \ln[B]^b)$$

$$= \Delta G_r^o + RT \ln([C]^c[D]^d / [A]^a[B]^b) \quad (2.10)$$

$$= \Delta G_r^o + RT \ln Q \quad (2.11)$$

And ΔG_r^o is the standard Gibbs Free Energy of the reaction and Q the reaction quotient.

When chemical equilibrium is reached, $\Delta G_r = 0$, and Q is replaced by K_{eq}, thus by (2.11),

$$\Delta G_r^o = -RT \ln K_{eq} \quad (2.12)$$

(practically, ΔG_r^o may be determined from the Gibbs Free Energy of formation of a substance, but this will not be covered and the interested reader is referred to Langmuir, 1997)

Combining (2.11) and (2.12) leads to

$$\Delta G_r = \Delta G_r^o + RT \ln Q = -RT \ln K_{eq} + RT \ln Q = RT \ln (Q/K_{eq}) \quad (2.13)$$

Now one is in a position to translate knowledge of Gibbs Free Energy, into the direction a reaction will progress to achieve equilibrium

At equilibrium $\Delta G_r = 0$ and Q = Keq. If $\Delta Gr < 0$, Q must be $< K_{eq}$ and the reaction (equation 2.7),proceeds in the forward direction, to the right, while if $\Delta Gr > 0$, Q must be > Keq, and the opposite is true.

The saturation index (SI), is similar to ΔG_r, with

$$SI = \log_{10}(Q/K_{eq}) \quad (2.14)$$

and

$$SI = \Delta G_r / (2.303RT) \qquad (2.15)$$

Following the convention that the mineral reaction is written as a dissolution reaction, one arrives at the important result:

when SI (and ΔG_r) is less than zero, the reaction proceeds in the forward direction (i.e. mineral is undersaturated and dissolves), whereas when both are greater than zero, the reverse reaction is favoured (mineral is oversaturated and precipitates).

Before ending the discussion pertaining to mineral phase reactions, it is important to understand that not all systems may be at equilibrium, for example a reaction may be rate-limited, that is, limited by kinetics. Reactions may thus vary from attaining equilibrium within the duration of an experiment, to mineral reactions evolving at a geological timescale. Reactions which proceed sufficiently quickly to potentially influence the laboratory experiments in this thesis, and which are expected given the system geochemical inputs (pore water and OSPW chemistry, and mineralogy of the till sediments) are listed in Table 2-2.

Table 2-2
Potential mineral phases of importance in glacial till sediments on site

Category	Mineral Name	Chemical Formula
Carbonates		
	Calcite	$CaCO_3$
	Dolomite	$CaMg(CO_3)_2$
	Siderite	$FeCO_3$
	Rhodochrosite	$MnCO_3$
Sulfates		
	Gypsum	$CaSO_4$-$2H_2O$
	Celestite	$SrSO_4$
	Barite	$BaSO_4$
Sulfides		
	FeS(a)	FeS
	Mackinawite	$Fe_{(1-x)}S$
Aluminosilicates		
	Chalcedony	SiO_2
	Kaolinite	$Al_2Si_2O_5(OH)^a$
Oxyhydroxides		
	$Fe(OH)_3$(a)	$Fe(OH)_3$
	Geothite	α-FeOOH
	Gibbsite	α-$Al(OH)_3$
	Birnessite	MnO_2
	Manganite	$Mn(OH)_3$

(Donahue, 2006)
[a] dissolution only

2.3 Clay Mineralogy, Sorption, Ion exchange and Cation Exchange Capacity (CEC) (Langmuir, 1997)

2.3.1 Review of Clay Mineralogy

With a thesis focus on OSPW ingress into clay-rich glacial till sediments, it is important to begin by first reviewing some of the fundamentals concerning clay mineralogy. The following section briefly introduces the different types of clay minerals, their structure, and the different sources of net layer charge giving rise to cation exchange capacity and the presence of exchangeable cations.

Clay minerals have been defined as “phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing” (Guggenheim et al., 2006). The fundamental building blocks are tetrahedral and octahedral units. The former typically consist of a silicon atom surrounded by 4 oxygens or hydroxyls in a tetrahedral geometric orientation; the latter, typically an aluminum atom in coordination with 6 oxygens or hydroxyls, yielding an octahedral geometric orientation. A tetrahedral sheet is then a 2D continuous arrangement of tetrahedrons in a hexagonal network, where the tetrahedron tips point in a common direction and base oxygens are shared between neighboring tetrahedrons. An octahedral sheet is similarly a continuous 2D network of octahedral units, which share corner oxygens/hydroxyls. If the central cation is trivalent, only 2 of 3 octahedral positions will be filled to achieve a charge-balanced structure, and the sheet is termed dioctahedral, while if the cation is divalent, 3 of 3 are filled, leading to a trioctahedral sheet. Tetrahedral and octahedral sheets are combined to form one of two different types of layers. In 1:1 layers, one octahedral sheet joins to one tetrahedral sheet (tips pointing towards octahedral sheet and corner oxygens are shared between the two sheets). Conversely, a 2:1 layer is comprised of an octahedral sheet sandwiched between two opposing tetrahedral sheets (tetrahedron tips pointing inward).

Stacks of 1:1 or 2:1 layers are separated by an interlayer space which may be vacant or populated with interlayer cations, hydrated cations, hydroxide octahedral sheets or organic material. For example, in kaolinite (a 1:1 mineral), little substitution of structural cations occurs in the layers, and the interlayer is vacant, with neighboring layers bound fairly tightly by hydrogen bonds (formed between tetrahedral oxygens and octahedral hydroxyls). In smectites (2:1 minerals), substitution of Al for Si in tetrahedrons, or of Mg, Fe, Zn, Ni, etc. for Al in the octahedrons, creates a charge imbalance in the layer that typically results in a net negative charge. The imbalance is satisfied by adsorption of cations in the interlayer space or to layers edges. (Notes: smectites have very weak interlayer bond between the oxygens of adjacent layers). For illites (also 2:1 minerals), substitution of Al for Si in the tetrahedrons creates a charge imbalance satisfied by interlayer potassium ions, which forms strong interlayer bonds.

Table 2-3, from Guggenheim et al. (2006), summarizes the composition and characteristics of phyllosilicates, including their typical net layer charge per formula unit. Further details may be found in Thomas (2004) and Grim (1953).

Table 2-3
Classification of planar hydrous phyllosilicates (Guggenheim et al., 2006)

Layer Type	Interlayer Material[1]	Group	Octahedral Character	Species[2]
1:1	None or H_2O only ($x \approx 0$)	Serpentine-kaolin	Trioctahedral	Lizardite, berthierine, amesite, cronstedtite, nepouite, kellyite, fraipontite, brindleyite
			Dioctahedral	Kaolinite, dickite, nacrite, halloysite (planar)
			Di,trioctahedral	Odinite
2:1	None ($x \approx 0$)	Talc-pyrophyllite	Trioctahedral	Talc, willemseite, kerolite, pimelite
			Dioctahedral	Pyrophyllite, ferripyrophyllite
	Hydrated exchangeable cations ($x \approx 0.2$-0.6)	Smectite	Trioctahedral	Saponite, hectorite, sauconite, stevensite, swinefordite
			Dioctahedral	Montmorillonite, beidellite, nontronite, volonskoite
	Hydrated exchangeable cations ($x \approx 0.6$-0.9)	Vermiculite	Trioctahedral	Trioctahedral vermiculite
			Dioctahedral	Dioctahedral vermiculite
	Non-hydrated monovalent cations, ($\geq 50\%$ monovalent, $x \approx 0.85$-1.0 for dioctahedral)	True (flexible) mica	Trioctahedral	Annite, phlogopite, lepidolite, aspidolite
			Dioctahedral	Muscovite, celadonite, paragonite
	Non-hydrated mono- or divalent cations, ($x \approx 0.6$-0.85)	Interlayer-deficient mica	Trioctahedral	Illite, glauconite, brammallite
			Dioctahedral	Wonesite[3]
	Non-hydrated divalent cations, ($\geq 50\%$ divalent, $x \approx 1.8$-2.0)	Brittle mica	Trioctahedral	Clintonite, kinoshitalite, bityite, anandite
			Dioctahedral	Margarite, chernykhite
	Hydroxide sheet (x = variable)	Chlorite	Trioctahedral	Clinochlore, chamosite, pennantite, nimite, baileychlore
			Dioctahedral	Donbassite
			Di,trioctahedral	Cookeite, sudoite
			Tri,dioctahedral	none
2:1	Regularly interstratified (x=variable)	Variable	Trioctahedral	Corrensite, aliettite, hydrobiotite, kulkeite
			Dioctahedral	Rectorite, tosudite, brinrobertsite
1:1,2:1			Trioctahedral	Dozyite

1 x is net layer charge per formula unit, given as a positive number
2 not an exhaustive list of species
3 net layer charge may be <0.6, but this is an exception

2.3.2 Factors giving rise to Surface Charge and Cation Exchange Capacity

When evaluating water-sediment interactions in a contaminant transport scenario (e.g. OSPW seepage), it is important to consider the sorption properties of materials in the system. This in turn, first requires that one understand some of the factors which give rise to surface charge.

The ability for a material to bind or sorb aqueous species, is dependent on its surface area (with fine-grained soils and sediments having higher sorption capacity than those with larger particle sizes), as well as the density of charge sites on its surface. Surface-site density is reflected in the term exchange capacity, which typically has units of charge per mass: milliequivalents per 100g (of sediment). When the surface has an overall net negative charge, the material has an affinity for positive species and hence a cation exchange capacity.

In clay minerals, the typically negative surface charge may arise from three different mechanisms: isomorphous substitution, lattice imperfections and broken or unsatisfied bonds.

(1) Isomorphous substitution occurs when a cation replaces a structural Al^{3+} or Si^{4+} cation in the clay mineral crystal lattice. Common substitutions include Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+}, which results in a local, permanent charge deficiency. The surface charge of illites, smectites and vermiculites is largely determined by this mechanism. (Note: lattice structure of clay minerals will not be discussed, and the interested reader is instead referred to other sources, including Langmuir, 1997 Chapter 9).

(2) Lattice imperfections are defects, for example, a missing Al^{3+} cation in the octahedral layer. This mechanism determines smectite surface charge and, to lesser degree, that of illites. It too yields a permanent charge.

(3) Lastly, broken or unsatisfied bonds occur at lattice edges and corners, and generally result in an exposed OH^- or O^{2-} molecule that is not charge balanced. The resulting strength of the charge imbalance is not as great as by

> the other two methods. This mechanism impacts all clay varieties, but is the dominant mechanism for kaolinite's surface charge. Unlike the other mechanisms, broken bonds are not a source of permanent charge, but rather are highly dependent on solution chemistry, particularly pH.

Concerning other mineral groups, including oxides, hydroxides, phosphates and carbonates, the principal cause of their surface charge is chemical reactions with, or ionization of, surface groups. The notation of metal oxide or hydroxides surface sites, helps to visualize this mechanism: the site may be expressed by MOH_n^{n-1}, where M is the metal cation, the superscript the net charge and the subscript the molecular formula (with n numerically between 0 and 2). Surface charges on these materials are highly sensitive to pH. For example, for ferric oxide, surface complexes may progress from $FeOH_2^+$ to FeOH, and FeO^-, as surrounding solution chemistry becomes more basic.

To summarize, with regard to pH dependency, smectites and illites have relatively stable surface charge (or CEC) with pH, whereas kaolinites and metal oxyhydroxides are highly pH dependent (more negative at high pH).This can have important consequences for techniques which measure CEC, as depending on the sediment composition, the experimentally determined value could be sensitive, and specific to the pH of the extractant. Also, amongst the species discussed, cation exchange capacity is smallest for kaolinite, and potentially largest for Mn and Fe oxyhydroxides: at pH 7, CEC for kaolinite is generally between 3 and $15meq100g^{-1}$, $10\text{-}40meq100g^{-1}$ for illite and chlorite, $80\text{-}150meq100g^{-1}$ for smectite-montmorillonite, and $100\text{-}740meq100g^{-1}$ for the metal oxyhydroxides. Naturally, in native sediments, which may represent a mixture of sands, clays, oxyhydroxides, organic material (which itself has CEC $\sim 100\text{-}500meq100g^{-1}$ at pH 7), and more, the CEC will reflect this composition both in its overall pH dependency and net magnitude.

2.3.3 Exchangeable Cations

While the cation exchange capacity describes the potential capacity of a surface to bind positively charged species, the similarly named exchangeable cations instead describes the composition of cations that exist, pre-bound, to sediment surface sites. Their characterization can be important to contaminant transport applications, because they represent weakly bound species which may be displaced into the pore water, by incoming seepage.

The partitioning of exchangeable cations on a surface is a complex subject, and only a basic overview will be provided here. Several important factors which influence this partitioning are:

- ion charge;
- ion size – particularly the hydrated radius;
- the properties of the solid (sorbent) surface (e.g. those of the clay mineral);
- the quantity and ratios of the various solutes in the contacting solution; and
- the total solution concentration (Fonstad, 2004).

2.3.4 Theoretical Models of Sorption and Ion Exchange (Langmuir, 1997)

A variety of models exist to describe the sorption and ion exchange behavior of systems. As a note: adsorption describes the process in which an atom, molecule or ion is bound or adheres to the surface of a material, while absorption reflects incorporation of that species into the material volume, and sorption is a generic term referring to either process. Adsorption may be characterized experimentally, through batch tests, wherein sediment samples of a set mass, are mixed with a set volume of solution containing the chemical species of interest. The concentration of solution is varied amongst samples, and the resultant dataset is used to create a plot of the quantity sorbed as a function of the final solution concentration. This plot is called an isotherm. The three primary models used to describe adsorption are the linear, Freundlich and Langmuir isotherms.

Mathematically, the linear isotherm is given by:

$$x/m = K_d C \tag{2.16}$$

where x/m is the concentration adsorbed to the sediments (with x the mass of the species, m, the mass of the sediment or sorbing substance), C is the concentration in solution and K_d is a constant known as the distribution coefficient.

One use against which this model is recommended, is to describe trace element uptake, when several processes may be involved, such as sorption, precipitation, co-precipitation into another mineral phase etc. Under these conditions, the calculated K_d value is only relevant to the specific system at hand and cannot be used to depict another system.

However, adsorption behavior under most circumstances does not correspond to the linear representation afforded by the linear sorption isotherm. Instead, sorption tends to be greatest at very low concentrations of a species, and gradually plateaus, with a smaller fraction sorbed at higher concentrations, resulting in an isotherm that is curved and not linear as shown in Figure 2-2. Thus, the linear isotherm representation finds application, for example, at very low concentrations of molecular organic species, where the curve is still approximately linear, and additional processes like precipitation are not present.

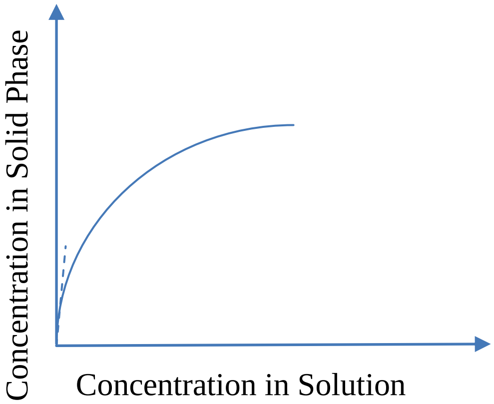

Figure 2-2 Typical shape of experimental sorption data (Langmuir, 1997).

Alternately, the Freundlich isotherm, which can characterize non-linear sorption, is governed by:

$$x/m = KC^n \tag{2.17}$$

again, with x/m is the concentration adsorbed to the sediments, C is the concentration in solution, and K and n are both constants.

A practical shortcoming to the previous two models, is that both assume an infinite number of unreacted surface sorption sites exist. This is improved upon by the Langmuir isotherm, which assumes a finite number of sites exist, and after these are filled, the isotherm plateaus, and further sorption is no longer possible.

The Langmuir isotherm is given by

$$x/m = (bCN_{max}) / (1+ bC) \tag{2.18}$$

where x/m is the concentration adsorbed to the sediments, C is the concentration in solution, N_{max} is the maximum sorption achievable, and b is a constant. Competition between different species in solution for sorption sites can be somewhat accommodated, if separate isotherms are plotted for each individual species, though whether this truly reflects competition is debatable.

Adsorption of dissolved ions, always involves the exchange of a competing ion. A competitive ion exchange between two species may be generalized as follows:

$$aA^{z} + B_{b}X = bB^{y} + A_{a}X \qquad (2.19)$$

where X is a negative surface site, A and B are cations with charge z and y respectively, and a and b the number of moles involved in the reaction.

The equilibrium constant (K_{exch}) for this expression is:

$$K_{exch} = [B^{y}]^{b}[A_{a}X] / [A^{z}]^{a}[B_{b}X] \qquad (2.20)$$

Sodium is the dominant cation in oil sands process-affected water, thus a possible reaction of relevance to the sediment system in this thesis could be:

$$Na^{+} + ½Ca\text{-}X_{2} = ½Ca^{2+} + Na\text{-}X \qquad (2.21)$$

and

$$K_{Na/Ca} = [Ca^{2+}]^{0.5}[Na\text{-}X] / [Na^{+}][Ca\text{-}X_{2}]^{0.5} \qquad (2.22)$$

In the above equation, the activities of aqueous species ($[Ca^{2+}]$, $[Na^{+}]$) can be determined using measured concentrations and Debye-Huckel theory. Activities of exchangeable cations (e.g. [Na-X]) may be calculated individually as a molar fraction (of the bound moles of that species compared to the total number of exchangeable cations) or as an equivalent fraction (amount of that species bound (in units of milliequivalents) compared to the total number of exchange sites, or

CEC. The former adheres to the Vanselow convention, the latter, the Gaines-Thomas convention (Appelo and Postma, 2005).

Thus, for example, following the Gaines-Thomas convention, for Na in our system,

$$\beta_{Na} = meq_{\ Na\text{-}X} / CEC \qquad (2.23)$$

and from (2.22) and (2.23)

$$K_{Na/Ca} = [Ca^{2+}]^{0.5}\beta_{Na} \ / \ [Na^{+}]\beta_{Ca}^{\ 0.5} \qquad (2.24)$$

Lastly, from a practical perspective, the equilibrated concentrations of major cations bound to the solid phase can be measured via desorption experiments, yielding beta values, from which an equilibrium ion exchange coefficient can be calculated (e.g. a $K_{Na/Ca}$ value), solving the equation.

This system of equations is known sometimes as ‘simple’ competitive ion exchange (as opposed to a power exchange function – not discussed) and can be used to represent competitive exchange of most metal cations onto clay surfaces.

It should be noted however, that more complex models do exist, for example, electrostatic adsorption models including the constant capacitance, diffuse-layer, and triple-layer models. These models find application in more complex scenarios, for example modeling trace element adsorption onto surfaces, against the net surface charge (Langmuir, 1997). However, such models are beyond the scope of the present work, wherein the emphasis is on ion exchange behavior of major species, and only preliminary/rudimentary understanding of trace element behavior is sought.

2.4 Geochemical Complexity and Non-Uniqueness

To summarize from above, the ingress of OSPW into the glacial till, may result in a series of mineral phases precipitation-dissolution reactions, oxidation-reduction reactions (including those microbially-mediated), competitive exchange reactions amongst major ions and trace elements, sorption, aqueous or surface complexation reactions, and more. Some reactions will be kinetically quick and reach equilibrium, while others may be sluggish and therefore ruled by kinetics over the duration of the proposed laboratory experiments. The result is a complex system of interrelated biogeochemical processes. The experiments proposed in this thesis attempt to disentangle the dominant processes, through a series of experiments of increasing complexity, thereby allowing for understanding of system processes to be developed in a step-wise manner.

However, a challenge is to characterize the key processes taking place, in a unique manner. Consider for example the caution above (section 2.3.3), where it was noted that linear sorption (K_d) constants should not be used to describe general uptake of trace elements, in systems in which sorption and precipitation both existed. If the underlying batch sorption test were conducted, measuring only the before and after aqueous concentrations of the trace element, this could lead to incorrect assertions that ion exchange was taking place, when in fact precipitation may have been responsible. At the same time however, this example identifies the solution. With the measurement of a greater number of parameters (for example, if mineral phase analysis were conducted in this example), true behaviors are more likely to be identified. Experiments in this thesis have included extensive aqueous and (collaborative) solid phase geochemical analyses. Thus, instances of non-uniqueness are less likely; however, situations still remain when more than one explanation is possible. These instances of non-uniqueness will be identified in the thesis, and some of the possible driving reactions identified.

Having now introduced some basic concepts, the background knowledge necessary for the reader will be completed by a literature review of relevant research conducted to date.

2.5 Environmental Challenges Associated with the Oil Sands Industry

There is widespread research concerning the impacts of the oil sands industry on surface and ground waters. This includes baseline characterization of groundwater quality prior to anthropogenic contamination, in effect, ‘before’ studies; investigation into ongoing contamination, e.g. the fate and transport of oil sands tailings pond seepage into the environment (which may be considered ‘during’ studies); and studies directed towards remediation and reclamation at mine closure (‘after’ studies). Thus according to this division, research on the aqueous environmental impacts of the oil sands industry may be subdivided into ‘before’, ‘during’ and ‘after’ anthropogenic contamination has taken place. Each of these will be expanded upon, in turn.

2.5.1 Identifying Baseline (Native) Aqueous Concentrations and Indicators of Anthropogenic Influence

An increasing amount of attention is now being placed on i) differentiating water quality signatures based upon anthropogenic versus natural oil sands exposure, ii) establishing baseline concentrations, which themselves could naturally exceed legislated water quality guidelines and iii) the effects of anthropogenic and indigenous oil sands contamination on sediments, biota or water quality in surface waters (e.g. Conly et al., 2007, Headley et al., 2005, McMaster et al., 2006, Kelly et al., 2010, Gibson et al., 2011).

2.5.2 Future Impacts and Long-Term Management of Oil Sands Mining Wastes

With the coming closure of the first oil sands mining facilities, and increasingly strict compliance legislation, science is scrambling to address the many different perspectives concerning mine closure, and the management, remediation or reclamation of residual contamination in the mining environment. Research includes both abiotic and biotic perspectives. With regard to the former, several investigators have explored issues pertaining to the remediation or reclamation of oil sands mining wastes (e.g. Elshayeb et al. (2009), Farwell et al. (2009), Headley et al. (2010), Kessler et al. (2010), Nix and Martin (1992)). Instead, others have adopted a biotic focus, for example, having begun to explore the ecological effects of moderately saline OSPW. Research to date suggests that such impacts could include altering the composition of phytoplankton communities (Leung et al, 2001, 2003), mortality and reduced numbers of offspring of daphnid species (Harmon et al., 2003), and osmotic stress (Crowe et al., 2001), inhibited germination characteristics, and lower wetlands diversity in plant species (Crowe et al., 2002).

2.5.3 Investigation of Ongoing Contamination in the Oil Sands Mining Industry

Still other studies have been directed towards the monitoring and better understanding of ongoing contamination in the oil sands mining industry (e.g. Kelly et al., 2010); including the biogeochemical reactions and reaction products from source to receptors, along the contaminant transport pathway. In the context of surface and groundwater, an example of obvious relevance is the seepage of tailings pond fluids, beyond containment features, and into the adjacent environment.

2.5.3.1 Hydrogeological Characterization of Seepage from Oil Sands Tailings Ponds

A handful of recent studies have begun to explore the hydrology of seepage at tailings pond facilities. For example, Ferguson et al. (2009) studied the hydrogeological flow system within an existing tailings storage facility, including the potential for long-term seepage into the adjacent Athabasca River. Using a combination of field measurements and groundwater transport modeling, Yasuda et al. (2010) evaluated the effectiveness of seepage containment measures at an oil sands tailings impoundment. However, an important extension to seepage hydrology, is to add biogeochemistry, and thereby to explore ingress of tailings pond waters from a reactive transport perspective. Before reviewing studies which have evaluated seepage in such a manner, it is important to first discuss the different geological settings upon which tailings ponds exist.

2.6 Diversity of Geologic Foundations for North Alberta Tailings Ponds

In the surface-mineable portion of the Athabasca Oil Sands region, extending from the Clearwater and Athabasca Rivers in the south, to Muskeg Mountain in the east and the Birch Mountains in the northwest, the geology may be generalized as follows: Holocene atop a complex arrangement of Quaternary sediments, which overlie Cretaceous sediments (including the lower oil sand bearing McMurray formation). Finally, the Cretaceous sediments themselves rest atop Devonian carbonates. Lowlands comprise most of this area (Fox, 1980; King and Yetter, 2011).

Over time, the region has been influenced by the advancement and withdrawal of glaciers in several directions, which has modified surficial sediments into their present arrangement. As a result, surficial geology in the lowlands is variable and includes widespread deposition of outwash sands in the east to north quadrant, regions of glaciolacustrine silts and clays to the south, and glacial ice-contact kames or kame moraines (silt and silty sand) near Fort Hills and to the north (Fox, 1980). Glacial action has further created a variable and complex arrangement of sediments in these Quaternary deposits with depth. This includes the presence of as many as 16 buried glacial valley and meltwater channel systems throughout the region: isolated fluvial features which have eroded into the bedrock either due to regional drainage before the last glaciation (valleys), or by action of glacial meltwater (channels) (Andriashek and Atkinson, 2007). The result is a region mantled by combinations of silt, sand and clay, with a complex subsurface distribution of aquifers and aquitards (King and Yetter, 2011). A regional map is shown in Figure 2-3.

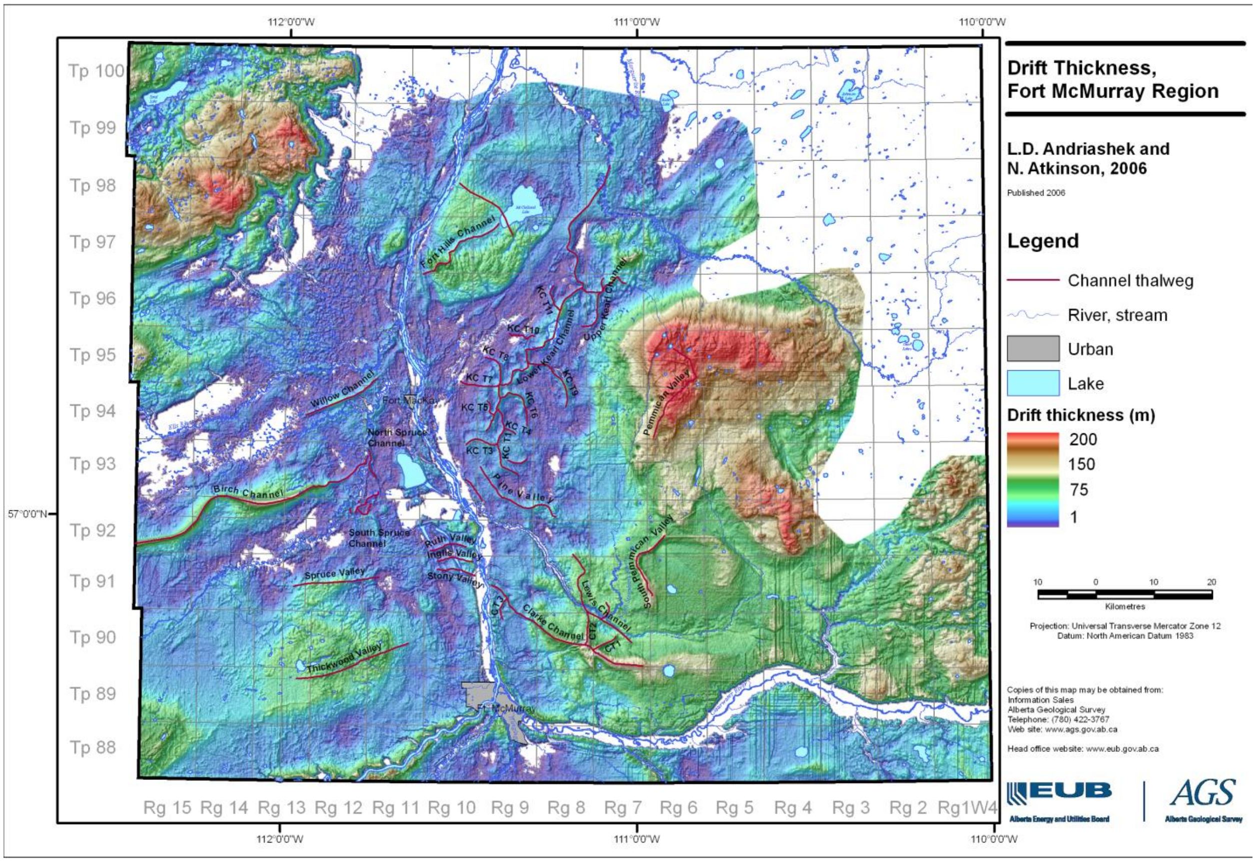

Figure 2-3 Thickness of drift above the bedrock surface, Fort McMurray region (from Andriashek and Atkinson, 2007).

Thus above-grade tailings impoundments in the region have been, or will be, constructed atop different surficial geological sediments or sequences. This includes external tailings ponds situated upon:

- glacial tills (sandy/silty till and clay till) overlying thick Clearwater clays
- sandy sediments or aquifers; and
- integrated systems of low permeable clay or till overlying sandy formations or outwash channels. Details are included in Table 2-4.

Table 2-4
The surficial geologic setting of several oil sands tailings ponds in northern Alberta

Setting	Example	References
glacial tills overlying thick Clearwater clays	Canadian Natural Resources Ltd. Horizon Oil Sands Project	AEUB and AE, 2002-2006 AEUB and CEAA, 2004b
sandy sediments or aquifers	east section - Syncrude Mildred Lake Settling Basin	MacKinnon et al., 2004 Oiffer, 2006
	Fort Hills Energy Limited Partnership, Project tailings area	AEUB, 2002
	south section - Shell Muskeg River Mine external tailings pond	Yasuda et al., 2010
clay or till overlying sands/outwash channels	Suncor Energy South Tailings Pond	Klohn Crippen Consultants Ltd., 2004
	Shell Jackpine Mine	AEUB and CEAA, 2004a
	Suncor Energy Tar Island Dyke and Pond 1 complex	Ferguson et al., 2009
	Imperial Oil-ExxonMobil Kearl Oil Sands external tailings area	Government of Alberta, 2005 AEUB and CEAA, 2007

Thus, diversity in geology among oil sands leases in Northern Alberta, dictates that tailings ponds by necessity, may be constructed in new and non-ideal hydrogeological settings.

2.7 Previous Literature Concerning Glacial till Aquitard Sediment Properties

Despite the fact that several tailings ponds exist in till or integrated till-sand channel settings, to date, little attention has been given to water-sediment interactions within surficial aquitards in the Athabasca Oil Sands region. Perhaps reflecting a historical focus on bitumen recovery and thus characterizing ore-bearing and not surficial sediments, there is scant published data concerning even basic sediment properties such as the mineralogy or cation exchange capacity, and in fact no evaluation of exchangeable cation composition, of these surficial, Pleistocene clay tills.

Across Alberta, surficial geology includes glacial till deposits which are derived from, and therefore reflective of, the underlying bedrock material – in the vicinity of Suncor's South Tailings Pond (the site of focus in this thesis), this is the Clearwater Formation (Klohn Crippen Consultants Ltd., 2004; Cathcart et al., 2008). At industrial sites near Fort McMurray, the topmost stratum of the Cretaceous Clearwater Formation was reported as having a montmorillonite/chlorite/illite/kaolinite composition of 13/13/38/38 (Suncor Southeast Waste Dump) or alternately 20/15/50/15 (Syncrude lease) (Klohn Crippen Consultants Ltd., 2004). Similar findings were reported by Jansen et al. (2008), who characterized two clay soils from the Fort McMurray region, intended for use as barriers for storage of sulfur blocks, as: a) cretaceous clay with mineralogical composition by weight of 25.9% smectite, 25.8% illite, 24.2% kaolinite and b) estuarine clay with mineralogical composition by weight 23.0% illite and 66.2% kaolinite. Together this suggests a predominantly illite/kaolinite composition of the Pleistocene glacial tills.

Similarly, limited research exists concerning the cation exchange capacity (CEC) of these Pleistocene glacial tills. Literature values are summarized in Table 2-5.

However, in these various studies, sediments either came from the A and B horizons, where humic substances and clays are most abundant and hence CEC values are generally highest (Langmuir, 1997), or were supplemented with peat (Peng et al., 2002) – so that reported values may not be of sufficient relevance to the present site.

Table 2-5
Reported values for cation exchange capacity of surficial sediments in northern Alberta

Value Predicted (meq/100g)	**Conditions**	**Source**
3 to 15 for kaolinite 10 to 40 for illite and chlorite 80 to 150 for smectite-montmorillonite 3 to 40 for STP clay-rich till sediments	pH 7[1] If clay composition is predominantly illite/kaolinite as expected	Langmuir (1997)
16 to 19	Peat-supplemented reclamation/salvage soils at the Syncrude site	Peng et al. (2002) (reiterated by Janfada et al., 2006)
30	Peace Lowland Ecoregion B horizon (15-30cm below surface) (similarly to the STP site, these clay tills are derived from Cretaceous marine shale)	Cathcart et al. (2008)
59 38	Fort Vermillion, AB (0-15cm below surface) Beaverlodge, AB (0-15cm below surface)	Whalen et al. (2000)
<1	Surficial sands (unconfined aquifer) at the Syncrude Mildred Lake site	Marsh (2006)

1 Langmuir data is a compilation from many sources and therefore offers only an approximation and may not be reflective of Alberta sediments

2.8 The Environmental Impacts of Oil Sands Tailings Ponds Seepage

The placement of tailings ponds in novel and operationally challenging settings, such as atop buried, groundwater-bearing channel deposits, increasing volumes of tailings waste generated by the rapid expansion of the industry, and stricter regulation for environment compliance and public scrutiny, demand that science better understand the environmental impacts of oil sands mining activities. Concerning the potential environmental risks associated with OSPW seepage, research has largely focused on the organic constituent principally responsible for its acute aquatic toxicity, naphthenic acids. This includes forays into naphthenic acid quantification by different analytical techniques, assessing its ecological impact through biological studies (e.g. Peters et al. 2007) or assessing its capacity for attenuation or biodegradation (e.g. Herman et al., 1994, Zou et al., 1997, Peng et al., 2002, Clemente et al., 2004, Janfada et al., 2006) - though with few studies having directly explored the fate and transport of naphthenic acids, following tailings pond seepage into surface or groundwaters (Mackinnon et al., 2004, Gervais and Barker, 2004, Oiffer et al., 2009, Tompkins, 2009).

In a review of process water quality and its implications in the oil sands industry, Allen (2008) identified not only naphthenic acids (NAs), but also sodium, chloride, sulfate, ammonium, and trace metals as target pollutants, due to their elevated concentrations compared to environmental water quality guidelines. Allen further noted that “the scarcity of recent [trace metal] data makes it difficult to determine if current concentrations are [even] problematic”. And yet, to date, very few studies exist with direct relevance to the evolution of major ions or trace metals within oil sands tailings pond seepage. Bennett et al. (1993) investigated long-term changes to the inorganic groundwater chemistry in a shallow sand and gravel aquifer, resulting from crude oil contamination. With similarity to the present work, the authors observed the evolution in inorganic geochemistry, in a

Pleistocene-era, moderately calcareous deposit, following addition of a source of organic carbon. In the strongly-reducing region, rich in dissolved organic carbon, below and directly downstream of the spill, proposed reactions taking place included: oxidation of carbon coupled with a) reductive dissolution of Fe and Mn, and to less extent b) reduction of nitrogen and sulfur species; and c) release of Sr by dissolution of silicates and upstream carbonate minerals. MacKinnon et al. (2004) investigated the use of characteristic features of OSPW, specifically its major ion, trace element and naphthenic acid concentrations, as indicators to monitor and assess tailings pond seepage migration and evolution into downstream surface water systems. En route, the authors noted that aqueous major ion concentrations changed only marginally following seepage through a subsurface fluvial sand deposit. However, they did not attempt to analyze or explain the limited variation that did occur. Boron concentrations decreased minimally during seepage through the sand, possibly by dilution. More recently, Oiffer et al. (2009) conducted a detailed, field-scale investigation within a portion of a shallow sand aquifer immediately adjacent to a Fort McMurray oil sands tailings pond. Here authors examined the fate and transport of naphthenic acids, and the potential for arsenic mobilization by a weakly reducing OSPW plume. As reported by Oiffer, at the time of publication, this was the "first assessment of the potential for trace metal mobilization due to the interaction of oil sand process-affected water with natural sediments." From this work, Oiffer concluded that evidence did not support the mobilization of arsenic by reductive dissolution by infiltrating tailings pond seepage waters, and that in general, under these conditions, little release of trace metals is to be expected. For example, boron was noted to be present in source OSPW seepage waters, yet strongly retarded downstream, possibly due to surface complexation reactions. In the seepage plume, Oiffer also observed retardation relative to conservative Cl of: bicarbonate species, attributed to calcite precipitation, and sodium and ammonium, attributed to cation exchange reactions.

Similarly, Tompkins (2009) evaluated the capacity for natural attenuation of naphthenic acids, and also for trace metal mobilization, through a series of aquifer injection experiments into the sand channel underlying the South Tailings Pond. In its native state, groundwater analysis identified the aquifer as mildly anaerobic with low trace element concentrations. Subsequent to the controlled injection of OSPW however, the concentrations of several species rose noticeably. This led Tompkins to postulate that the introduction of OSPW had stimulated microbially-mediated reduction of iron and manganese oxides and oxyhydroxides, thereby releasing Fe(II), Mn(II), Ba, Co, Sr and Zn into the groundwater. In a follow-up study intended to further clarify the biogeochemical processes taking place and hence the plausibility of this assertion, Haque et al. (2009) examined the solid phase partitioning of trace elements on pristine sediment samples from this same aquifer segment. Samples were analyzed using a modified sequential extraction procedure. A significant contribution to the total extractable element concentrations was found to be associated with the F2 fraction - poorly crystalline Fe, Mn oxides. Further to Tompkins' hypothesis, it was therefore suggested that ingress of OSPW may result in the dissimilatory reduction of poorly crystalline Fe and Mn oxides and oxyhydroxides, resulting in the mobilization of certain trace elements. However, just as environmental impact studies have focused on naphthenic acids owing to its more obvious toxicity, the few OSPW seepage investigations that exist, have focused on sandy aquifers, because they readily transmit water to wells or springs.

With a number of current or planned tailings facilities placed atop glacial till-mantled sand channels (Stephens et al., 2006), there is increasing need to understand the fate and transport of inorganic species as OSPW seeps through clay-rich till sediments, prior to reaching underlying water resources. However, only one applicable study exists, thus revealing a significant knowledge gap regarding the geochemistry of water-sediment interactions within surficial aquitards in the Athabasca Oil Sands Region. Abolfazlzadeh (2011) tracked the progression and evolution of OSPW seepage from a field-scale representation of a tailings pond, and subsequently derived a predictive flow model of the system. Inorganic chemistry and isotopic signatures were evaluated prior to pond filling, and after 2 years of infiltration. The investigation revealed that transport in the till is dominated by diffusion. Evidence also suggested that: a) ingressing Na was mitigated by ion exchange, which released Ca and Mg into solution, b) high concentrations of ingressing Cl behaved conservatively, c) there was notable attenuation of SO_4, and d) that there was Mo and Pb uptake from OSPW, but Sr and Ba release. However, pore water and pond source water composition were evaluated at only two discrete time points, limiting the extent to which detailed seepage evolution could be resolved. Also, potential biogeochemical processes taking place were proposed, though not validated. Finally, the infiltration pond, which possesses a tiny fraction of the volume present in true tailings ponds, was subject to significant and uncharacteristic dilution by rainfall and snow-melt events over time (e.g. pond pH changed from 8.5 to 7.3, conductivity from about 2.7mS cm^{-1} to <0.5mS cm^{-1}), creating a deviation from the true tailings pond seepage scenario. Thus, there remains a great need for detailed characterization of the attenuation capacity, and biogeochemical evolution and end products as OSPW seepage infiltrates through the glacial till - particularly as may be afforded by a comprehensive series of increasingly detailed experiments, under well-controlled conditions, along with supporting geochemical simulations.

2.9 Objectives

This thesis represents the first detailed assessment of the geochemical evolution and end products, as tailings pond OSPW seeps through a clay-rich glacial till, en route to an underlying aquifer. Glacial till influence has been overlooked to date, yet represents a key component of the contaminant transport pathway. Addressing this knowledge gap is a critical step towards protecting downstream aquatic resources.

The overall objectives of the present study are to:

1) Assess the potential for release (or attenuation) of trace elements and major ions from glacial tills when exposed to OSPW; and to
2) Characterize the key biogeochemical processes involved in controlling pore water and sediment chemistry.

These objectives will be addressed through a series of laboratory experiments and supporting geochemical simulations.

2.10 Overview of Doctoral Research Program

A series of laboratory experiments was carried out, to test these hypotheses. Experiments were designed to be increasingly complex, beginning with characterization of basic system properties, and culminating with a detailed laboratory representation of seepage under field conditions; thus gradually increasing understanding of system geochemical behaviors with each successive experiment. The first experiments focused on analysis of soil water content, specific density, and grain size distribution. Cation exchange capacity and exchangeable cation properties were next completed, which a) assess the capacity of in-situ sediments to bind possible inorganic contaminants; and b) characterize cations, initially bound to the sediments, that may be displaced and released through interaction with ingressing OSPW, respectively.

Batch sorption experiments offered initial examination of the impact of OSPW seepage into the environment; investigating the effects of adsorptive and ion exchange reactions on the mitigation/mobilization of major cations and trace metals. Experiments are performed by mixing glacial till aquitard samples with varying concentrations of OSPW. In addition to the traditional method, a little-known alternative was used, which keeps sediments within a relatively undisturbed state, thereby overcoming a significant failing of the traditional approach. Both simplified, laboratory-prepared OSPW and ‘real’ OSPW collected on site were used, in order to investigate the system response at different levels of complexity. Interpretations were supported by geochemical simulations using PHREEQC (Parkhurst and Appelo, 1999).

Lastly, seven radial diffusion cells were set up (in duplicate), to characterize the initial sediment pore water composition and also to examine the more representative, long-term outcome of geochemical reactions within aquitard sediments, in their native redox state, when exposed to diffusion-driven ingress of OSPW. Cells were kept in an anaerobic environment (mimicking field conditions), and monitored for approximately 6 months. Cells were further modeled using the software program, MIN3P (Mayer et al., 2002), in order to quantitatively define the migration and attenuation of OSPW constituents in a reactive transport framework. Modeling also serves as an interpretive aid, to verify or further refine understanding of the key reactions driving system behavior.

Little work has been done regarding inorganic species' transport and attenuation, due to the complex behavior involved. Dissolved metals and ions undergo many water-sediment interactions in the tailings/dyke system, affecting the nature of the persisting contamination. By addressing this issue, the present research directly impacts the areas of remediation, groundwater management, and environmental policy. It may also help to establish a scientific basis for revisiting long-standing or wide-spread policies in the oil sands, such as the necessity of maintaining a zero water discharge policy off site, or the viability of future tailings pond placement atop buried sand channels (which functionally may act as potential discharge pathways). Altogether, this research is expected to have industry-wide benefit.

2.11 Chapter 2 References

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Chapter 3: Site Overview, Materials and Methods

3.1 Site Description

3.1.1 South Tailings Pond (Klohn Crippen 2004, Stephens et al. 2006)

The South Tailings Pond (STP) is located on the Suncor Energy Inc. mine lease, approximately 35km north of Fort McMurray. Irregularly shaped, the STP is approximately 23km^2 in area: 4km North to South, and 5km East to West. The facility has a tailings holding capacity of 366Mm^3. It is designated for storage of fine tailings and oil sands process-affected water (OSPW), with placement having commenced June 2006 (Stephens et al., 2006). Three continuous retaining dykes make up the North, West and South portions of the STP. Containment to the East is provided by naturally elevated ground. Approximately 8 km of the South and West Dyke walls, and 50% of the STP footprint, overlies the Wood Creek Sand Channel, a buried, permeable, glaciofluvial sand channel (depicted in Stephens et al., 2006).

3.1.2 Site Geology and Hydrogeology (Klohn Crippen 2004, Stephens et al. 2006)

In descending order below the ground surface, the geology at the STP consists of Holocene organic soil, Pleistocene glacial till, Pleistocene glacial outwash channels (in some areas only), and the Cretaceous Clearwater, Cretaceous McMurray, and Devonian Waterways bedrock formations.

The Holocene organic soils typically extend to a depth of 1-2m deep, with a maximum depth of 4m, and are muskeg-based, featuring silts, peat, organic soil with roots and wood pieces, and trace clays.

The Pleistocene glacial till is approximately 8-15m thick (when atop the Wood Creek Sand Channel), and is composed of clayey tills, sandy tills, silty tills, and

Clearwater rafted, ice-thrusted or derived tills. Although the thickness of the glacial till deposit is generally uniform, thin (<5m) coverage has been observed at several locations across the site (Klohn Crippen Consultants Ltd., 2004). Upper regions can be sandy with a progressively higher clay fraction found with depth. Discontinuous lenses, approximately 2m thick, of Pleistocene glaciolacustrine soils (silts, clays, fine sands) are occasionally present atop the glacial till layer.

The Wood Creek Sand Channel, believed to be an extension of the Clarke Channel (Andriashek and Atkinson, 2007), is a Pleistocene glaciofluvial feature with a thickness of approximately 20-30m and consists of dense sands and gravels. In the vicinity of the STP, it is broadly oriented from SE to NW, although it is joined near the middle of the West Dyke by a secondary branch aligned SW to NE. Flow in this principal feature is towards the NW, while in the secondary branch, groundwater flows towards the SW. A third segment of the Channel underlies the body of the STP; however, initial data suggests it is not a major flow channel and was perhaps an overbank or flood feature. A “spill-point” of the Wood Creek Sand Channel into the McLean Creek, a tributary to the Athabasca River, exists beyond the NW corner of the STP dyke. Prior to dyke construction, the Wood Creek Sand Channel was predominantly confined, except for the NW (where it encounters the McLean Creek) and SE sections of the main channel.

The underlying formations include a) the Clearwater Formation, of marine origin, which is principally composed of clay shales and thin, carbonate-cemented siltstone beds, b) the McMurray Formation, composed of oil sands, water sands and clays, and c) the Devonian Waterways Formation, which consists of calcareous rocks.

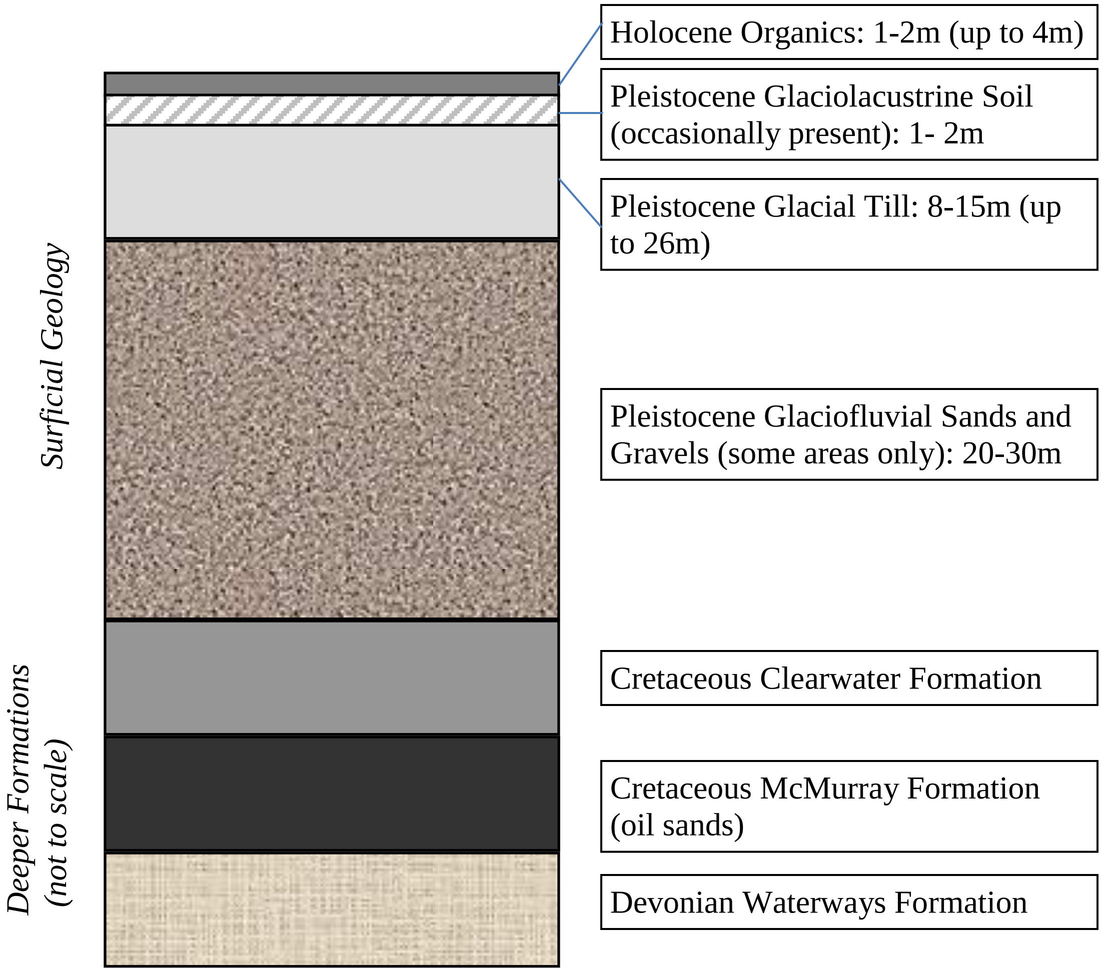

Figure 3-1 Simplified geological sequence at the STP site. Neither the Glaciolacustrine nor Glaciofluvial units are present throughout the site. Also, though the Wood Creek Sand Channel (Pleistocene Glaciofluvial Sands and Gravels) primarily rests atop the Clearwater clay shales, in some areas it is located directly atop the McMurray Formation. The Pleistocene glacial till is approximately 8-15m thick (when atop the Sand Channel); although the thickness of the till deposit is generally uniform, thin (<5m) coverage has been observed at several locations on site. (Klohn Crippen 2004, Stephens et al., 2006).

3.1.3 Environmental Controls on Site

Oil sands operators in Northern Alberta adhere to a policy of zero water discharge across their lease boundaries and into the environment. Suncor has identified three potential locations for seepage discharge into the environment and has mitigated them using the following controls: an interception pumping well field to the NW (groundwater is pumped into the STP), a cutoff wall to the SW, and if required, a pumping well system may be installed to the SE (Stephens et al. 2006). This system offers closed-loop containment of seepage waters on site; however, it cannot be maintained in perpetuity. Thus, investigation into the fate and transport of seepage is a necessity, and the knowledge gained can then be applied towards sustainable remediation and reclamation strategies.

3.1.4 Sample Collection

Uncontaminated sediment cores were collected during the construction of a groundwater monitoring well research transect in 2006. The wells were positioned across the primary sand channel flow system (underneath the NW dyke wall), immediately downstream of the STP. Boreholes were drilled using a 0.11m casing on a 1503 Nodwell SONIC Drill Rig. Polycarbonate resin (Lexan®) sleeves were used to line the drill stem such that cores were directly encapsulated as drilling progressed, with the core ends capped immediately upon retrieval, all to preserve the subsurface redox conditions. Cores were then shipped to the University of Alberta and stored at -20ºC at the Cold Regions Geoenvironmental Research Facility.

Samples for laboratory analysis were collected from various depths in the glacial till, the underlying till-sand channel transition or interface region, and occasionally, for interest, from the sand channel below (Figure 3-2). This was done for two reasons: first, to characterize sediment properties or response to OSPW with depth, thereby accounting for variability in mineralogy, clay content, etc. across the till. Secondly, tailings pond OSPW can infiltrate the till along two different pathways: i) from the saturated dyke downwards into the glacial till; or ii) through the pond floor, then laterally in the direction of local groundwater flow (Figure 3-3). Recent work by Ferguson et al. (2009) supports pathway i); however, using samples collected from various depths allows exploration of both possibilities.

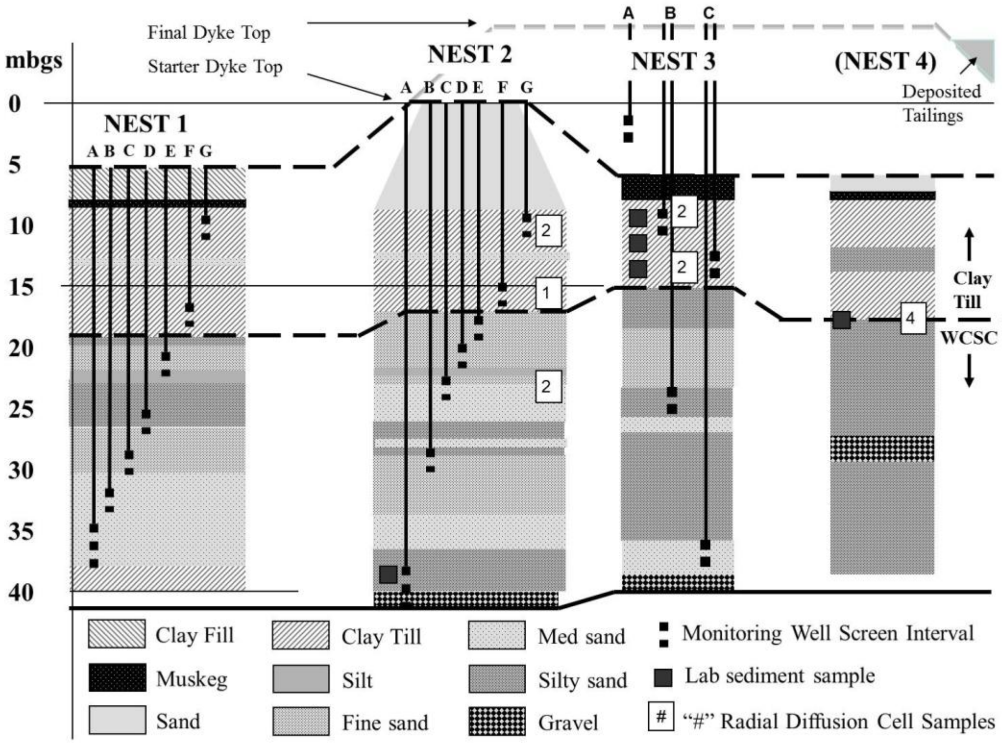

Figure 3-2 Cross section schematic of the surficial geology of the South Tailings Pond Groundwater Monitoring Network. Figure includes locations where laboratory sediment samples were taken from.

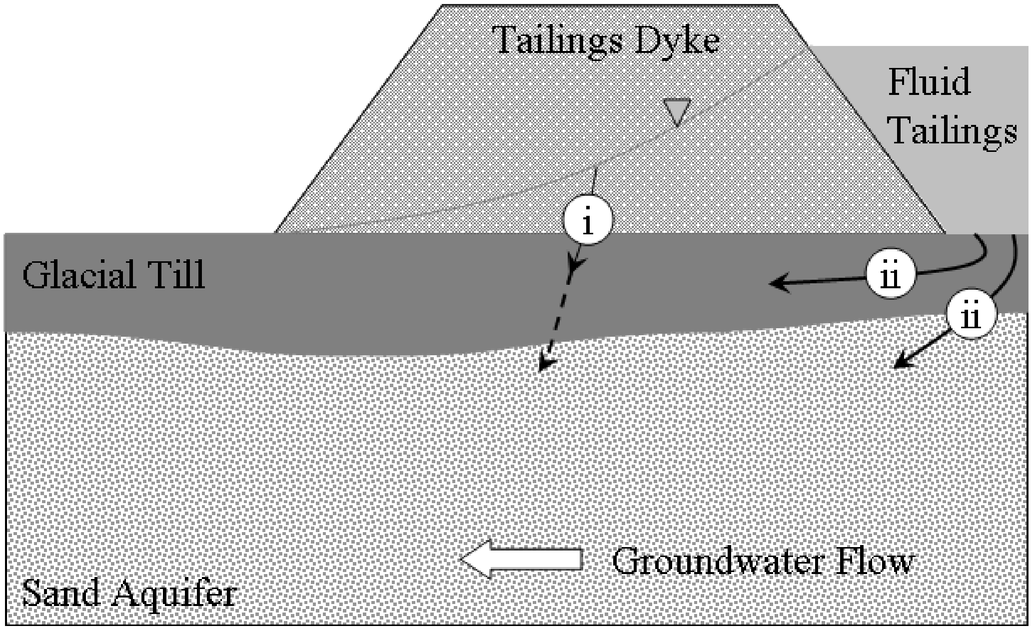

Figure 3-3 Potential hydraulic pathways of process-affected water from tailings pond source. (Numbers correspond to path descriptions in the text)

Core sections for laboratory use were cut using a radial arm saw, then wrapped in cling wrap and aluminum foil, sealed in air-tight plastic bags, and finally placed in cold storage (4^oC) to thaw for 24 hours. Moisture loss was monitored by mass measurements, before and after thawing. Once thawed, samples were kept at their native moisture content to prevent potential complications with drying, where mineral phases may precipitate but subsequently re-dissolve only to limited extent. Gravel, although rarely encountered, was removed by hand from small experimental samples, as it would immediately render that sample replicate an outlier. During sample preparation, rubber gloves were worn, and ethyl ether-disinfected stainless steel tools were used, to avoid cross contamination of microbial populations from one core to the next.

3.2 Materials

3.2.1 Oil Sands Process-Affected Water (OSPW)

Tailings pond OSPW includes high concentrations of dissolved ions that accumulate from ore extraction chemicals and oil sands ores, as well as organic compounds of concern, predominantly naphthenic acids (now termed acid extractable organics), which make the water toxic to many aquatic organisms (Allen, 2008, Oiffer et al., 2009). Dissolved solids are chiefly comprised of sodium (~500-700mg L^{-1}), chloride (~75-550mg L^{-1}), sulfate (~200-300mg L^{-1}) and bicarbonate (~750-1000mg L^{-1}) and pH is approximately 8.0–8.4 (Allen, 2008, Oiffer et al., 2009, Price, 2005). Trace elements present may include Al, As, Cd, Cr, Cu, Fe, Pb, Mo, Ti, V, Zn (Allen, 2008), of which As, Cd, Cr, Cu, Ni, Pb, Zn are classified as priority pollutants by the USEPA (USEPA, 2009).

Process-affected water was sampled from discharge lines feeding into the STP. Samples were collected August 25, 2008 and stored sealed, in the dark, at 4^oC. The inorganic composition, determined in-house using Ion Chromatography (Dionex ICS-2000 (cations) and 2500 (anions) systems) and Inductively Coupled

Plasma Mass Spectrometry (PerkinElmer SCIEX ELAN 9000), is reported in Tables 3-1 and 3-2.

Table 3-1
Chemical composition of baseline condition groundwater from glacial till and STP oil sands process-affected water (major species) [units: mg L^{-1}]

	Baseline Groundwater				**OSPW**
Species	**MW-1G (11-May-06)**	**MW-2G (11-May-06)**	**MW-1F (11-May-06)**	**MW-2F (23-Jun-06)**	**(25-Aug-08)**
Calcium	55.8	65.8	33.8	94.9	7.62
Magnesium	17.3	17.7	10.8	18.2	4.17
Potassium	2.8	3.9	6.2	3.8	10.05
Sodium	25.9	221	156	20.1	591.35
Ammonium	0.9	5.1	0.0	3.4	2.02
Lithium	0.02	0.07	0.05	0.03	0.16
Chloride	2.3	306	5.8	13.2	374.51
Fluoride	0.2	0.3	0.4	0.2	2.21
Bromide	0.0	0.0	0.0	0.0	0.93
Nitrite	0.0	0.8	0.1	0.1	b.d.
Nitrate	0.0	0.1	0.0	0.2	4.65
Phosphate	0.0	0.0	0.0	0.0	b.d.
Sulfate	12.0	48.2	148	5.4	150.39
Alkalinity (as $CaCO_3$)	457[a]	643[a]	204[a]	496[a]	491
pH	7.1	6.9	7.2	6.9	8.6
Total Organic Carbon	29[b]	55[b]	113[b]	not measured	83
Redox Potential[c]	247mV	248mV	182mV	263mV	not measured

[a] 20-Jun-06 samples

[b] 27-Sept-06 samples

[c] Redox potentials were typically not measured in this thesis - see Sections 2.1.2 and 6.3.2 for details.

Note: MW = monitoring well, b.d. = below detection limit, OSPW = oil sands process-affected water

Note: MW-1G, 2G are wells in monitoring well nests 1 and 2 from mid-elevation of the clay till deposit, and MW1F, 2F, the same but from low in the clay till deposit.

Table 3-2
Chemical composition of baseline condition groundwater from glacial till and STP oil sands process-affected water (trace element species) [units: μg L^{-1}]

	Baseline Groundwater				**OSPW**
Species	**MW-1G (23-Jun-06)**	**MW-2G (23-Jun-06)**	**MW-1F (23-Jun-06)**	**MW-2F (23-Jun-06)**	**(25-Aug-08)**
beryllium	b.d.	b.d.	b.d.	b.d.	b.d.
boron	88	438	1,118	14	1,784
aluminum	2,529	742	2,378	640	6,306
silicon	9,026	10,677	3,427	11,779	2,308
phosphorus	376	198	474	169	b.d.
vanadium	b.d.	2	1	b.d.	b.d.
chromium	9	14	9	6	11
iron	3,209	10,344	486	800	3,005
manganese	304	529	180	258	68
nickel	8	43	5	9	15
cobalt	2	13	1	1	6
copper	282	130	333	89	b.d.
zinc	b.d.	b.d.	39	b.d.	b.d.
gallium	1	b.d.	1	b.d.	6
arsenic	5	5	4	b.d.	b.d.
selenium	5	8	b.d.	b.d.	7
rubidium	1	3	5	2	24
strontium	266	277	419	370	198
molybdenum	1	4	126	1	264
silver	b.d.	b.d.	b.d.	b.d.	b.d.
cadmium	b.d.	b.d.	b.d.	b.d.	b.d.
cesium	b.d.	b.d.	b.d.	b.d.	b.d.
barium	215	230	170	283	66
thallium	b.d.	b.d.	b.d.	b.d.	b.d.
lead	14	3	16	2	14
uranium	1	1	9	b.d.	b.d.

Note: MW = monitoring well, b.d. = below detection limit, OSPW = oil sands process-affected water

Note: MW-1G, 2G are wells in monitoring well nests 1 and 2 from mid-elevation of the clay till deposit, and MW1F, 2F, the same but from low in the clay till deposit.

3.2.2 Glacial Till Sediment Characteristics

Scant published data exists concerning the characteristics of surficial glacial till sediments in Northern Alberta, and this extends to hydrogeology and groundwater chemistry. Although no detailed account was found in the literature, it seems likely that the uppermost few meters of the glacial till are fractured, as a result of repeated freezing/thawing and wetting/drying cycles (*Kevin Biggar, personal communication*, Hendry et al., 2000). Median hydraulic conductivity, measured by slug testing in the glacial till at various locations on the Suncor South Tailings Pond lease, was $2.4*10^{-7}$m s^{-1} (Stephens et al. 2006), which is higher than values traditionally assigned to very low conductivity clay-rich units (e.g.10^{-11}ms^{-1}, Hendry et al., 2000). In the radial diffusion study (Chapter 6), the porosity of the STP glacial till sediments was found to be 0.24; however, this does not preclude diffusion dominance, as in a study of Quaternary clay-rich tills in Saskatchewan, despite a high measured porosity of 0.31, Hendry et al. (2000) noted very low hydraulic conductivity - on the order or 10^{-11} to 10^{-12}m s^{-1}, moreover affirming that solute transport was dominated by molecular diffusion. Similarly here, on the basis of migration of conservative tracers into the upper portions of the glacial till immediately adjacent to the STP, Abolfazlzadeh (2011) recently demonstrated that diffusion was the dominant mechanism of transport, with estimated effective diffusion coefficients for chloride and δ^{18}O of$1.8*10^{-9}m^2s^{-1}$ and $1*10^{-9}m^2s^{-1}$ respectively. Moreover, under the assumption that surficial fractures are present, because the STP represents a constant source of contaminants and not an isolated spill event, it is expected that the fractures would fill with the process water, which then diffuses into the surrounding sediment matrix. And thus diffusive interaction with the matrix is still a major determinant of the aqueous geochemical outcome. Taken together, advection through the STP glacial till cannot be discounted; though it is anticipated that diffusive solute migration will be a major determinant of system behavior.

Regarding groundwater geochemisty, the pristine, or baseline groundwater concentrations measured in glacial till wells at the STP monitoring well transect consisted dominantly of calcium, sodium, sulfate and total inorganic carbon (alkalinity), with aluminum, iron, manganese, silicon and strontium the principal trace elements (Ulrich et al., 2007; Tables 3-1 and 3-2).

3.3 Methods

For an overview of the laboratory experiments conducted within this thesis, the reader is directed to Chapter 2, §2.10. Specific details concerning the cation exchange capacity and exchangeable cation experiments may be found in Chapter 4, §4.2.3 and Appendix A. Details concerning the subsequent series of experiments, batch sorption experiments, are presented in Chapter 5, §5.2.2, while the reader is directed to Chapter 6, §6.2.2-6.2.4, for detailed experimental methods for the radial diffusion cells and the accompanying reactive transport modeling.

However, important to each of these experiments' analyses, is the quantification of major ions present in solution. Thus details concerning Ion Chromatography analysis are included below.

3.3.1 Ion Chromatography

Aqueous lithium, sodium, ammonium, potassium, magnesium and calcium concentrations were quantified using a Dionex ICS-2000 Ion Chromatography system. 25.0μL of liquid sample is first injected into the sample loop (Dionex AS50 Autosampler) and thereafter merged with an isocratic eluent stream (20.00mM Methanesulfonic Acid). The eluent and sample are pumped through guard (IonPac® CG12A) and separator columns at a flow rate of 1.00mL min^{-1}. A Dionex CSRS300 4mm suppressor preferentially enhances the sample ions' signal relative to the eluent conductivity, with analyte quantification ultimately performed by Chromeleon Client v6.50 software. The mean detection limit is less than 0.2mg L^{-1} for each of these six cation species.

Aqueous fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate concentrations were characterized using a Dionex 2500 Ion Chromatography system. 25.0μL of liquid sample is first injected into the sample loop (Dionex AS50 Autosampler) and thereafter merged with an isocratic eluent stream (8.0mM $NaCO_3$ + 1.0mM $NaHCO_3$). A Dionex GP50 Gradient Pump forces the eluent and sample through guard (IonPac® NG1 and IonPac® AG14A) and separator (IonPac® AS14A) columns at a flow rate of 1.00mL min^{-1}. A Dionex ASRS300 4mm suppressor preferentially enhances the sample ions' signal relative to the eluent conductivity, with signal measurement and analyte quantification performed by a Dionex CD25 Conductivity Detector and Chromeleon Client v6.50 software respectively. The mean detection limit is less than 0.3mg L^{-1} for each of these seven anion species.

Five calibration standard solutions analyzed at the outset of each sequence enable Chromeleon characterization of the liquid sample (Dionex, Seven Anion Standard and Six Cation Standard II). A quality control check standard and blank are run after these calibration standards and after approximately every 10 to 15 experiment samples.

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Chapter 4: Evaluating Methods for Quantifying Cation Exchange in Mildly Calcareous Sediments in Northern Alberta*

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*A version of this chapter has been submitted for publication.
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4.1 Introduction

A great variety of methods exist for characterizing the exchangeable cations or cation exchange capacity (CEC) of sediments and soils. In select mineralogically uniform sediments, several methods may yield comparable results; however, in more complex systems, differences can arise, highlighting that certain methods are better suited to the conditions at hand. An application that has long caused challenges, is quantifying cation exchange properties in sediments containing partially soluble carbonate minerals. While select studies have explored this issue in the past (e.g. Bascomb, 1964; Van Bladel, 1975), re-visitation is warranted, considering sediments and mineralogy unique to one's site of interest, and using new or commonly used methods at the present time. To date, a critical evaluation of the suitability of commonly used methods for characterizing the cation exchange capacity and exchangeable cation assemblage of carbonate mineral-bearing glacial sediments near Fort McMurray, AB, has not been conducted.

Characterization of the cation exchange capacity and exchangeable cations is an important first step towards assessing the potential environmental impact of contaminant seepage into the subsurface, which therefore has great relevance to the oil sands industry, where contaminants from tailings ponds may seep or diffusively ingress into surrounding sediments and ground waters (e.g. Holden et al., 2011b). Despite the importance of this scenario, little attention has been given to the geochemistry of such water-sediment interactions in the Athabasca Oil Sands region, including either the capacity for surficial, Pleistocene clay tills to attenuate ingressing solutes, or how composition of ingressing contaminants might change by release or uptake of exchangeable cations.

The objectives of this chapter are:

1) To conduct an up-to-date evaluation of several conceptually distinct methods, for their suitability in characterizing the exchangeable cations and

cation exchange capacity in mildly calcareous sediments; and thereafter to use the most suitable method(s)

2) To evaluate these properties in low carbonate content, surficial glacial sediments near Fort McMurray, Alberta.

The focus of the present study is on major cation mobility through ion exchange reactions. Detailed understanding of trace element behavior, which may be additionally influenced by surface complexation reactions, is beyond the scope of this study.

4.2 Materials and Methods

4.2.1 Review of Common Methods

Many different methods have been proposed for evaluating the CEC and exchangeable cation composition of sediments, each possessing different strengths and weaknesses. Lithium Chloride (LiCl) extraction, as per Husz (2001), is an example of a CEC summation method using an unbuffered salt solution. A saturated sediment paste (Rhoades, 1982) is mixed with the extractant salt solution (LiCl) and displaced cations are measured in the supernatant to estimate the exchangeable cations, and summed to estimate the CEC. An advantage of the method is that it preserves the native sediment pH (Bache, 1976; Husz, 2001); however, it is possible that the method would solubilize partially soluble minerals present in the sediment, leading to an overestimation of the exchangeable cations. The most common CEC method involves the surplus addition of an index cation (e.g. Na^+), which is then displaced by a second species (e.g. NH_4^+) and quantified (with or without intermediary washes to remove residual free phase cations) (e.g. Bascomb, 1964; Chapman, 1965; USEPA, 1986). Such methods have been widely used; therefore, previously published CEC values for many sediments exist for comparison; however, these methods are time consuming and laborious (Ammann et al., 2005; Bache, 1976; Dohrmann, 2006a) and quantification can be impacted by the presence of partially soluble mineral phases (Dohrmann, 2006a). Alternate methods ensure complete displacement of exchangeable cations not by applying excessive quantities of exchanging cations, but by using high affinity cation complexes (Ammann et al., 2005; Dohrmann 2006b, 2006c; Meier and Kahr, 1999). The higher selectivity of these complexes allows extraction to be completed quickly, in a single step, and the modified Silver Thiourea method of Dohrmann (2006b), for example, is reported to be insensitive to the presence of partially soluble carbonate mineral phases. Methylene Blue, an organic, cationic dye, ($C_{16}H_{18}N_3S^+$) may be used to characterize the CEC as well as other sediment properties. It too has a very high binding affinity compared to inorganic cations (Margulies et al., 1988). Two implementations of the Methylene Blue method exist: a batch sorption method (Hang and Brindley, 1970) and a titration or spot test method (AFNOR, 1993; ASTM C837, 2009). Advantages of Methylene Blue extraction include its simplicity, and its wide use within certain fields (e.g. the oil sands industry standard (Kaminsky, 2008)). However, its CEC values have been, on occasion, observed to be significantly smaller than those derived using the Ammonium Acetate method (e.g. Kahr and Madsen, 1995; Yukselen and Kaya, 2008).

It must also be appreciated that different methods are not likely to report identical CEC values, because they may be sensitive to different exchange mechanisms or establish different exchanging environments. For example, as discussed in Chapter 2 §2.3.2, the negative surface charge of clay minerals, particularly kaolinite, exhibits a measure of pH dependence. Also, calcium carbonate solubility is greater at circumneutral pH than with buffered extractants of pH 8.2. Therefore extractant pH would clearly be expected to influence CEC in general, and particularly in calcareous sediments. Lower ionic strength solutions may induce less dissolution of mineral phases, such as calcite, which dissolve into ionic components (Langmuir, 1997), while the concentration and relative speciation of bound cations may change as the contacting solution becomes more dilute (Appelo, 1996). Finally, methods accounting for soluble mineral presence estimate exchangeable cations, while those that do not, are in fact instead measuring ‘extractable’ not exchangeable cations (Rengasamy and Churchman, 1999). These key differences must be kept in mind, when comparing results from different methods.

4.2.2 Sample Collection and Preparation

Laboratory-grade kaolin was selected to act as a sediment standard in this method comparison study, since it is homogenous, without confounding pore fluids, and has similar clay mineralogy to the field samples (kaolinite-illite composition is anticipated, e.g. Jansen, 2008). Samples were prepared using kaolin alone, or as a baseline approach to test the influence of soluble carbonate minerals at estimated field concentrations, kaolin spiked with 1% by mass of calcium carbonate (certified ACS powder, Fisher Scientific, U.S.A.). Modifications to ionic strength, pH, or applied calcium carbonate concentration were not pursued, and are left to future research.

Sediment samples were collected from the Suncor Energy Inc. lease, approximately 35km north of Fort McMurray, AB (site geology and sediment sample collection, preservation and preparation are described in detail in Chapter 3, §3.1.2 and §3.1.4). To characterize the exchange properties across the depth of surficial sediments, samples were selected from the middle and lower glacial till, the underlying sand channel, and from the intermediary clay till-sand channel transition zone (Appendix A, Table A-1).

Clay mineralogy of select samples was investigated by X-ray diffraction using ethylene glycol solvated oriented clay slides (AGAT Laboratories, Edmonton, Canada) (Tables 4-1 and 4-2).

Table 4-1

Mineral phases[a] present in the glacial till.

Sample ID	Type of Analysis[b]	Weight (%)	Qtz	Plag	K-Feld	Cal	Dol	Anhy	Pyr	Musc	Bar	Sid
High Till	Bulk Fraction:	87.5	86	2	2	2	6	0	1	1	0	0
	Clay Fraction:	12.5	7	1	1	0	0	0	0	0	0	0
	Bulk and Clay:	100	76	2	2	1.8	5.0	0	1	0	0	0
Mid Till	Bulk Fraction:	87.9	90	2	1	1	5	0	2	0	0	0
	Clay Fraction:	12.1	4	0	1	0	0	0	0	0	0	0
	Bulk and Clay:	100	79	2	1	0.8	4.2	0	1	0	0	0
Low Till	Bulk Fraction:	86.4	90	2	1	1	4	0	1	0	0	0
	Clay Fraction:	13.6	12	1	1	0	0	0	0	0	0	0
	Bulk and Clay:	100	80	2	1	0.5	3.9	0	1	0	0	0

[a] Qtz (quartz), Plag (Plagioclase Feldspar) K-Feld (K-Feldspar), Calc (calcite), Dol (dolomite), Anhy (anhydrite),
Pyr (pyrite), Musc (muscovite), Bar (barite), Sid (siderite)

[b] bulk fraction is >3μm and clay fraction is <3μm

Table 4-2

Composition of clay minerals[a] in the glacial till.

Sample	% FOC	% Clay in Bulk Sample	Composition of Clay Fraction (%)					Predicted CEC[b]
	(by weight)	(by weight)	kaol	chl	ill	ML	smec	(meq $100g^{-1}$)
High Till	1.53+0.06	12.53	39	0	43	0	9	14.1
Mid Till	3.69+0.03	12.09	24	13	49	0	9	21.4
Low Till	0.99+0.02	13.56	49	0	32	0	5	13.0

[a] kaol (kaolinite), chl (chlorite), ill (illite), ML (mixed layer), smec (smectite)

[b] from CEC = 0.1* (7 * (%clay) + 35 * (%Carbon)), Appelo and Postma (2005)

4.2.3 Experimental Methods

For each method, samples were prepared at two different sediment:water ratios, to later assess the method’s robustness to the presence of partially soluble minerals (Carbonate and Sulfate Field test (Dohrmann, 2006a) – see §4.4 Discussion). Experiments were conducted at 20°C and all samples were tested in triplicate. Before each experiment, a portion of the sediment section (~10-20g) was oven-dried at 105°C for 24 hours to determine the water content. Mass balance calculations accounting for water content, initial pore fluid and added extractant solution chemistries were used to provide context for final, observed, equilibrium concentrations. A brief summary of the experimental procedures is provided below, with full details in Appendix A.

4.2.3.1 Lithium Chloride (Husz, 2001, modified)

Undried sediment was mixed with deionized water to create a saturated paste (Rhoades, 1982). Ten grams (or 20g) of paste was then mixed with 0.4mol L^{-1} LiCl, shaken, centrifuged (4150 rpm for 14 minutes) and the supernatant collected. This process was repeated twice and all supernatants combined. The inclusion of a third rinse represents a method modification, chosen after preliminary experiments returned exchangeable cation values that were lower than CEC values observed using other methods (also reported in Husz (2001)), and was based upon the hypothesis that two rinses with a weak exchanger were insufficient for displacing all pre-bound cations. Exchangeable cations were quantified by Ion Chromatography (described in Chapter 3 §3.3.1) and summed to estimate the CEC. Trace elements were quantified using Inductively Coupled Plasma Mass Spectrometry (PerkinElmer SCIEX ELAN 9000), to assess whether their inclusion or omission would noticeably impact the resultant, summed CEC value.

4.2.3.2 Sodium Acetate, Ammonium Acetate (USEPA, 1986)

Briefly, 4g (or 8g) of undried sediment was mixed four times, with high pH-buffered, 1N Sodium Acetate (NaOAc), to saturate the binding sites with sodium.

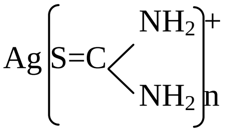
The alkaline pH8.2 buffer provides a means of mitigating carbonate dissolution (Bache, 1976; Tucker, 1954). The sample was then thrice washed with 2-propanol Optima (Fisher Scientific, U.S.A.) to remove free phase ions. Lastly, the sample mixed three times with 1N Ammonium Acetate (NH_4OAc) (pH 7), and the supernatant retained. The concentration of displaced sodium was quantified by Ion Chromatography and used to estimate the CEC.

4.2.3.3 Methylene Blue (based upon AFNOR, 1993)

A mixer was used to uniformly disperse the undried sediment sample (22.5g or 45g for clayey samples and 45g or 90 g for sandy ones) and 500mL deionized water into suspension. Increments of 0.01N Methylene Blue were titrated into the slurry. Following each addition of titrant, a glass stirring rod was used to apply one drop of the slurry onto filter paper. The end point is reached when the deposited drop develops a light blue halo.

4.2.3.4 Silver Thiourea (Dohrmann, 2006b)

The structural formula of Silver Thiourea is:



$$\mathrm{Ag}\left[\mathrm{S{=}C}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right]_n^{+}$$

where n is less than or equal to 4, and dependent upon thiourea concentration (Chhabra et al., 1975). Herein, the complex will be referred to as AgTU.

AgTU solution (0.01N) and 2g (or 4g) of undried sediment were mixed into a slurry, then shaken, centrifuged and the supernatant collected. In the next rinse, deionized water was mixed with the remaining sediment in a similar manner. The third rinse resembled the second, although shaking was omitted. The supernatants were combined and analyzed for exchanged major cations by Ion

Chromatography and for change in silver content, and therefore CEC, by Inductively Coupled Plasma Mass Spectrometry, where

$$\mathrm{CEC[meq\ 100g^{-1}]} = 100 * (\mathrm{Ag[meq]}_{(\text{final, blank})} - \mathrm{Ag[meq]}_{(\text{final, sample})}) / \text{sample mass[g]} \qquad (4.1)$$

A fluid-only blank was also run to assess losses to the system.

4.3 Results

4.3.1 Cation Exchange Capacity – Kaolin Samples

Although intended to be an analytical 'standard', different methods did not report the same sorptive capacity when using identical laboratory grade kaolin. The triplicate mean CEC's, using method-prescribed sample masses, and kaolin (no calcite added) were: 7.0 meq $100g^{-1}$ (NH_4OAC), 4.2 meq $100g^{-1}$ (LiCl), 4.0 meq $100g^{-1}$ (Methylene Blue) and 6.8 meq $100g^{-1}$ (AgTU). In the presence of calcite, the measured values rose to 7.4 meq $100g^{-1}$(NH_4OAC), 6.5 meq $100g^{-1}$(LiCl), 4.2 meq $100g^{-1}$ (Methylene Blue), and 7.4 meq $100g^{-1}$ (AgTU). Among methods, Methylene Blue values were the most consistent when calcite presence was altered or sample mass doubled. CEC data are summarized in Figure 4-1.

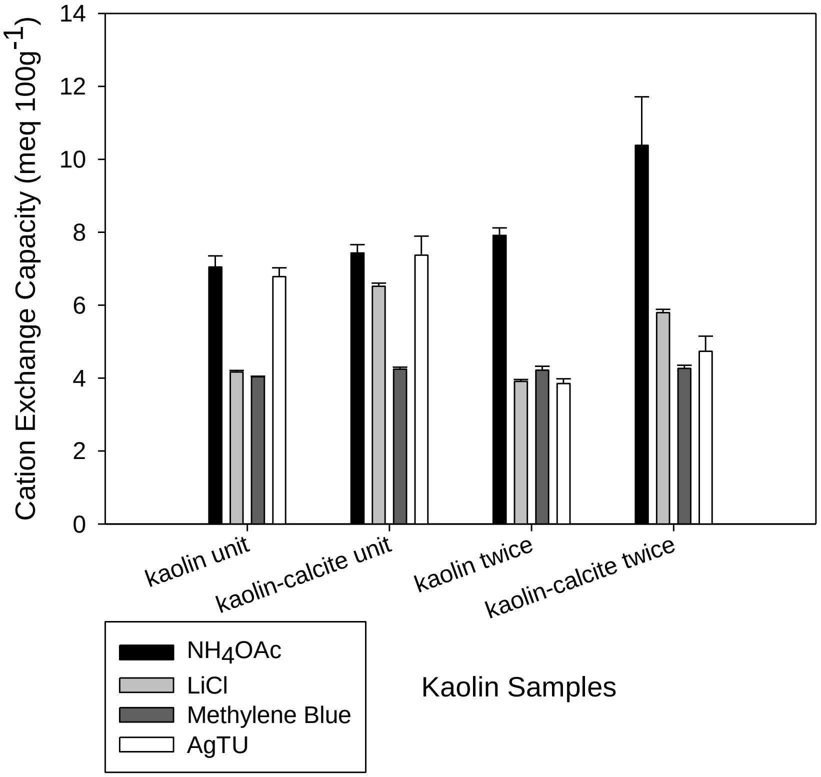


Figure 4-1 The cation exchange capacity of kaolin samples as determined by different methods. Two sample types were tested: kaolin or kaolin spiked with calcite. Two sample masses were tested: the method prescribed ‘unit’ mass or twice that. The average pH of the unbuffered method’s (Lithium Chloride) equilibrium solutions was 4.6 for kaolin and 7.9 for kaolin-calcite samples. Error bars represent the standard deviation of cation exchange capacities from triplicate samples.

4.3.2 Cation Exchange Capacity – Field Sediments

Across methods, the mean cation exchange capacity was 7.8meq 100g^{-1} in the clay till, 7.4meq 100g^{-1} in the clay till-sand channel transition and 1.6meq 100g^{-1} in the sand channel. However, CEC values varied significantly among methods with NH$_4$OAc and AgTU typically reporting the highest values and LiCl and Methylene Blue the lowest values. CEC also varied noticeably among sampling elevations within the same geological unit, when using the same method, reflecting in-situ variability. CEC field sample results are summarized in Figure 4-2.

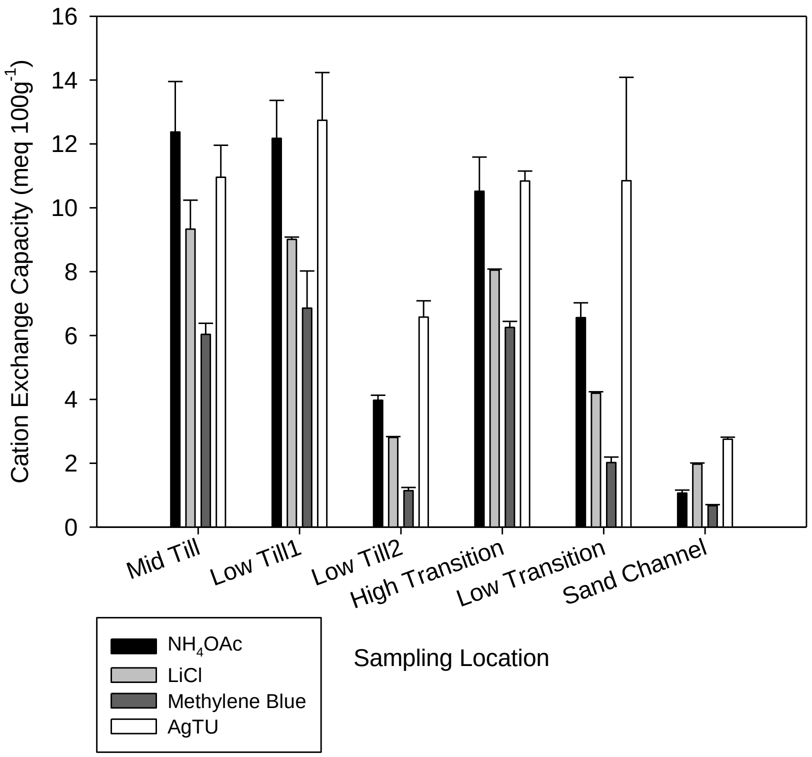


Figure 4-2 The cation exchange capacity values of surficial sediments near Fort McMurray, as determined by different methods. The graph depicts results using only method-prescribed or ‘unit’ samples masses. The pH of the unbuffered method’s (Lithium Chloride) equilibrium solutions ranged from 7.5-8.8 with mean 8.3. Error bars represent the standard deviation of cation exchange capacities from triplicate samples.

4.3.3 Exchangeable Cations – Kaolin and Field Samples

The data suggest that the AgTU method is not suitable for determining the exchangeable cation concentrations when calcite is present. The sum of exchangeable cations determined by this method, and often even the exchangeable calcium concentration alone, exceeded the cation exchange capacity determined by the AgTU (via silver quantification), Methylene Blue or NH$_4$OAc methods. In contrast, the sums of exchangeable cations by the LiCl method lie between the CEC’s measured for Methylene Blue versus those of either the AgTU (silver quantification) or NH$_4$OAc methods. This assessment does not validate LiCl results, but simply suggests that they are plausible. Results are summarized in

Table 4-3.

Table 4-3
Comparison of AgTU and LiCl exchangeable cation results
[units: meq $100g^{-1}$ dried sediment]

	Silver Thiourea				**Lithium Chloride**			**MB**	**NH_4OAc**
Sample	**Exch. Ca^{2+}**	**Exch. Mg^{2+}**	**Sum Exch. Cations**	**CEC via Ag^+**	**Exch. Ca^{2+}**	**Exch. Mg^{2+}**	**Sum Exch. Cations**	**CEC**	**CEC**
Kaolin	1.24	1.66	3.37	6.79	1.25	1.79	4.17	4.04	7.05
Kaolin +Calcite	11.85	1.67	14.32	7.37	3.88	1.61	6.52	4.25	7.43
Mid Till	9.70	2.07	11.90	10.96	7.37	1.61	9.33	6.04	12.37
Low Till1	19.72	2.18	22.05	12.74	7.29	1.38	9.01	6.86	12.18
Low Till2	13.02	1.62	14.76	6.58	2.03	0.66	2.81	1.14	3.97
Upper Transition	18.84	2.89	21.94	10.84	5.08	2.63	8.05	6.25	10.52
Lower Transition	14.24	1.61	15.96	10.85	2.83	1.20	4.19	2.02	6.56
Sand Channel	11.74	0.57	12.38	2.75	1.60	0.34	1.97	0.67	1.06

Exch. = Exchangeable, CEC = cation exchange capacity, MB = methylene blue
Note: Table shows results from method-prescribed (i.e. 'unit') masses, and averages of triplicate data

Exchangeable cation abundance can be expressed in terms of milliequivalent (meq) fractions (β) as:

$$\beta_I = meq_{I\text{-}Xi} / sum(meq_{I\text{-}Xi}) \qquad (4.2)$$

where I is an exchangeable cation possessing charge i, on exchange site X (Appelo and Postma, 2005). These values, across all field sediments, show that the assemblage of exchangeable cations, in decreasing abundance, consists of Ca>Mg>K>NH_4>Na (Table 4-4).

Table 4-4
Bound exchangeable cation fractions on field sediments (LiCl results). [unitless]

Sample	β_{Ca}	β_{Mg}	β_{K}	β_{NH4}	β_{Na}
Mid Till	0.79	0.17	0.01	0.02	0.00
Low Till1	0.81	0.l5	0.02	0.02	0.00
Low Till2	0.72	0.24	0.04	0.00	0.00
Upper Transition	0.63	0.33	0.03	0.01	0.00
Lower Transition	0.67	0.29	0.03	0.01	0.00
Sand Channel	0.80	0.17	0.04	0.00	0.00

Note: Table shows results from method-prescribed (i.e. 'unit') masses, and averages of triplicate data

Easily exchangeable trace elements were present only at very low concentrations. In LiCl extractions, the most abundant trace metals observed were: Mn (~0.002meq 100g^{-1}), Sr (~0.01meq 100g^{-1}), Ba (~0.01meq 100g^{-1}), and V (~0.3mg L^{-1})[1]. For AgTU, B, V, Ba and Al were all detected both in samples' equilibrium solutions and also at similar concentrations in fluid-only controls; therefore while they may have been present, they could not be accurately quantified. Mn was sparsely present (at ~0.03meq 100g^{-1}), and Sr was found in the Upper Transition and Sand Channel samples (~0.03meq 100g^{-1}). These trace elements' trace presence (compounded by the fact that most form surface complexes which may dominate species present on the exchanger) suggests their exclusion or inclusion will only negligibly impact summed CEC calculations (e.g. for LiCl).

4.4 Discussion

Section 4.5.1 explores which methods performed best in sediments containing carbonate mineral phases (objective 1) while Section 4.5.2 explores the plausibility of cation exchange values measured in the glacial till sediments (pertaining to objective 2).

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[1] Redox state was not determined thus oxidation state (and speciation) of V is unknown, precluding meq 100g^{-1} determination. In addition V is suspected to be an anionic not a cationic complex under the experimental conditions.

4.4.1 Evaluating the Suitability of Cation Exchange Methods in Mildly Calcareous Sediments

Evaluating methods' ability to accurately assess cation exchange properties in carbonate mineral-bearing sediments is a challenging task. Unlike other realms of analytical chemistry, there is no reference material with a pre-determined cation exchange capacity, against which methods' performance can be assessed. One approach, to examine the validity of a cation exchange method when soluble or partially soluble mineral phases, such as calcite or gypsum, are present, is the Carbonate and Sulfate Field (CSF) model (Dohrmann, 2006a). The underlying principle is that as a sediment property, the CEC or exchangeable cation values should remain constant despite experimental variations in sediment to solution ratios. If, on the other hand, changes in solid to solution ratios result in dissimilar CEC values, this may be indicative that partially soluble mineral phases are present and confounding extraction. Under such circumstances, a higher relative amount of solution will impart greater dissolution of the partially soluble minerals. CSF analysis is implemented by testing a sample at two different sediment:water ratios and plotting the results – with one axis capturing the CEC value at one sediment:water ratio, the other axis, the CEC value at the other ratio (e.g. Figure 4-3). If the method is robust to the presence of these mineral phases (or if they do not exist), the measured CEC will be the same at both sediment:solution ratios and the data points will plot along a linear x=y line.

For cation exchange capacity, the CSF model clearly shows that the four methods do not perform equally well in the presence of partially soluble minerals (here, calcium and magnesium carbonates – Table 4-1) (Figure 4-3). Methylene Blue appears unaffected by the presence of these mineral phases. The limited deviations from linearity for that method are attributed not to mineral presence but to sediment variability, as core samples were not mixed/homogenized prior to subsamples being selected for testing in order to minimize drying out the sample.

Lithium Chloride appears to be mildly affected by the presence of carbonate mineral phases. The CSF model results lastly suggest that the NH_4OAc method and especially the AgTU method are noticeably impacted by the presence of partially soluble carbonate mineral phases.

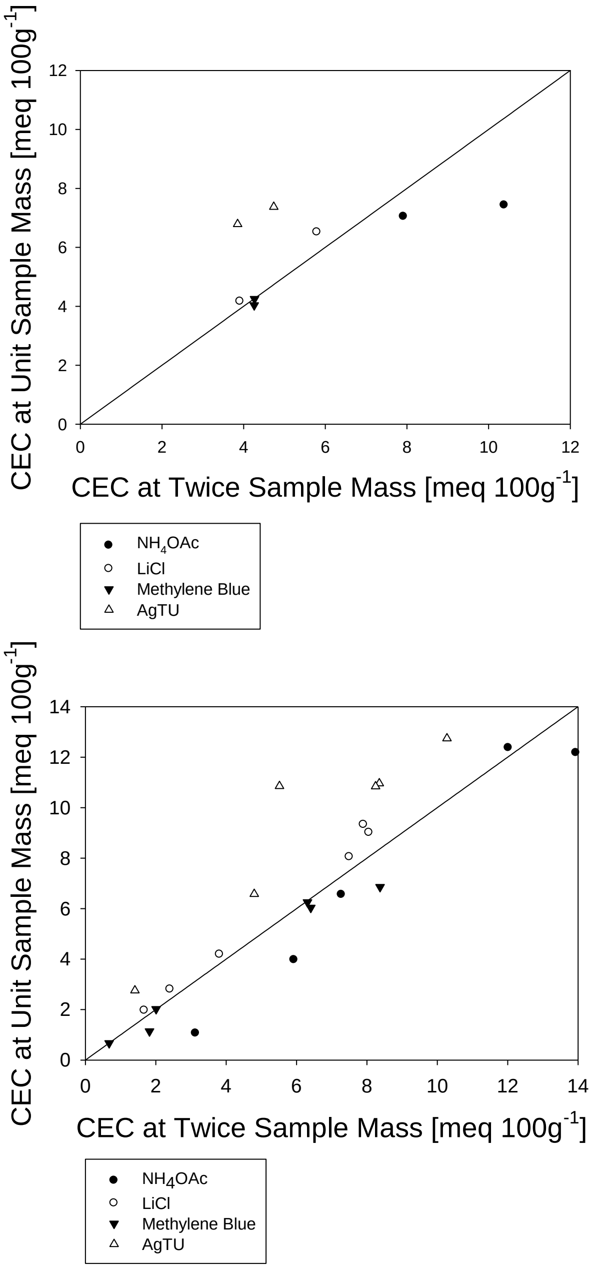

Figure 4-3 The Carbonate and Sulfate Field model (Dohrmann 2006a) for (top) laboratory-grade kaolin (top) and field sediments (bottom). CEC = cation exchange capacity.

4.4.1.1 Evaluating the Exchangeable Cation Data

CSF analysis may be extended to exchangeable cation methods in an analogous manner, except that individual cation concentrations are analyzed in place of the CEC. As before, CSF analysis suggests that the LiCl extractable cation concentrations are largely unaffected, though not entirely indifferent, to the presence of partially soluble calcite (Figure 4-4). Specifically, potassium and calcium were slightly elevated at lower sediment:solution ratios, reaffirming limited sensitivity to the presence of soluble minerals.

For the AgTU method, CSF analysis shows that Na^+, K^+ and Mg^{2+} exchangeable concentrations were not largely influenced by the presence of carbonate minerals; however, the quantification of exchangeable calcium was greatly affected by their presence. These findings are in agreement with Dohrmann (2006c) who also noted that the method largely overestimated the exchangeable cations in calcareous clays.

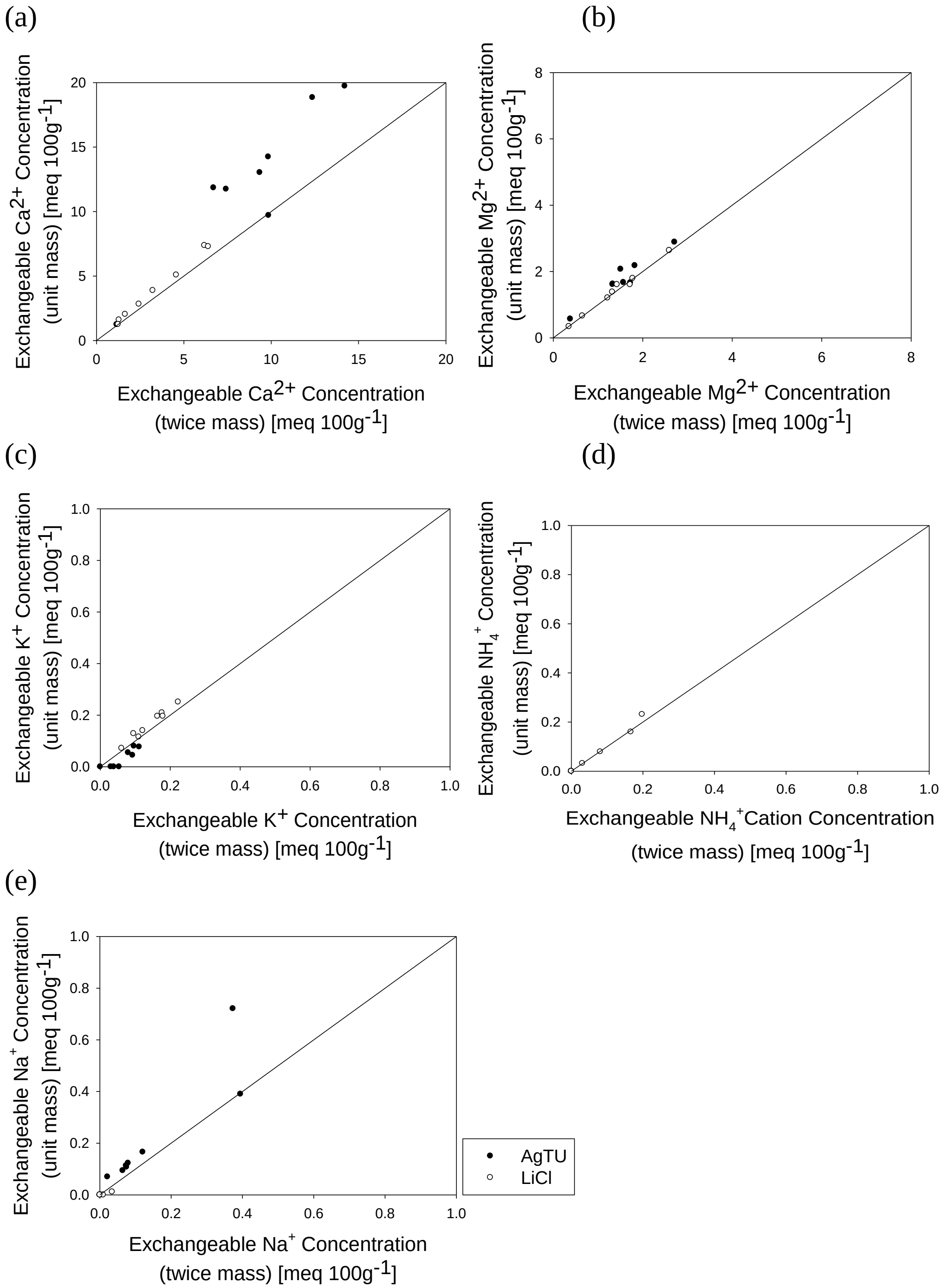

Figure 4-4 The Carbonate and Sulfate Field model (Dohrmann 2006a) applied to exchangeable cations characterized by the Silver Thiourea (AgTU) and Lithium Chloride (LiCl) methods. Plots show the model applied to (a) calcium, (b) magnesium, (c) potassium, (d) ammonium, and (e) sodium.

4.4.1.2 Statistical Evaluation of Differences Amongst Cation Exchange Methods

Method comparison was achieved, in part, through statistical evaluation of a series of a priori research questions[2]: For kaolin samples (without calcite), is the CEC the same across methods and if not, is it equivalent amongst any two methods? Within each method, does doubling the mass of kaolin+calcite samples alter the CEC, and do kaolin+calcite samples yield significantly different CEC values than kaolin (only) samples? The same statistical analysis was repeated with field sediments, except for the lattermost question.

For exchangeable cation data, questions governing method comparison were: For field sediments, within each method, does doubling the sample mass alter the exchangeable Ca^{2+} or Mg^{2+} values? Do the AgTU and LiCl methods yield the same exchangeable Ca^{2+}, Mg^{2+}, or K^+ values? Using kaolin samples, does the presence of calcite impact the value of exchangeable Ca^{2+}, Mg^{2+}, or $K^{+}{}_{,}$ in either method?

Questions were investigated using SPSS software (PASW Statistics 18, Release 18.0.0 Jul 30, 2009) using nonparametric techniques (Independent Samples Kruskal-Wallis Test or Independent Samples Mann-Whitney U Test) in place of multi-factor ANOVA because the requirement that within-group variability in measurements was common amongst groups could not be met (Levene’s Test of Equality of Error Variances). Within-method comparisons were assessed by hand, using t-test and paired t-test comparisons. A significance level of 0.05 was used in all tests.

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[2] Kaolin ‘controls’ were analyzed separately from field samples because the former are without pore fluids or confounding mineral phases and homogenous, thus expected to be consistent among replicates, while the latter may show natural, extensive variability even amongst ‘replicate’ samples, which could skew analysis.

Cation Exchange Capacity – Kaolin

Statistical analysis rejected the null hypothesis that the CEC from kaolin (only) samples is the same across testing methods (significance 0.005, Independent samples Kruskal-Wallis). Further analysis however, revealed that the CEC for kaolin samples was not significantly different between the following pairs of methods: LiCl-Methylene Blue, LiCl-AgTU, Methylene Blue-AgTU, and AgTU-NH_4OAc. Kaolin+calcite samples did not yield a significantly different CEC than kaolin (only) samples for the NH_4OAc and Methylene Blue methods (paired T-test). Using kaolin+calcite samples, doubling the sample mass did not significantly alter the CEC, only for the Methylene Blue method (two independent means t-test).

Cation Exchange Capacity – Field Sediments

Similarly, the null hypothesis was rejected that the CEC for field samples is the same across testing methods (significance 0.000, Independent samples Kruskal-Wallis); although, the CEC for field sediments was not significantly different between the Methylene Blue-LiCl, LiCl-AgTU, and AgTU-NH_4OAc method pairs. Unlike kaolin samples, doubling the sediment sample mass did significantly alter the CEC for all four methods (significance 0.006 (Methylene Blue), 0.0003 (NH_4OAC), 0.0000 (LiCl), 0.0000 (AgTU); paired t-test).

Exchangeable Cations

Using the Independent Samples Mann-Whitney U test, there was no evidence that sample mass significantly impacted the exchanged calcium or magnesium values in field sediments for LiCl, though it did impact exchanged calcium in the AgTU method (significance 0.004). Evidence suggested that exchangeable calcium, magnesium and potassium values were all significantly different if characterized by the AgTU versus the LiCl method (significance 0.000 (Ca^{2+}), 0.009 (Mg^{2+}) and 0.000 (K^{+}), Independent Samples Mann-Whitney U test). Finally, paired t-tests reveal that the presence of (spiked) calcite in kaolin samples impacted the value of exchangeable calcium (for both AgTU and LiCl methods), and exchangeable magnesium (LiCl method only), but not the values of exchangeable potassium or sodium.

To summarize, statistical analysis suggests that:

i. The Methylene Blue method may be least impacted by the presence of calcite;

ii. Even when using well-controlled kaolin samples, methods reported different CEC's. However, LiCl and Methylene Blue, LiCl and AgTU, and AgTU and NH_4OAc tended to report similar values of CEC to one another.

iii. Within sediment cores, intra-sample variability can be large, to the extent that no method reported statistically similar CEC's at their method-prescribed unit mass, versus twice that sample mass. Homogenizing field sediment material and testing larger sample masses (e.g. as in the Methylene Blue method) should lessen this effect.

iv. The AgTU method is not suitable with sediments which have a carbonate mineral presence.

v. For exchangeable cations, the LiCl method is more robust than AgTU for the mildly calcareous glacial till sediments; although it too gave unsatisfactory results with calcite-spiked kaolin controls. This may be related to kinetics: calcite powder added to kaolin samples may have dissolved readily compared to calcium carbonate minerals in field samples, which may not have fully dissolved in the experiment timeframe.

4.4.1.3 Lithium Chloride

Results from statistical analysis and CSF modeling (Figures 4-3 and 4-4) suggest that Lithium Chloride is mildly affected by the presence of carbonate mineral phases; CSF modeling showed the sum of extractable cations using unit sediment masses (low sediment:solution ratio) was consistently slightly higher than that at twice sediment mass. This is the pattern expected by mineral-sensitive methods, since low sediment mass implies a greater relative volume of solution, which in turn results in increased dissolution of the partially soluble mineral phase.

The relative insensitivity of this method to minerals present in the sediment may seem surprising, given that the method does not use sediments in their native (undried) state, but as a pre-mixed saturated paste, which in itself might pre-dissolve existing minerals. This hypothesis was tested using a PHREEQC (Parkhurst and Appelo, 1999) simulation of the LiCl procedure, using Low Till1 as a case study. All PHREEQC simulations in this study used the WATEQ4F database from Ball and Nordstrom (1991). The results reveal that only limited calcite dissolution occurs during creation of the saturated paste, or after, during subsequent extraction (Table 4-5), reiterating that the method is only mildly sensitive to carbonate presence.

Table 4-5
PHREEQC (Parkhurst and Appelo, 1999) simulation of calcite consumption during various conditions of the LiCl experiment.

	Moles in Calcite Assemblage		
Experimental Condition	**Initial**	**Final**	**Change**
Unit mass, Saturated Paste Creation	7.31E-04	7.31E-04	-9.43E-07
Unit mass, LiCl Extraction	7.31E-04	7.27E-04	-4.00E-06
Twice mass, Saturated Paste Creation	1.47E-03	1.47E-03	-1.90E-06
Twice mass, LiCl Extraction	1.47E-03	1.47E-03	-3.54E-06

However, in general, creation of the saturated paste does present several challenges: addition of dilute water may impact the relative composition of bound cations (Appelo, 1996), confounding cations in the pore fluids are not removed, simply diluted, and it is possible that soluble mineral phases would be subject to some measure of dissolution. This new saturated paste system is expected to equilibrate with the sediment surfaces, to some extent modifying the native exchangeable cation assemblage prior to characterization. In accordance, Bache (1976) noted that if soluble mineral phases exist in the sediment, and if CEC summation methods such as the unbuffered LiCl extractions are used, the soluble minerals should be first washed out or otherwise accounted for.

The LiCl method was also unable to measure all exchangeable cations. Exchangeable lithium cannot be measured (Li is the confounding extractant), though this may be only a minimal drawback since Li is not present at significant concentrations in most natural systems. Of greater relevance, it was difficult to quantify exchanged sodium, as its concentration was small and often overwhelmed by the neighboring lithium peak on the Ion Chromatography chromatogram.

Husz (2001) noted that in comparison to $BaCl_2$ extractions, the LiCl extractions yielded similar relative abundance amongst cations, albeit at approximately half the magnitude of bound concentrations extracted by $BaCl_2$. Such a finding was reiterated during pilot studies (data not shown): the relative cation content, as given by the beta values in equation4.2, were in good agreement with the relative exchange assemblage composition predicted by PHREEQC (Parkhurst and Appelo, 1999), and yet the magnitude of the sum of exchangeable cations was smaller than the NH_4OAc-derived CEC for all preliminary samples tested. In this light, a modified method was used in this study, wherein not two but three LiCl rinses were performed. Easily detectable concentrations of cations were still measured in the third rinse and therefore included in the calculated CEC's presented above.

Because cations were detected in the third rinse, it is logical to question whether or not all cations had been exchanged even by this third rinse. To investigate this, a simple PHREEQC (Parkhurst and Appelo, 1999) simulation of the three-rinse LiCl extraction was run. The simulation revealed that by the conclusion of the simulated exchange, the lithium exchange fraction (LiX) was not equal to 1.0 (Table 4-6) - suggesting that three 25mL rinses of 0.4mol L^{-1}LiCl were not sufficient to displace all pre-bound cations. A follow-up simulation was run to determine what concentration of LiCl is required to fully displace all pre-bound cations (using three rinses). The simulation results suggest that 1.0mol L^{-1} should be sufficient (Figure 4-5).

Additional suggested future improvements:

i. Using three rinses and higher molarity LiCl solution to ensure complete exchange occurs.

ii. First forming the sediment into a saturated paste may not be required and instead it may be advisable to simply apply the three LiCl washes to the undried sediment.

Table 4-6

Predicted solid phase exchange fractions at different rinse stages using LiCl extraction (Low Till1 sediment sample, 10g paste).

Bound Species	**PHREEQC-predicted Fraction Rinse1**	**PHREEQC-predicted Fraction Rinse2**	**PHREEQC-predicted Fraction Rinse3**
LiX	5.97E-01	7.88E-01	8.77E-01
CaX_2	3.61E-01	1.95E-01	1.15E-01
MgX_2	3.43E-02	1.46E-02	6.94E-03
KX	5.82E-03	2.13E-03	8.31E-04
NH_4X	2.30E-03	5.80E-04	1.57E-04
NaX	2.55E-04	2.64E-05	2.98E-06

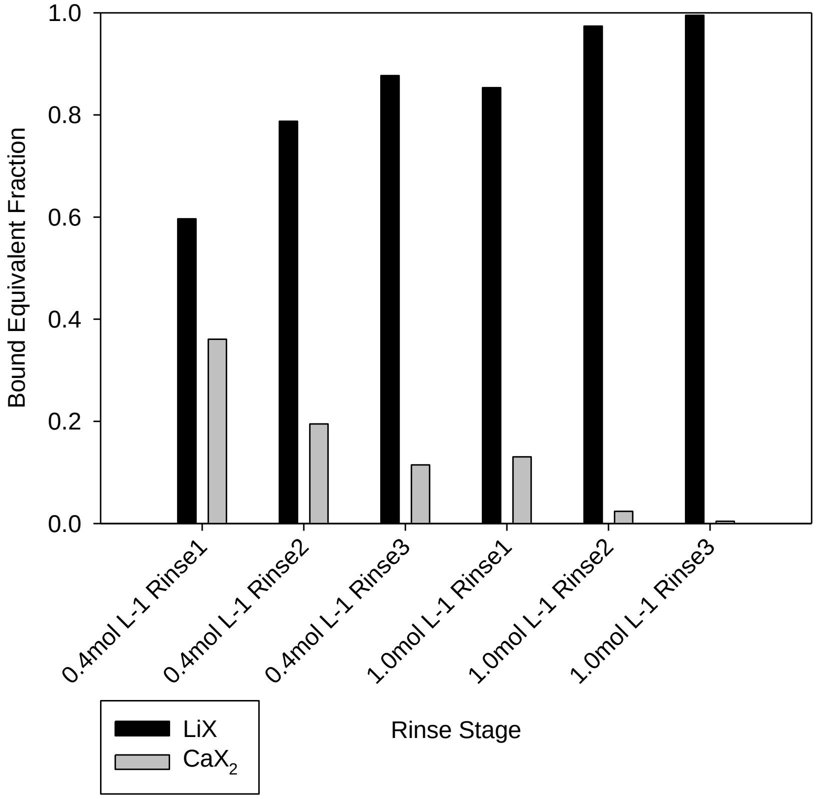

Figure 4-5 The simulated exchange assemblage for the two predominant cations, lithium and calcium, during extraction rinses at two different Lithium Chloride (LiCl) concentrations (Low Till1 Sample using 10g saturated paste).

4.4.1.4 Silver Thiourea

The results and analyses above demonstrate that the Silver Thiourea procedure (Dohrmann, 2006b) is noticeably impacted by the presence of partially soluble carbonate mineral phases. This is in contrast to the results from Dohrmann (2006b), who found that across a variety of clays, the method was unaffected by their presence. However, in a companion paper (Dohrmann, 2006c), it was also observed that the method, particularly for exchangeable magnesium and calcium, was not robust in the presence of calcite and dolomite mineral phases. As a solution, Dohrmann (2006c) proposed pre-saturating the AgTU exchange solution with the confounding mineral of concern, e.g. calcite, to minimize unwanted dissolution. This modification is expected to improve results with the field sediments studied here. Unfortunately the limitation of this improvement is that it allows one to compensate for only a single mineral phase. XRD mineralogy results (Table 4.1) and previous batch sorption experiments with these sediments (Holden et al., 2011a) suggest that Fort McMurray sediments include dolomite and perhaps sulfate-bearing mineral phases as well.

Early implementations of Silver Thiourea extractions (e.g. Chhabra et al., 1975) were criticized for overestimating the cation exchange capacity – particularly for smectite clays (Dohrmann, 2006b). The underlying mechanism was postulated to be the hydrophobic binding of free phase Silver Thiourea complexes by Silver Thiourea complexes already adsorbed to the clay surface. Dohrmann (2006b) further suggested that at low solution to solid ratios, there exist fewer cations in solution relative to the number of sorption sites, minimizing the erroneous 'excess' sorption that takes place. Although the method of Dohrmann used here includes additional rinses specifically designed to remove these hydrophobically bound complexes, the present findings, particularly the CSF results, support the possibility that the rinses may not have been fully successful so that higher solution to solid ratios (i.e. 'unit' mass test cases) indeed resulted in greater excess adsorption and thus a higher measured CEC.

Method performance did not appear attributable to stock solution properties, although non-sorptive losses could have impacted results. The pH of the AgTU stock solution was acceptable, ~6.8, (pH >8 may lead to silver loss via silver sulfide precipitation), the solution was the correct light-green color, and solutions were kept only for 48hours, which should have avoided other silver precipitation reactions. However, there were very large errors in quantifying silver content in solution-only controls: final silver concentrations in controls were approximately 10% or 20% of initial stock concentrations. The cause of this loss is unknown, but it appears to have been isolated to the controls, as AgTU CEC values for sediments were comparable to those determined by other methods and not, for example, 80% smaller.

An additional consideration is whether or not sufficient index cations existed in solution to populate all sorption sites. Dohrmann (2006b) implied that a 30% excess of AgTU is necessary, compared to the expected cation exchange capacity, in order to ensure complete coverage. Assuming a maximum possible cation exchange capacity of 13meq $100g^{-1}$ for the present sediments (Figure 4-2), and with 4g of sediment mixed with 48mL of 0.01M Ag^+ solution, 0.48meq of silver complexes would exist, compared to 0.52meq of sorption sites. Thus, when 4g of sediment were used, full coverage could not have occurred. This offers another possible explanation for the higher observed CEC at low sediment:water ratios in the CSF analysis.

Additional suggested future improvements:

i. For characterization of carbonate-rich sediments, the calcite-modified Silver Thiourea method (Dohrmann, 2006c) or alternatively a different organo-metal complex (e.g. Ammann et al., 2005) may offer an improvement to the method used here.

ii. Owing to the poor performance of fluid-only controls, it may be prudent to not only prepare the stock solution fresh, every 48hours, but to also conduct analytical characterization within a similar timeframe.

iii. Exchangeable NH_4^+ cannot be quantified using Ion Chromatography, due to interference by a much larger silver peak, necessitating an additional analytical procedure.

iv. One must ensure that enough AgTU complexes will be added to fully populate all sorption sites – by increasing added stock solution volume or concentration.

4.4.1.5 Methylene Blue

Methylene Blue is advantageous over other extractants in that it has a very high binding affinity compared to inorganic cations (Margulies et al., 1988). This could be attributed to its structure: the molecule has polar and non-polar components making it well suited to bind to clay surfaces, which are not uniformly negative, but similarly, have regions of charge (e.g. by isomorphous substitution) interspersed within relatively neutral areas. In addition, the present analyses consistently found the Methylene Blue method to be best suited for use with mildly calcareous, clay till sediments.

The Methylene Blue test is taken to be a standard method for characterizing sediment properties (specifically tailings properties) in the Oil Sands Industry in Alberta (Kaminsky, 2008, Sethi, 2012). Its adoption as an industry standard may stem, at least in part, from initial work by Sethi, who established a correlation relating the methylene blue values with the clay content of oil sands samples. Clay content was itself subsequently demonstrated to be correlated with clay activity (combination of clay content and surface area of sediments), which was found to be useful for monitoring tailings properties, at the time that Consolidated Tailings processing was introduced at a commercial scale at Suncor. Similar support was repeated by Mikula et al. (1998) who found that tailings slurry properties were inadequately explained by traditional use of fines content, while instead segregating characteristics were much better explained by clay activity – again, a parameter which could be rapidly and inexpensively determined by the methylene blue test.

The present results support the use of this method in oil sands applications, in particular providing a scientific underpinning for its future application in characterizing surficial sediments in the Alberta oil sands, as part of remediation and reclamation efforts.

The Methylene Blue spot or halo test was not without shortcomings however. Input stock concentration is not explicitly measured, and the endpoint, the blue halo, is (subjectively) judged by eye, and its appearance not always obvious. Improvements might be achieved by using photometry to assess input stock concentration, or perhaps by using a photometry-based batch method in place of the spot test (e.g. Kahr and Madsen, 1995; Yukselen and Kaya, 2008).

A caution with using this extractant is that clay-methylene blue interactions are not straightforward, and particularly for kaolinites, could create slight uncertainty in the meaning behind the reported Methylene Blue Index (or CEC) value. For example, spectroscopic analysis of smectites has shown that clay surface coverage by cationic dyes is governed not only by electrostatic dye-surface reactions, but also by interactions between dye molecules themselves (Bergaya et al., 2006). This is manifested by aggregation or interaction of dye molecules at the surface of such clays, and would result in overestimation of the CEC (Margulies et al., 1988). However, while smectite and illite interactions with methylene blue are fairly well understood (e.g. from spectroscopy investigations), kaolinite-methylene blue spectroscopy results are atypical, suggesting that how the molecule interacts with kaolinite is not yet properly understood (Cliff Johnston, personal communication).

There are conflicting reports in the literature regarding the pre-treatment of clays before applying the Methylene Blue test, particularly, with regard to dispersion and testing of clays in their lithium or sodium form. In support of Kahr and Madsen (1995) and Kaminsky (2008), we believe that it is very important that clays be well-dispersed in order to achieve good, reliable Methylene Blue results. This could be implemented by adding a dispersant (e.g. $Na_4P_2O_7$-$10H_2O$, $NaHCO_3$, NaOH) to the sample and then sonicating it for at least 20-30 minutes. In the present context, dispersion may explain why the Methylene-Blue-derived CEC was similar to that of other methods (LiCl, AgTU) for commercial kaolin, and yet noticeably smaller for field sediments: as a commercially available product, kaolin was likely subject to extensive dispersion during pre-treatment purification (Bergaya et al., 2006), which would help ensure that complete exchange by methylene blue was achieved for those samples. One may postulate similar explanation to the findings of Yukselen and Kaya (2008), who observed that Methylene Blue values were smaller than Ammonium Acetate-derived cation exchange capacities for several clay sediments. There too, no apparent attempt was made to disperse the clays before analysis, which would result in lower Methylene Blue values than otherwise attained. By contrast, like Yukselen and Kaya (2008), Meier and Kahr (1999) also tested several clay mineral types with both methods; however here using dispersion via sodium hexametaphosphate. The results were the opposite, showing larger CEC values for Methylene Blue across samples, we believe, reinforcing the need to fully disperse clays when using this method.

Additional suggested future improvements:

i. It may be of interest to quantify the cations exchanged into solution, to confirm that divalent cations are displaced by methylene blue, and that sediments need not be pre-treated into a Li or Na-form.

4.4.1.6 Sodium Acetate-Ammonium Acetate

CSF results suggest that the method is noticeably influenced by partially soluble carbonate mineral phases (in accordance with Van Bladel et al., 1975), despite statistical analysis reporting more favorable behavior, e.g. kaolin+calcite did not yield a significantly different CEC than kaolin only. Once again, the influence of calcite was greater at lower solid:solution ratios, though this had different manifestation in the CSF plot. One may postulate the mechanisms behind this behavior as follows: calcium released by dissolution during the initial Sodium Acetate rinses competes with the introduced, desorbing sodium ions for exchange sites, such that despite the overwhelming number of Na^+ ions, some small fraction of calcium is bound to the exchange sites. Being buffered to pH 8.2, the Sodium Acetate solution is not expected to dissolve large quantities of calcium carbonate (e.g. Van Bladel et al., 1975); however, this does not preclude dissolution altogether, and such dissolution was observed over the course of the present experiments. A lower sediment:solution ratio (i.e. higher relative fluid content) exacerbates these effects - resulting in greater dissolution of partially soluble minerals, increased calcium concentrations, and by competition, a lower relative binding of the index cation (sodium). Because the index cation is ultimately desorbed and quantified as an estimate of the number of sorption sites, a lower fraction of bound sodium yields a lower CEC estimate. Thus a lower sediment:solution ratio would underestimate the CEC compared to a higher such ratio - resulting in the CSF data point falling below the x=y line, as was observed.

The Ammonium Acetate method also tended to report a higher CEC than the other methods tested. One possibility is that the method overestimates the true sorption capacity. In support, Bache (1976) noted that the solid phase may contain positively charged surfaces, such as proton-bound oxide/hydroxide surfaces, in addition to negative surfaces. Solutions with high ionic strength compress the diffuse double layers of each surface, permitting each to be quantified separately; however, with weak ionic strength solutions, which may be more representative of in-situ conditions, the surfaces' layers may overlap, effectively neutralizing one another. In such a circumstance, the use of a high ionic strength extractant will incorrectly characterize CEC by the larger magnitude negatively charged surface, as opposed to the lower magnitude 'net' charge, reflective of in-situ conditions (and recall that the ionic strengths were: 1.0N (Sodium Acetate), 0.4N (LiCl), 0.01N (AgTU) and 0.01N (Methylene Blue)). Dohrmann (2006b) offers a similar argument with AgTU, where higher concentration solutions were thought to compress the 'Stern layer', whereby a greater number of cations could be adsorbed.

Furthermore, the effects of using a buffered, high-pH solution (e.g. NaOAc, pH8.2) need to be considered. Since the field sediments in this study contain a large proportion of kaolinite, whose surface charge is highly pH dependent, and given that the surface charge will be increasingly negative at higher pH, such a method could potentially over-evaluate the true CEC, or the CEC determined by other non-buffered methods. Similarly, Bache (1976) notes that the addition of a basic solution may stimulate acid-dissociation-like reactions of surface OH groups to O^-, which would create a greater net negative sorption capacity, while Ross (2009) suggests that buffered extractants often yield higher CEC values than unbuffered methods.

A final possibility is that the relatively high CEC values determined by the NH_4OAc method, could be related to the presence of iron oxides in the sediments. No attempt was made to quantify these phases within the sediments, and different extractants may have differing susceptibility to their presence.

Additional suggested future improvements:

i. It may be good practice to tailor the extractants to the conditions expected on site. The present work is part of broader work investigating the seepage of high-pH (8.3), sodium-rich waters into adjacent clay till. Natural groundwater recharge will be circumneutral pH and contain mostly sodium and calcium. Thus, perhaps a more representative extraction would be pH8.2 NaOAc rinses followed by rinses with pH7 calcium chloride[3].

4.4.2 Measured Exchange Results in the Context of Pre-existing or Predicted Values

As with assessing which methods performed best, validating the results is not a straightforward task. Empirical relationships and guidelines offer some value though, by providing context for observed values. As an example, Appelo and Postma (2005) relate the CEC (meq $100g^{-1}$) to the sediment organic carbon content (%C) and clay content (%clay), at circumneutral pH, as:

$$\text{CEC} = 0.1 * (7 * (\%\text{clay}) + 35 * (\%\text{C})) \qquad (4.3)$$

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[3] As a further benefit, chloride based salts may be more appropriate for calcareous applications, e.g. Tucker (1954) noted that calcium carbonate displayed a much greater solubility in acetate over chloride solutions.

Using observed values of FOC and clay content (Table 4.2), yields a predicted CEC of 21meq $100g^{-1}$ in the mid clay till and 13meq $100g^{-1}$ in the low clay till. By comparison, across methods the CEC was found to be ~6-12meq $100g^{-1}$ in the Mid Till, ~7-13meq $100g^{-1}$ in Low Till1 and ~1-7meq $100g^{-1}$ in Low Till2. Thus observed values appear plausible, though lower than anticipated. This difference should not be overemphasized however, as such an empirical equation is simply a broad guideline, and does not take into account detailed and important factors like clay mineralogy (different clays have substantially different sorption capacity).

To further complicate matters, very little data has been published regarding the cation exchange properties of surficial Pleistocene sediments in the Athabasca Oil Sands region, so that references for comparison largely do not exist. Peng et al. (2002) (reiterated by Janfada et al., 2006) reported values of 16.2 to 19.4meq $100g^{-1}$ for reclamation/salvage sediments at the Syncrude site, which is comparable to the CEC measured in the nearest likely strata, the Mid Till, at 6.0 to 12.4meq $100g^{-1}$. The sediments in the Peng et al. (2002) study were supplemented with peat, and additionally, may have been collected from higher soil horizons, where humic substances and clays are most abundant (Langmuir, 1997) - likely accounting for the higher values observed. Marsh (2006) reported CEC's generally less than 1meq $100g^{-1}$ within surficial sands from an unconfined aquifer at the Syncrude Mildred Lake site, which is comparable to the 0.7-2.8meq $100g^{-1}$ (Sand Channel) values determined here.

A PHREEQC (Parkhurst and Appelo, 1999) simulation was conducted to check whether or not the LiCl experimental results were plausible (AgTU was not included, since its suitability with carbonate-rich sediments had already been ruled out (Results, Section 4.4.3)). The simulation equilibrated measured pore fluid solutions[4] with the number of exchange sites predicted by NH_4OAc CEC experiments, in order to characterize the assemblage of bound cations in the

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[4] Pore fluid data did not include pH or alkalinity measurements. These values for the simulation were estimated from groundwater values collected at the same time and location as the tested sediment sample.

sediments' native state. Such a comparison has limitations, namely that it can confirm only the relative distribution of cations and not their absolute value concentrations. Nevertheless, as shown in Table 4-7, the results of the comparison were quite similar, reaffirming the LiCl method's potential usefulness with calcareous sediments. Furthermore, while such analysis does not offer insight into the observed CEC value, being an input parameter in the simulation, the good fit of the simulated values suggests the exchanger complies with the Gaines Thomas model using standard selectivity coefficients. This in turn implies that one should be able to predict the exchange composition, once the CEC is known.

Altogether, the CEC and exchangeable cation data observed in the present study appear plausible in the context of pre-existing and predicted values.

Table 4-7
Comparing LiCl and PHREEQC-predicted (Parkhurst and Appelo, 1999) estimates of native sediment exchangeable cation fractions.

	Low Till1		**Mid Till**		**Upper Transition**	
Bound Species	**PHREEQC-predicted Fraction**	**LiCl-derived Fraction**	**PHREEQC-predicted Fraction**	**LiCl-derived Fraction**	**PHREEQC-predicted Fraction**	**LiCl-derived Fraction**
CaX_2	8.6E-01	8.1E-01	8.2E-01	7.9E-01	6.8E-01	6.7E-01
MgX_2	1.1E-01	1.5E-01	1.6E-01	1.7E-01	2.8E-01	2.9E-01
KX	1.9E-02	2.2E-02	4.5E-03	1.4E-02	2.0E-02	3.3E-02
NH_4X	1.3E-02	1.8E-02	1.3E-02	2.5E-02	7.0E-03	7.6E-03
NaX	3.5E-03	0.0E+00	1.9E-03	0.0E+00	1.2E-02	0.0E+00

4.5 Conclusions

Four methods were tested for cation exchange capacity assessment (Lithium Chloride, Silver Thiourea, Methylene Blue, Ammonium Acetate), and two for exchangeable cation determination (Silver Thiourea, Lithium Chloride), in sediments known to contain several percent, by weight, of partially soluble carbonate mineral phases. Among CEC methods, the Methylene Blue method was least impacted by the presence of these carbonate minerals supporting its ongoing use as the Oil Sands industry standard, but more importantly, justifying its future use in characterizing surficial sediments, as focus shifts towards remediation and reclamation with the impending closure of the area’s first mines.

The LiCl method was suitable for assessing the relative abundance of exchangeable cations, but not their absolute bound concentrations, likely due to lithium’s weak exchanging power. The AgTU method was not suitable for either CEC or exchangeable cation determination in mildly calcareous sediments. Thus, additional method comparisons are required to determine an optimal exchangeable cation extractant for use with mildly calcareous, clay-rich sediments.

Although the Methylene Blue and LiCl extractants performed best in the mildly calcareous sediments, no method was without shortcomings, and hence improvements were proposed. Most notably, complete extraction by LiCl requires additional rinses at a higher concentration extractant solution. Methylene Blue samples must be fully dispersed before testing, for example by using a chemical dispersant as well as 20-30minutes of sonication. For all methods, inhomogeneous field cores or samples should be well homogenized before sub-sampling for CEC testing, and, to decrease variability among replicates, sub-samples should be on the order of 10g or more.

This study also characterized, for the first time, the cation exchange properties of surficial glacial sediments near Fort McMurray, Alberta. The mean cation exchange capacity, using the Methylene Blue method, was found to be 4.7±2.7meq $100g^{-1}$ in the clay-rich glacial till, 0.7±0.0meq $100g^{-1}$ in the underlying sand and 4.1±2.3meq $100g^{-1}$ in the till-sand transition zone. The exchangeable cation assemblage in decreasing order consisted of $Ca>Mg>K>NH_4>Na$. In the context of seepage from oil sands tailings facilities, these findings suggest sediments possess only a mild capacity to bind potential contaminants (likely Na, the dominant cation in process waters), while ingress of Na-rich process water will displace exchangeable Ca and Mg into solution, raising their aqueous concentrations.

4.6 Chapter 4 References

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Chapter 5: Geochemical Interactions between Process-Affected Water from Oil Sands Tailings Ponds and North Alberta Surficial Sediments*

*A version of this chapter has been published.
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5.1 Introduction

In Northern Alberta, the South Tailings Pond is the first of several tailings facilities to be sited atop buried sand channels - relicts of previous glacial rivers. Preliminary hydrogeological modeling of this case study site, as part of the initial site assessment, suggests that oil sands process-affected water (OSPW) from the pond will diffuse through the clay-rich till and into the underlying sand channel; however, the development and extent of this impact are not known (Hall et al., 2004).

As part of a larger research program investigating the geochemical impact of oil sands tailings seepage on native surficial sediments and groundwater resources, the objectives of the present work are:

1. To investigate the influence of adsorptive and ion exchange reactions on the mitigation/mobilization of major cations – in both the glacial till and sand channel sediments. This will be achieved using traditional batch sorption experiments, and also a recent modification of the traditional method that uses less disturbed sediment samples.

2. To further understanding of the geochemical processes driving system behavior, through use of geochemical simulations.

Based on existing literature, the present study offers the first detailed laboratory characterization of the adsorption and ion exchange processes to be expected when ingressing inorganic components present in OSPW interact with surficial sediments in the Athabasca Oil Sands region. In Chapter 4, exchangeable cation experiments (Lithium Chloride (Husz, 2001, modified)), revealed that in the glacial till, the easily displaceable cations consist of Ca > Mg > K > NH_4> Na, in decreasing abundance. And, as presented earlier (Chapter 3 §3.2.1), OSPW is known to contain high concentrations of sodium, chloride, sulfate and bicarbonate ions (Marsh, 2006; Oiffer et al., 2009; Price, 2005). A reasonable expectation therefore, is that interaction of OSPW with the native surficial sediments and pore water will result in the sorption of ingressing sodium with the subsequent displacement of pre-bound cations such as calcium and magnesium. Depending on the saturation indices of mineral phases in the resultant solution, this may further lead to precipitation of sulfate or carbonate minerals.

5.2 Materials and Methods

5.2.1 Sediment Sampling and Characterization

To investigate variations in sediment response with depth, samples were selected from the upper, middle and lower glacial till, from the lower portion of the clay till-WCSC transition zone, and for additional interest, from deep in the WCSC. The respective depths are: 3.4 - 4.6meters below ground surface (mbgs) (upper till), 6.1 – 6.4mbgs (mid-till), 8.2 – 9.1mbgs (low till), 12.2 – 13.7mbgs (till-WCSC transition), and 37.7 and 38.7mbgs (deep WCSC). The site description and details concerning soil core collection or sample preparation are included in Chapter 3 (§3.1.2, §3.1.4).

Several experiments were conducted to assess the physical properties of the sediments. Select samples were analyzed for fraction of organic content by collaborative researchers at the University of Waterloo. In addition, grain size analysis was conducted using both sieve tests, and for select samples, hydrometer analysis.

In accordance with standard grain size analysis techniques, sediments were first dried then gently ground prior to sieving (e.g. Das, 2002). However, sediments dried into clumps that could not be sufficiently ground down, and thus small silt/clay clusters could be observed as having been incorrectly retained by sieves in the sand-sized fraction. Therefore a revised approach was adopted wherein samples were first washed using a 0.075mm sieve, thereby removing the silt/clay clusters or coatings on sand particles. The amount passing through the sieve was dried and quantified as the fines portion. The retained fraction of coarser sediments was dried and characterized by sieving analysis in the normal manner. Two of the sediment samples were (qualitatively) observed to have a high clay content, therefore in order to better resolve the distribution of fines in these samples, they were also analyzed using a hydrometer. Sediment properties are presented in Table 5-1.

Table 5-1
Physical properties of the tested sediments

Sample ID	**Soil Core Sampling Location**[d]	**CEC**[c] **(meq $(100g)^{-1}$)**	**Specific Gravity (20ºC)**	**Grain Size Summary**	**Gravi-metric WC**	**% FOC by weight**	**Description from Borehole Logs**
MW3-4	Monitoring well 3B, 3.4 to 4.6 mbgs	11.32	2.614	0.5% > 0.475mm 67.5% < 0.475mm > 0.075mm 32.0% < 0.075mm 19.2% < 0.0023mm	0.142	1.530+0.057	Clay (till), silty, sandy, low-medium plastic, brown, moist
MW3-6	Monitoring well 3B, 6.1 to 6.4 mbgs	4.02	2.633	4.0% > 0.475mm 70.3% < 0.475mm > 0.075mm 25.6% < 0.075mm	0.121	3.690+0.028	See above (experimentally noted to be sandy, red-brown compared to other till samples)
MW3-9	Monitoring well 3B, 8.2 to 9.1 mbgs	15.50	2.643	0.6% > 0.475mm 45.3% < 0.475mm > 0.075mm 54.0% < 0.075mm 30.0% < 0.0022mm	0.124	0.986+0.018[a]	See above
M4-13	Monitoring well 4B, 12.2 to 13.7 mbgs	3.51	2.660	3.7% > 0.475mm 74.4% < 0.475mm > 0.075mm 22.0% < 0.075mm	0.056	0.978+0.028[b]	Transition zone, clay till to sand (silty)
M2-38	Monitoring well 2A, 37.7 mbgs	6.50	2.669	9.0% > 0.475mm 42.5% < 0.475mm > 0.075mm 48.6% < 0.075mm	0.169	not tested	Sand: dark grey, fine-gr., very silty, wet, some fine gravel, trace coarse gravel, occasional CL clay lens 4-6” thick with gravel (till-like)
M2-39	Monitoring well 2A, 38.7 mbgs	5.59	2.733	19.1% > 0.475mm 56.9% < 0.475mm > 0.075mm 24.0% < 0.075mm	0.103	not tested	Sand/gravel: dark grey, fine to med. grained, clean gravel: med. to coarse-grained, occasional cobble

FOC = fraction of organic content, CEC = cation exchange capacity, WC = water content, mbgs = meters below ground surface
Grain size distribution curves are numerically summarized to show the major features.
[a] Tested sample came from a marginally lower elevation of 9.1 to 9.8mbgs
[b] Tested sample came from a marginally higher elevation of 11.0 to 12.2mbgs
[c] Sodium Acetate method (USEPA, 1986).
[d] Nests of monitoring wells are situated linearly, with approximately 100m spacing from 2A to 3B and again from 3B to 4B.

5.2.2 Batch Sorption Experiments

In order to investigate the utility of a recently proposed method of laboratory sorption experiments, and in order to examine the system behavior at an increasing level of complexity, a total of four different treatments were applied:

- standard batch sorption tests using a simplified, simulated process-affected water;
- standard batch sorption tests using process-affected water collected on site;
- a new method of sediment cube sorption tests (modified from Zhang et al., 1998) using simulated process-affected water; and
- sediment cube sorption tests using process-affected water collected on site.

Process-affected water was collected from a discharge line feeding directly into the South Tailings Pond. Samples were collected August 25, 2008 and stored sealed, in the dark, at 4^{o}C. In addition, a simplified synthetic or simulated process-affected water was created, based upon the chemical composition of STP process-affected water averaged across 6 sampling events between September 2006 and August 2008. This water was comprised only of major ions, and in order to evaluate system response at future, potentially higher discharge concentrations, the concentration was conservatively selected to be 1.2 times that of Suncor OSPW averaged across these dates[5] (Table 5-2). The simulated process water possesses similar ionic characteristics to the actual process water but does not contain the complex organic compounds. A comparison of the simulated process water results to the actual process water results should therefore provide some insight into the role of organic compounds in the attenuation and release of inorganic species.

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[5] Synthetic process-affected water was comprised of Fisher Scientific (USA) reagents: NaCl (certified A.C.S. crystal), Na_2SO_4 (certified A.C.S. anhydrous), $NaHCO_3$ (certified A.C.S), KCl (certified A.C.S) and ACROS Organics (ES) $CaSO_4$-$2H_2O$ (A.C.S.) and BDH Chemicals (Canada) $MgSO_4$-$7H_2O$ (A.C.S.).

5.2.2.1 Traditional Method

Sorption and ion exchange behavior were investigated as a function of process-affected water concentration. Six different aqueous solutions were used: deionized water as well as 5 different concentrations of OSPW. A concentration range was used as a means of modeling the geochemical response to an advancing plume of OSPW. For simulated OSPW, the maximum concentration was conservatively selected to be 1.2 times the average concentration of Suncor OSPW observed to date. The concentrations of the 4 intermediate stock solutions were selected to be 20%, 40%, 60%, and 80%, by volume, of this proposed maximum. Similarly, South Tailings Pond-destined or hereafter known as real OSPW stock solutions were prepared to 20%, 40%, 60%, 80% and no dilution or 100% strength of the water collected on-site. Immediately after preparation, a portion of each stock solution was retained for pH (Thermo Electron Corporation, pH electrode 9107BN) and alkalinity analysis (potentiometric titration), while additional samples were filtered (0.2μm) and major ion and trace metal speciation ascertained by Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry[6], respectively. (Details regarding Ion Chromatography analysis may be found in Chapter 3 (§3.3.1))

Based upon preliminary experiments to optimize the procedure, batch samples were created at a soil to water ratio of 1:2. Fifteen grams of undried sediment were added to 30g of stock solution, within a 50mL plastic centrifuge vial, and mixed into a slurry using a glass stirring rod. (Plastic containers were deemed permissible given our focus on inorganics and the short-term 24 hour duration.) Order of preparation of batch vials was randomized across solution concentrations. Samples were prepared quickly to minimize sediment desiccation. Vials were agitated at room temperature (20°C) for 24 hours (ASTM Standard D4646, 2003) using a wrist-action shaker (Burrell Wrist-Action ® Laboratory

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[6] Samples were preserved in 1% nitric acid, and analyzed via PerkinElmer SCIEX ELAN 9000 – results not shown.

Shaker, Model BB,10° amplitude, 400±20 Osc. min^{-1}). Subsequently, samples were centrifuged at 4150rpm for 15 minutes (Heraeus Multifuge ® 3 L-R). Any changes to the physical characteristics of either the solid phase or solution such as color, opacity, etc. were noted. A portion of the resultant supernatant was analyzed for pH and alkalinity, while the remainder was filtered (0.2μm) and major ion and trace metal speciation ascertained by Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry, respectively. Tests were conducted in triplicate.

A sample of the soil core was placed in a drying oven for gravimetric water content analysis before the first batch vial was prepared, and another after the final vial was created. Two fluid-only blanks were prepared at each concentration – one before batch vials were created, one after - and subject to the same treatment as the sediment-water vials to measure non-adsorptive losses to the system. Mass measurements were taken at all stages of the experiment to further record any such losses.

Following final decantation and conclusion of the sorption experiment, a simple desorption procedure was applied to the remaining solid phase. The procedure reflects the latter portion of the Sodium Acetate cation exchange capacity method (USEPA, 1986); in short, three 33mL rinses with 2-propanol Optima (Fisher Scientific) followed by three rinses with a prepared 1N ammonium acetate solution (pH 7.0).

5.2.2.2 Cube Batch Sorption Method

A modification of a recently proposed method was critically evaluated, as a means to investigate sorption and ion exchange behavior as a function of process-affected water concentration, by diffusive equilibration of an intact sediment sample (Zhang et al., 1998). The details of the applied stock solution concentrations are the same as above (see 5.3.2.1).

Samples were prepared by carefully cutting a 15g cube of undried sediment, with approximate dimensions of 2 x 2 x 2cm, from the soil core section, using a stainless steel palette knife. The procedure was designed so that both the traditional and cube methods would utilize the same sediment sample size and soil to water ratio, to facilitate later comparisons between results from the two methods. Pre-tests were conducted at 5day, 6day, 7day, 8day and 11day durations and a preliminary simulation was run using PHREEQC (Parkhurst and Appelo, 1999) in order to establish the length of time needed for the system to equilibrate, using a cube of these dimensions. The simulation considered 1D diffusive, non-reactive transport, for sodium and chloride, at their concentrations within full strength OSPW (0.026mol kgs^{-1} and 0.010mol kgs^{-1} respectively). The diffusion coefficient was estimated to be $10^{-10}m^2s^{-1}$ and the diffusion path length for 1D transport was assumed to be half the length of the cube (i.e. assuming diffusion would occur from each side of the cube into its center). Results from both laboratory analyses and the simulation predicted that equilibration would be achieved in 5 days for a cube of these dimensions. Sediment cube location within the core section and order of preparation of the batch samples were randomized across solution concentrations. Given the greater duration of this experiment, 5 days and not 24 hours, glass jars (Fisher Scientific, I-Chem 200series 4oz, clear) were used to minimize the sorption of organics onto container walls, which could have altered the inorganic system response. The undried sediment cube was placed in a jar and 30g of solution carefully added using a syringe (B-D 20cc luer lok, bulk, non-sterile – Fisher Scientific). The jar was then sealed and left in the dark, at 20°C for 5 days. After this period, any changes to the physical characteristics of either the solid phase or solution were noted. The equilibrated solution was decanted and analyzed for pH, alkalinity, major ions by Ion Chromatography and trace metals by Inductively Coupled Plasma Mass Spectrometry. A portion of the soil core was dried at 100°C for 24 hours for gravimetric water content analysis. A fluid-only control was prepared at each concentration. Mass measurements were conducted throughout the experiment to record evaporative losses to the system. Tests were conducted in triplicate.

Table 5-2
Chemical composition of full strength oil sands process-affected waters (OSPWs) used in batch sorption experiments (average of source solutions used for each of the five sediment regions' samples) [units: mg L^{-1}]

Species	**Simulated OSPW**	**Real OSPW**
Calcium	16.07	7.62
Magnesium	12.14	4.17
Potassium	12.59	10.05
Sodium	720.62	591.35
Ammonium	0.47	2.02
Lithium	not added	0.16
Chloride	398.00	374.51
Fluoride	0.01	2.21
Bromide	not added	0.93
Nitrite	not added	not detected
Nitrate	not added	4.65
Phosphate	not added	not detected
Sulfate	228.03	150.39
Alkalinity (as $CaCO_3$)	709	491
pH	8.3	8.6
Total Organic Carbon	not added	83

5.2.2.3 Batch Sorption Analysis

Linear and Langmuirian sorption models are commonly used to analyze batch sorption data. As introduced in Chapter 2 §2.3.4, the linear sorption model is specified as:

$$K_d = Cs / Cw \tag{5.1}$$

with K_d representing the non-equilibrium 24 hour distribution coefficient (ASTM Standard D4646, 2003), Cs the solute mass sorbed per unit mass of dry soil (mg kg^{-1}) and Cw, the solute concentration remaining in solution (mg L^{-1}).

The Langmuirian model in turn, is given by:

$$Cs = (bN_{max}Cw) / (1+bCw) \tag{5.2}$$

where b is a constant, and N_{max} the maximum possible sorption by the solid (Langmuir, 1997).

Mass balance calculations accounting for non-adsorptive losses, and initial pore fluid and added OSPW solution chemistries were used to provide context for final, observed, equilibrium concentrations. Analysis was conducted as a two-step process:

1) Is sorption behavior sufficiently represented by either the linear or Langmuirian models, and over what concentration range of OSPW solutions?
2) If neither model is suitable, do other models exist that are able to better account for the observed data?

5.3 Results

5.3.1 Batch Sorption Experiments - Control Case

Fluid-only controls were used to quantify non-adsorptive losses to the system. In cube batch experiments, the difference between the initial stock solution and final control concentrations was less than 10% for each of the principal cations: potassium, sodium and magnesium, but not for calcium. In the traditional (slurried) batch experiments, the difference between the initial stock solution concentration and the final concentration, averaged from the before and after controls, was typically less than 5% for potassium, and sodium. The difference was less than 5% for magnesium in simulated OSPW solutions but less than 10% for magnesium in real OSPW solutions, and the difference was greater than 10% for calcium in both solutions. Together, this suggests that linear partitioning coefficients calculated for calcium may be unreliable (ASTM Standard D4646, 2003). Non-adsorptive losses were accounted for within the mass balance calculations.

5.3.2 Batch Sorption Experiments – Deionized Case

Batch sorption samples created using deionized water are conceptually similar to saturated paste extractions (Janzen, 1993), and serve to identify the distribution of chemical species available to interact with ingressing OSPW seepage. Each of the sediments tested showed that interaction with deionized water led to the dissolution of calcium and magnesium sulfate and carbonate minerals. The concentration of released ions was greatest in the sand channel, with the most abundant cation and anion species being: Ca^{2+} 9.09meq $kg_{dry\ sediment}^{-1}$ and SO_4^{2-} 10.15meq $kg_{dry\ sediment}^{-1}$(averaged across cube and traditional trials, from MW2-38 and MW2-39 combined). Conversely, the concentration of released ions was smallest in the lower clay till and adjacent till/sand interface region. For example, in the latter, the most abundant cation and anion species were: Ca^{2+} 2.12meq $kg_{dry\ sediment}^{-1}$ and alkalinity 2.71meq $kg_{dry\ sediment}^{-1}$ (averaged across cube and traditional trials).

These results support earlier, unpublished findings from saturated paste extractions performed at the University of Alberta on these same sediments (2006). Those studies noted that with increasing depth from the upper clay till through to the base of the Wood Creek Sand Channel: a) there was a general increase in the concentrations of ions released into solution, attributed primarily to the dissolution of calcium and magnesium sulfates, although calcium and magnesium carbonate dissolution was also proposed in some sections of the till; and b) anions became increasingly dominated by sulfate with an increasingly marginal relative contribution attributable to alkalinity.

For the Deionized case, cube batch samples tended to show an identical, albeit subdued response when compared to traditional (disturbed) batch samples; approximately 70% of the magnitude of the traditional samples' response. This likely reflects the fact that sample stirring and shaking inherent to the traditional experiment procedure exposes a greater sediment surface area available for reaction, and may also introduce particle grinding and milling effects (Burgisser et al., 1993), which cause an increased amount of dissolution to occur.

5.3.3 Batch Sorption Experiments – Zero to Full Strength OSPW Cases

Cation sorption was best represented by a linear isotherm only for sodium, and selectively for ammonium and lithium. The sodium response was linear from 0 to full strength (100%) OSPW, with possible evidence of approaching a Langmuirian plateau at full strength. Sediment partitioning coefficients for sodium are tabulated below (Table 5-3). Lithium was well characterized by simple linear desorption for all solution strengths, although only for simulated OSPW experiments. Samples mixed with real OSPW, which includes aqueous lithium, displayed more complicated sorption behavior than samples mixed with lithium-devoid, simulated OSPW. The ammonium response was variable, but showed evidence of linear desorption from 0-100% for simulated OSPW samples and also occasionally for real OSPW, traditional batch samples.

Table 5-3
Linear sorption partitioning coefficients (K_d) for sodium [units: L kg^{-1}]

Sample ID	**Geology**	**Real OSPW, Traditional Batch Experiment**	**Simulated OSPW, Traditional Batch Experiment**	**Real OSPW, Cube Batch Experiment**	**Simulated OSPW, Cube Batch Experiment**
MW3-4	upper glacial till	0.51±0.01	0.57±0.08	0.46±0.03	0.44±0.04
MW3-6	mid glacial till	0.26±0.06	0.15±0.04	0.25±0.03	[a]
MW3-9	lower glacial till	0.58±0.07	0.60±0.03	0.63±0.01	0.73±0.01
MW4-13	till/sand interface	0.12±0.01	0.17±0.07	0.16[b]	0.17±0.15
MW2-38	deep sand channel	0.22±0.01[d]	0.27±0.02[d]	[c]	[c]
MW2-39	deep sand channel	not measured	0.14±0.04[d]	[c]	[c]

[a] data was non-linear
[b] only one sample so no standard deviation possible
[c] sediment too cohesionless for cube batch tests
[d] isotherm possessed non-zero intercepts

For the majority of cation species, including calcium, magnesium and potassium, neither the linear nor Langmuirian models suitably captured the system behavior. For example, although calcium displayed a relatively linear desorption isotherm, it was most often with non-zero y-intercept so that the simple linear model no longer applied. Calcium concentrations from 0-100% OSPW strengths were often clustered about a region apart from the origin, including those from low concentration input stock solutions, reaffirming the presence of soluble minerals, which complicate system behavior beyond simple desorption. Figure 5-1 illustrates an example dataset showing cations both well and poorly characterized by the linear sorption model.

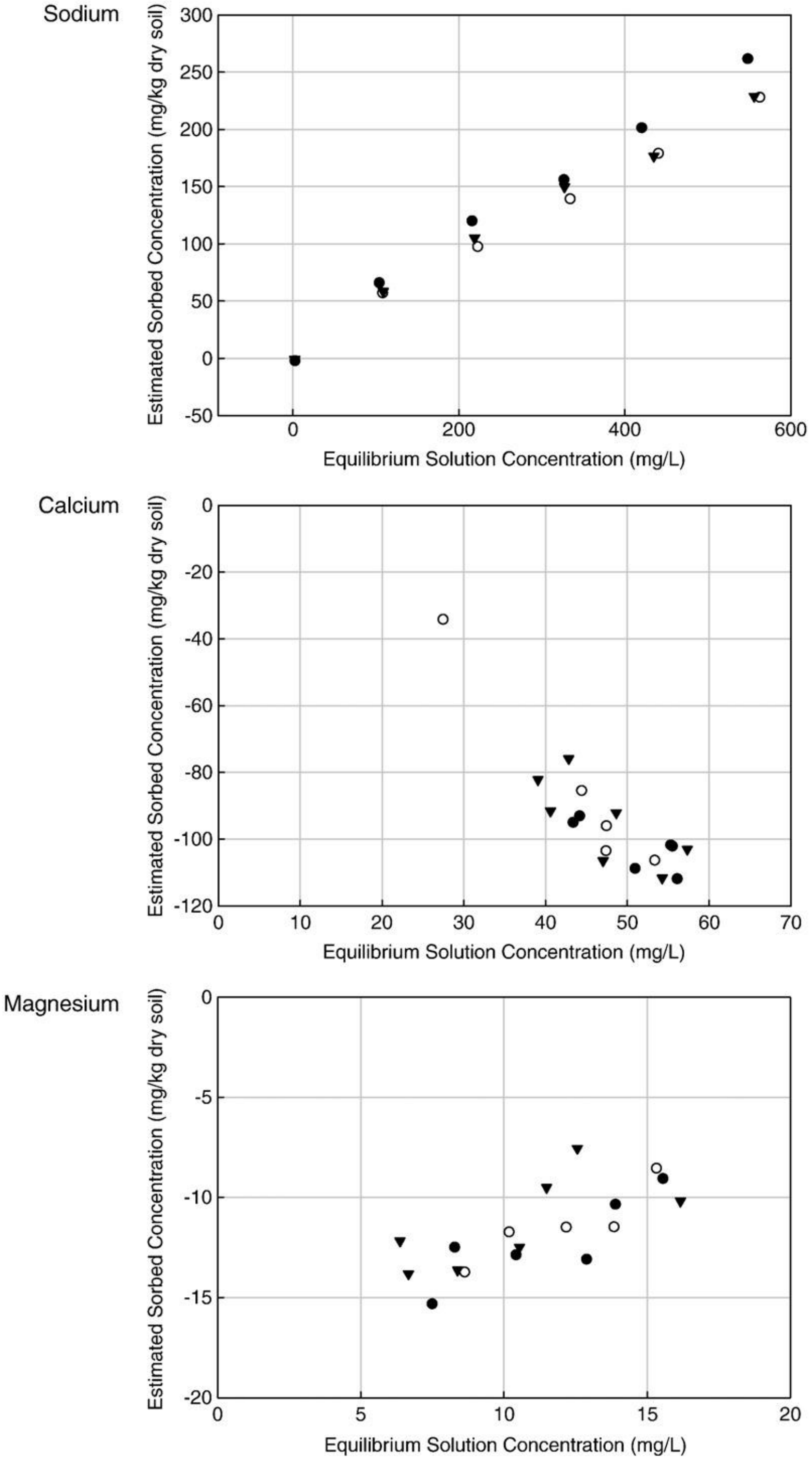

Figure 5-1 Applying linear sorption isotherms to experimental data for MW3-4 (upper till) batch cube samples mixed with simulated process-affected water (sodium – top, calcium - middle, magnesium – bottom). Series shown are method triplicates.

The experimentally-determined, final, equilibrium solutions were modeled using PHREEQC (Parkhurst and Appelo, 1999), to ascertain their degree of saturation with respect to carbonate and sulfate mineral phases. Results consistently found equilibrium solutions to be oversaturated with respect to calcite and dolomite, at all OSPW strengths except, usually, the Deionized case. Solutions from all OSPW strengths tended to be very near the saturation point of magnesite, typically crossing into oversaturation when higher OSPW strengths were mixed with the sediment. All solutions were well undersaturated with respect to gypsum. These results suggest that regardless of OSPW strength, in reaching the equilibrium state, carbonate minerals would be precipitated out of solution, while sulfate minerals, if present, would dissolve, being released into solution.

The trends of equilibrium solution ion concentrations with increasing OSPW strength were examined for each batch sample created (Figure 5-2). Mass balance calculations permitted a comparison of a predicted final concentration (based upon non-adsorptive losses and initial pore fluid and added OSPW solution chemistries) with the observed, final equilibrium concentrations. A positive value for the difference between the predicted and observed values is indicative of uptake of that ion while a negative value represents release, for example, by dissolution or desorption.

Consistent findings were observed in the ion trends - across sediment treatment (cube vs. traditional disturbed), OSPW solution (real vs. simulated) and sediment type (clay vs. sand). Chloride showed evidence of a constant, near zero response across OSPW strengths, suggesting neither its uptake nor further chloride release. Sulfate showed evidence of a constant to slightly increasing extent of release with OSPW strength. The amount of sulfate released was much greater than the chloride response, but smaller than the calcium or magnesium release, except in the Sand Channel. Magnesium typically showed a constant release across all OSPW strengths. Calcium behavior was similar, with a constant to slightly increasing extent of release with OSPW strength, although at approximately twice the magnitude of magnesium. By contrast, sodium showed evidence of increasingly large uptake with OSPW strength, beginning with a near-zero response or very slight release in the Deionized case. The alkalinity response tended to begin with release at low OSPW strengths, quickly switching into often large uptake by high OSPW strengths. Here, again the Sand Channel response was slightly different, showing a more significant initial release and subsequent reduced uptake of alkalinity-based species with increasing OSPW strength.

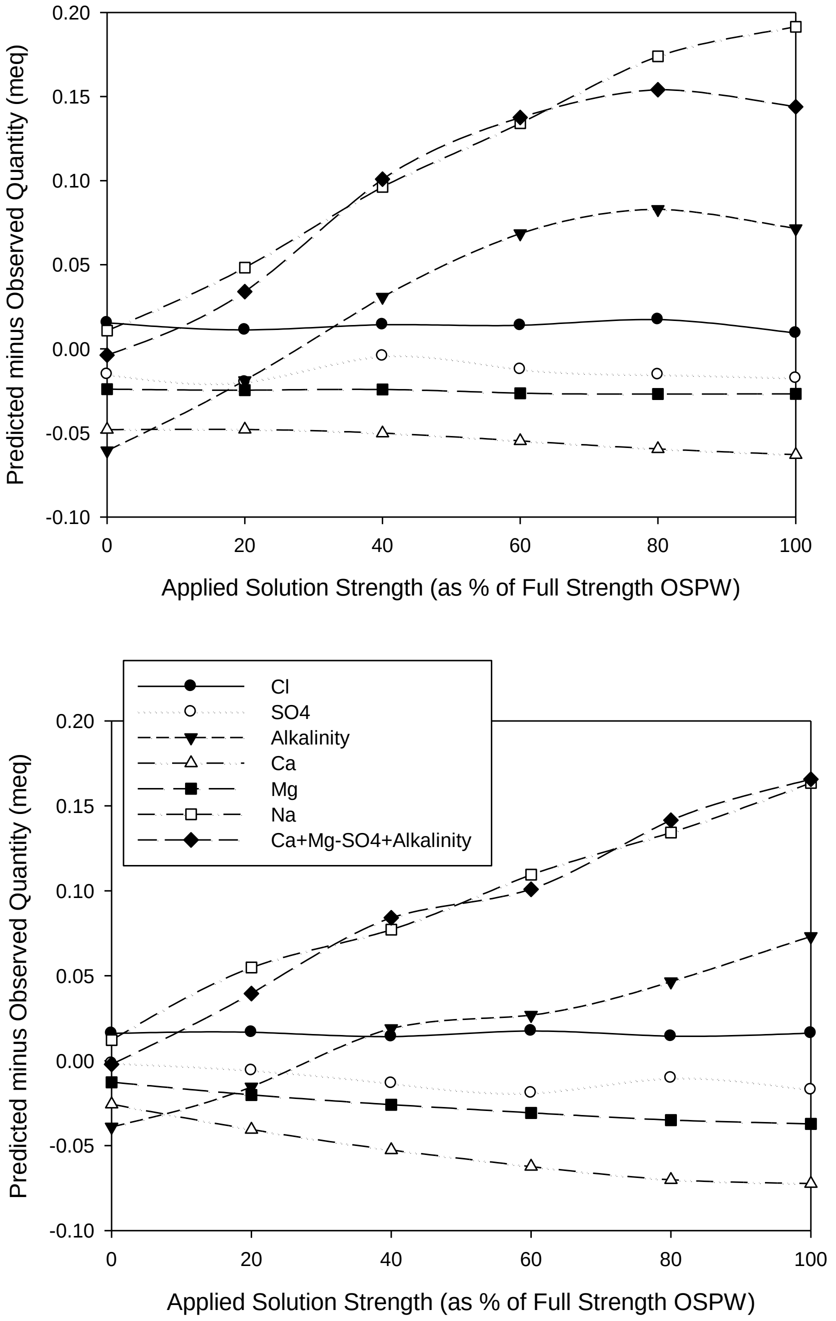

Figure 5-2 Example trends of equilibrium ion concentrations with applied solution strength for MW3-9 (lower till) sediments: (top) simulated process-affected water, traditional batch sample, sample #1 in triplicate series; (bottom) real process-affected water, cube sample, sample #1 in triplicate series).

5.4 Discussion

5.4.1 Linear Sorption

In descending geological order, the linear sorption partitioning coefficients for sodium range from about 0.45L kg^{-1} in the till, to 0.15 in the interface region and 0.19 deep in the Wood Creek Sand Channel (WCSC). This suggests that sodium attenuation may be possible in the till. However, given that the South Tailings Pond may effectively act as a constant contaminant source, attenuation in the till may not be manifested as a reduction in concentration, but rather in retardation of the sodium plume relative to more conservative species such as chloride. Alternately, the WCSC may act as a preferential pathway for seepage from the South Tailings Pond, in areas of limited till coverage. By either transport pathway, it is predicted that most incoming ions in full strength process-water seepage, where sodium concentrations near 600mg L^{-1}, will remain in solution.

Migration of sodium through the till could have an additional consequence. As a reversible process, it is reasonable to expect that the future interaction of ingressing fresh groundwater with the sodium-saturated sediment surfaces, would subsequently desorb sodium back into solution. Thus, glacial till sediments could act as long term sources of sodium following tailings pond closure.

Neither linear nor Langmuirian sorption was able to account for the behavior of most ions in the laboratory experiments; however, important clues to their behavior can be inferred from simple plots of the equilibrium solution response versus input OSPW strength (Figure 5-3). Across all samples, plots revealed strikingly similar behavior between the trends of sulfate and the more abundant calcium - and also to a lesser extent, magnesium. Plots further show that all three species are released and that their concentrations remain relatively constant despite interaction with increasingly concentrated OSPW. Together, these behaviors suggest the dissolution of pre-existing minerals within the sediments:

calcium, and to a lesser extent, magnesium sulfates. Saturation indices of resultant, equilibrated solutions support this interpretation as gypsum was undersaturated at all OSPW strengths. Finally, the minor increases in the amount of calcium and sulfate released with OSPW strength that were observed could reflect a greater extent of dissolution at higher ionic strength.

The chloride response was constant and near zero across OSPW strengths. In other words, the predicted final concentration, based only upon mixing the pore fluid with added stock solution chemistries, suitably predicted the experimental equilibrium solution composition. This suggests that chloride ions are neither uptaken, nor released through interaction with native pore water or sediments and hence that incoming ions, present within a contaminant plume, will remain in solution. Given the high concentrations of chloride in the OSPW (375mg L^{-1}), unchecked, conservative chloride, like sodium, may therefore impact surrounding aquatic environments.

The plotted alkalinity trends, corroborated by the saturation indices of calcite in the equilibrated solutions, suggest that except at low OSPW strengths, alkalinity is lost from the system – believed to be by the precipitation of carbonates. (At low strengths, for example in the Deionized case, both the plots and the saturation indices instead suggest alkalinity release – likely the dissolution of pre-existing carbonate mineral phases).

A proper understanding of the divalent cations' behavior is not immediately obvious from the graphs. Comparing ion trends with increasing OSPW strength, calcium behavior, mild release, is opposite to the strong sorption of sodium, and the amount of calcium and magnesium released is greater than can be attributed to sulfate mineral dissolution alone – both, as ion exchange would require. Confusion arises though, as the trends suggest calcium release, while saturation indices instead propose calcite precipitation. However, if the divalent ions' responses are combined, correcting for the quantity believed released by sulfate mineral dissolution, and using precipitated carbonate (alkalinity) to estimate additional calcium and magnesium that may have been exchanged, then precipitated, the resultant curve (Ca+Mg-SO4+Alkalinity) is almost identical to the sodium response. Therefore, it is hypothesized that calcium and magnesium are released into solution both by dissolution of pre-existing sulfate minerals and by sodium-induced desorption, followed by their limited precipitation as a carbonate mineral phase.

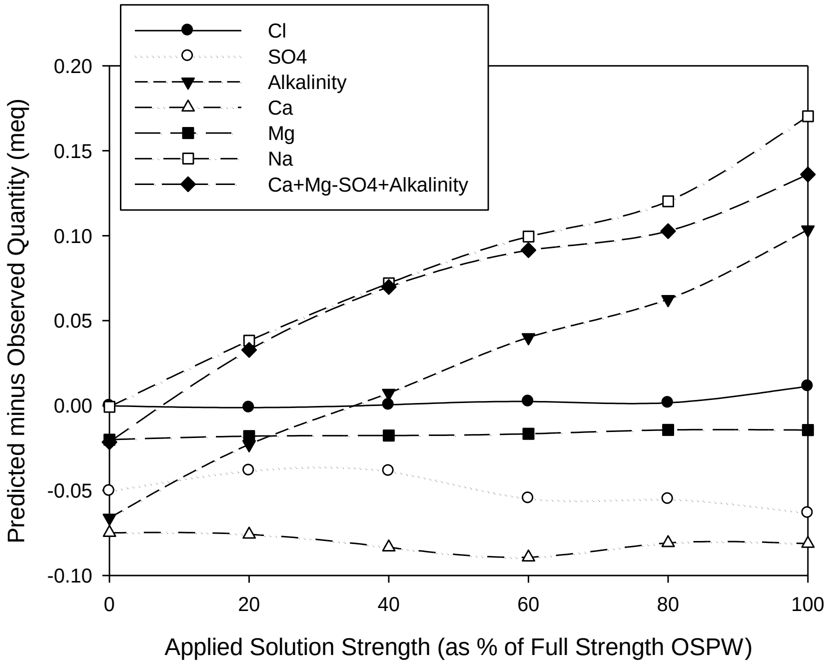

Figure 5-3 Sample dataset depicting ion behavior versus applied solution strength (MW3-4 (upper till), simulated process-affected water, traditional batch sample, sample #1 in triplicate series).

5.4.2 Broader Implications – Is Ion Exchange Theory a Sufficient Model to Predict System Behavior?

Ion exchange between sodium and calcium may be represented as follows:

$$Na^+ + \frac{1}{2}Ca\text{-}X_2 = Na\text{-}X + \frac{1}{2}Ca^{2+} \qquad (5.3)$$

with the equilibrium ion exchange coefficient characterizing the reaction,

$$K_{Na/Ca} = \frac{[Na\text{-}X][Ca^{2+}]^{0.5}}{[Na^{+}][Ca\text{-}X_2]^{0.5}} \qquad (5.4)$$

The square brackets represent activities, or effective concentrations, either in solution or bound to exchange sites (X).

Solution activities at the low ionic strengths relevant to these experiments (I ~ 0.04mol L^{-1}) may be approximated using the Debye-Huckel equation, whereas the activities of exchangeable cations may be determined by following the Gaines Thomas convention. The latter involves calculating the equivalent fraction of each exchangeable cation, compared to the overall exchange capacity (summarized in Chapter 2 §2.3.4).

Different approaches exist for implementing Ion Exchange theory. By measuring the equilibrated concentrations of major cations, both in solution and bound to the solid phase (the latter via desorption experiments), an equilibrium ion exchange coefficient (a K value) can be calculated. This coefficient can then be evaluated against established values for similar sediments. In the present experiments, this approach was not possible since both desorption and initial-most exchangeable cation experiments (Sheldrick, 1984 and USEPA, 1986) were ammonium acetate-based, and found to be confounded by carbonate and sulfate mineral dissolution acting concurrently with exchange reactions. Alternately, ion exchange coefficients (e.g. $K_{Na/Ca}$) may instead be assigned previously established, empirical values, and used to back-calculate estimates of bound exchangeable cation activities. Constrained by these estimated activities, the equilibrated aqueous and solid phase systems predicted by simulations can then be compared against laboratory observations. PHREEQC (Parkhurst and Appelo, 1999) may be used to facilitate this latter approach.

5.4.2.1 Geochemical Modeling of Batch Sorption Experiments using PHREEQC

The United States Geological Survey software program PHREEQC (Parkhurst and Appelo, 1999), in conjunction with the WATEQ4F database (Ball and Nordstrom, 1991), was used to evaluate whether or not Ion Exchange theory could account for the observed response of the batch sorption experiments. Several scenarios were modeled, each sharing the same basic structure. First, a surface of exchange sites was equilibrated with the adjacent groundwater, to derive the initial, assumed in-situ, composition of the exchange assemblage. Previously determined CEC values (Table 5-1) were used to quantify the number of exchange sites, while groundwater chemistry was determined by in-house analysis of field samples collected at the same time and physical location as the sediment samples being modeled. This modeled assemblage was then mixed with 30g of OSPW, mimicking the treatment applied during the batch experiments. At this point, the models deviate from one another. One model included only the steps described above ("PHREEQC no mineral" in graphs). However, earlier saturation index simulations had found carbonate solids to be oversaturated. In order to improve the fit of the modeled calcium and magnesium responses to the experimental data, mineral phase equilibration was therefore added to different stages of the conceptual experiment. First, mineral precipitation of the most oversaturated component, calcite, was simulated by equilibrating the resultant, mixed solution, by itself, with calcite ("PHREEQC Calcite at End"). However, this fails to account for oversaturated magnesium carbonates and furthermore, empirical evidence suggests that naturally occurring minerals exist more often as solid solutions than as pure phases (Appelo and Postma, 2005). Therefore, another approach instead equilibrated the final solution not with the pure phase calcite, but with an ideal solid solution comprised of calcite and magnesite. A potential conceptual shortcoming of these two models, is that mineral equilibration is applied only to the final solution, once it has equilibrated with the exchange sites. A more complicated model was therefore run, in which calcite precipitation was permitted during the mixing reaction of the 30g OSPW with the exchange surfaces, thereby impacting both the solution and exchange site compositions ("PHREEQC Calcite with Mix").

Further improvement to the fit of the modeled response, particularly at low OSPW strengths, required that sulfate mineral dissolution, predicted by earlier analysis but hitherto ignored, be included in the model. In an attempt to achieve the same extent of dissolution as observed in the batch experiments, equilibration with gypsum was included in the models, at the precise saturation indices noted in the laboratory solutions. Gypsum equilibration was included either during the mixing reaction of the 30g OSPW with the exchange surfaces ("PHREEQC CalciteGypsum w Mix"), again, thereby impacting both the aqueous and bound chemistries, or alternatively applied to the final solution in isolation ("PHREEQC SolidSlnGypsum at End").

5.4.2.2 Simulation Results

Ion exchange models including both calcite and gypsum mineral phase equilibration simulated the observed batch experiment data very closely for the major cation species (Figure 5-4). The sodium response was predicted very well, by all of the models attempted.

For calcium, accounting for calcite precipitation improved the fit of the model to the observed data, particularly in terms of shape but often in terms of the magnitude as well (either "Calcite with Mix" or "Calcite at End" vs. "no mineral" model). The refinement of including gypsum equilibration led to further improvement, especially at low OSPW strengths, so that "CalciteGypsum w Mix" and "SolidSlnGypsum at End" both very closely predicted the observed behavior. (Owing to the solution chemistry, the resulting solid solution mineral phase is predominantly calcite-based. Therefore, it is not surprising that these two models' results appear similar, since essentially both equilibrated with calcite and gypsum). The model best fitting the observed data was the "SolidSlnGypsum at End".

For magnesium, concentrations were often under-predicted, regardless of the model. Once again, the combination of shape and magnitude of response were typically best represented by the "CalciteGypsum with Mix" model, and next by the "Calcite w Mix" or "SolidSlnGypsum at End" models.

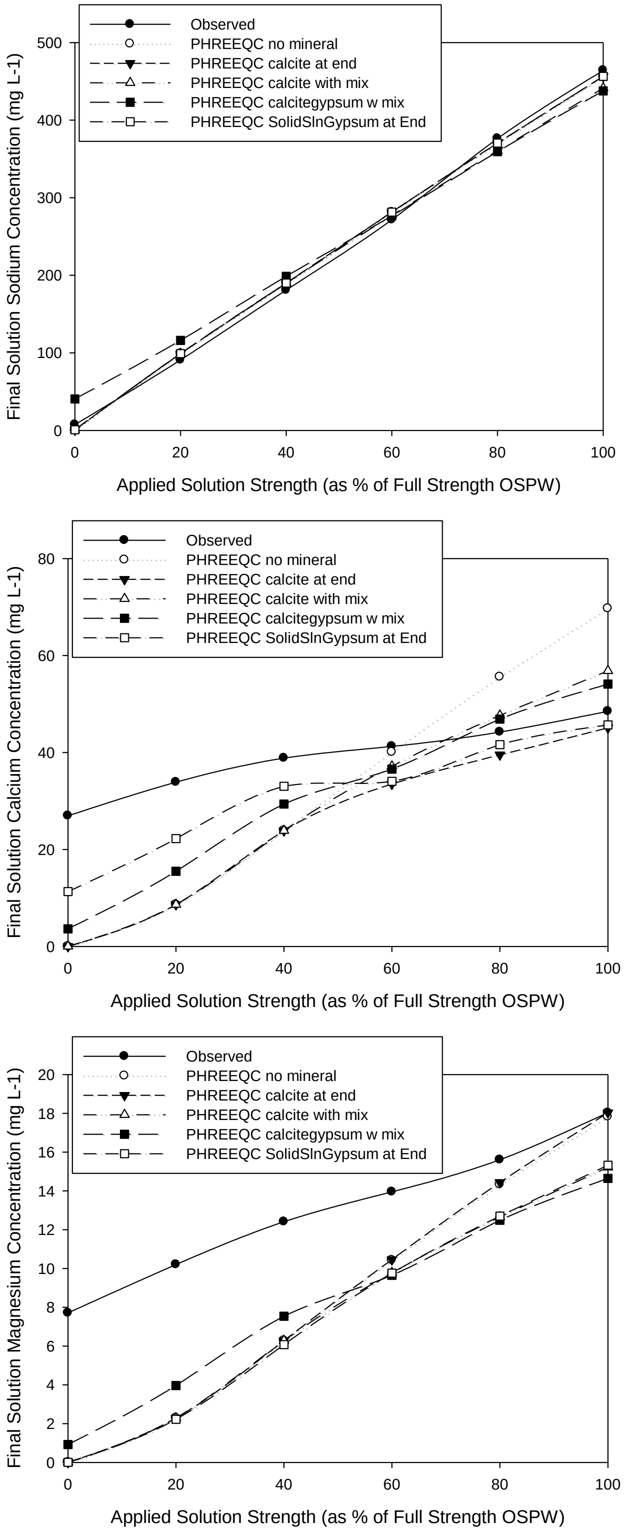

Figure 5-4 Comparison of observed concentrations (average of triplicates) with results predicted by PHREEQC (Parkhurst and Appelo, 1999) models (for traditional batch experiments, sediment MW3-9 (lower till), using real process-affected water; sodium – top, calcium – middle, magnesium – bottom).

The strong similarity between the best models' output and the observed experimental data suggests that particularly for divalent species, Ion Exchange theory, supplemented by carbonate mineral precipitation and sulfate mineral dissolution offers a suitable explanation of the observed calcium and magnesium system behavior.

5.4.2.3 Further Validating the PHREEQC Models

Both hand calculations (not shown – Appelo and Postma, 2005 p256) and experimental data were used to validate the output from PHREEQC (Parkhurst and Appelo, 1999) models during their development.

For calcium and magnesium, the Ammonium Acetate-based batch desorption data were not of use, as they influenced by the same carbonate and sulfate mineral dissolution confounds as observed during recent exchangeable cation experiments on these same sediments. However, there was no such evidence to discredit the sodium desorption data. Experimentally-derived exchangeable sodium fractions were calculated as the milliequivalent-based fraction of bound sodium relative to the cation exchange capacity, using traditional samples from region MW3-4. These observed exchangeable sodium fractions were then evaluated against the corresponding values calculated by the two best PHREEQC simulations (Parkhurst and Appelo, 1999): one with the calcite, magnesite solid solution and gypsum equilibration after mixing OSPW with the exchange assemblage, the other with calcite and gypsum equilibration during the mixing of OSPW with exchange sites. The results show excellent similarity between the modeled and experimental-derived sodium fractions, supporting the assertion that the models are accurately representing system behavior (Table 5-4).

Table 5-4
Batch desorption experiment validation of PHREEQC (Parkhurst and Appelo, 1999) models (MW3-4)

Case	$\beta_{\text{Na, desorb, experimental}}$	$\beta_{\text{Na, Phreeqc, SolidSlnGypsum at End}}$	$\beta_{\text{Na, Phreeqc, CalciteGypsum w Mix}}$
Deionized	0.001	0.013	0.005
20	0.032	0.051	0.048
40	0.061	0.083	0.080
60	0.092	0.110	0.112
80	0.121	0.133	0.138
100	0.157	0.158	0.172

Values in each column were averaged across real OSPW and simulated OSPW samples

5.4.3 Integration of Results

Laboratory results and corroborative geochemical simulations establish a unified conceptual model elucidating the complex geochemical interactions expected to take place when migrating OSPW encounters surficial sediments. In light of observed equilibrium ion trends, exchangeable cation and saturation index data, and PHREEQC ion exchange modeling, it is expected that ingressing OSPW will cause the dissolution of pre-existing calcium and magnesium sulfate minerals. Therefore high concentrations of sulfate, in addition to conservative chloride, are expected to persist. Furthermore, evidence suggests that sodium present in the OSPW, by competitive exchange, releases pre-bound calcium and magnesium into solution. However, aqueous concentrations of these divalent cations are subsequently mitigated by limited precipitation as a carbonate mineral phase. These findings are supported by observations made during recent field studies. At a road salt storage facility in Massachusetts, Ostendorf et al. (2009) noted that an advancing de-icing agent plume with dissolved sodium fraction of 0.975, desorbed calcium and magnesium that were initially bound to glacial till drumlin sediments. Oiffer et al. (2009) investigated the evolution of a OSPW seepage plume in a shallow sand aquifer adjacent to a Fort McMurray oil sands tailings pond. In that study, researchers proposed that observed retardation of bicarbonate migration, relative to conservative chloride, was due to calcite precipitation in the calcite-oversaturated plume. In further affirmation of the present findings, ingressing ammonium and sodium were retarded – believed to be attributable to cation exchange processes.

Meaningful predictions regarding the potential ecological consequences of OSPW seepage reaction products, such as sodium, chloride or sulfate release cannot be made at this time. The present experiments offer qualitative understanding and not quantitative estimates of concentrations of ions that could ultimately appear in downstream waterways. Furthermore, in general, the ecological effects of moderately saline oil sands process-affected water are not well understood. However, research to date suggests that such impacts could include altering the composition of phytoplankton communities (Leung et al, 2001; Leung et al., 2003), mortality and reduced numbers of offspring of daphnid species (Harmon et al., 2003), and osmotic stress (Crowe et al., 2001) and inhibited germination characteristics of plant species (Crowe et al., 2002).

5.4.4 Traditional Batch Method versus Cube Diffusion Batch Method Response

Overall, the results of the cube batch sorption experiments were very similar to those of the traditional set-up, featuring highly disturbed slurried sediment samples, affirming the utility of this newer approach. The magnitude of ion concentrations in the equilibrium solutions was noticeably smaller for cube samples; however, this did not impact the analysis in any apparent manner. For example, the calculated sodium linear sorption partitioning coefficients, the shape and magnitude of ammonium, sodium and lithium linear isotherms, and the shape and magnitude of batch sorption ion trends versus OSPW strength were all essentially the same across both methods. Similarly, Zhang et al. (1998) reported that the adsorption coefficients for benzene using Regina clay were quite similar between the traditional and diffusion sorption methods, at 5.1±1.6mg/L and 4.2±0.9mg/L respectively. Thus the cube diffusion method appears to offer a viable alternative to the standard batch method and a conceptual improvement in simulating sorption behavior within unperturbed geologic settings.

5.4.5 Influence of Organics: Comparing the Simulated OSPW to Real OSPW Response

The results from the batch sorption experiments using simulated OSPW were comparable to those using (real) OSPW collected on-site, with observed differences more likely reflecting parent solution concentration differences than the impact of organics. Sodium linear sorption partitioning coefficients were not statistically different between simulated and real OSPW samples (paired sample t-test, alpha = 0.05). However, equilibrium concentrations tended to be larger within simulated OSPW systems, particularly for sodium, magnesium, chloride and sulfate. Plots of ion trends versus OSPW strength were similar in shape and magnitude across both cases, although sediments mixed with simulated OSPW tended to show greater uptake of sodium and alkalinity and a marginally smaller release of calcium.

These effects are believed to reflect concentration differences between simulated and real OSPW solutions. Simulated stock solutions were created to a maximum of 1.2 times the strength of real OSPW in order to conservatively investigate system response at a greater OSPW concentration than observed to date. Additionally, the simulated solution attempted to broadly recreate real OSPW using only major ions; therefore, certain species' concentrations, such as calcium, were significantly greater in the simulated stock solutions (Table 5-2). The greater sodium concentration in simulated OSPW mixing solutions not surprisingly resulted in greater sodium uptake. Similarly, simulated solutions, with much higher calcium and alkalinity concentrations, were inherently more saturated with respect to calcite (confirmed by saturation index analysis), resulting in greater precipitation of that mineral phase, and hence alkalinity uptake and reduced aqueous calcium concentrations. Together these results suggest a minimal impact of organics as complexing agents upon system behavior.

5.4.6 Next Steps in the Research

Batch sorption experiments allow for easy, rapid determination of ion exchange tendencies and sorption capacities of sediments. However, despite its widespread use, the conventional procedure suffers from several limitations including that sediments are disturbed greatly, reaction times are very short and redox state is not controlled for – all of which limit the representativeness to on-site conditions. These limitations will be minimized by the next stage in this research project, radial diffusion cell experiments (van der Kamp et al., 1996), which will build upon the present findings, evaluating the mitigation or mobilization of major ions and trace metals in the subsurface, in response to the diffusion-driven ingress of OSPW. Radial diffusion cells permit geochemical investigations over longer durations, featuring minimally disturbed sediments and a controlled redox environment. Results from the radial diffusion cells will be additionally interpreted in light of collaborative anaerobic microcosm experiments featuring these same sediments. This will enable better understanding of the biogeochemical processes and end products expected on site.

5.5 Conclusions

This study offers the first detailed laboratory evaluation of the adsorption and ion exchange reactions to be expected, following diffusive ingress of solutes from oil sands process-affected water into surficial sediments in Northern Alberta.

The batch sorption experiments indicate that chloride will behave conservatively, with high concentrations remaining in solution (375mg L^{-1}). The results further reveal that where amply present, glacial till sediments have the capacity to mitigate the high concentrations (600mg L^{-1}) of ingressing sodium (K_d = 0.45 L kg^{-1}), though since the tailings pond is expected to act as a constant contaminant source, mitigation may be realized as a retardation of the sodium plume. Moreover, it should be noted that in localized areas on site, the glacial till coverage is thin (<5m) or altogether absent. Together, it is reasonable to expect that high concentrations of ingressing sodium and chloride ions may remain in solution. Unchecked these species are a potential risk to neighboring aquatic environments.

In addition, this study offers new and important insights into the complex nature of geochemical reactions within glacial till and sand channel sediments in this setting. The analysis shows that the prevalent cations' behavior is not suitably represented by the simple linear sorption isotherm model. Instead, system behavior is shown to be controlled by a combination of competitive ion exchange, dissolution and precipitation reactions. Specifically, the observed ion trends in equilibrated solutions, in conjunction with geochemical simulations, suggest that the ingress of process-affected water will induce the dissolution of pre-existing sulfate minerals. Furthermore, sodium present in the process-affected water will exchange with sediment-bound calcium and magnesium, increasing the divalent ions' pore fluid concentrations, and leading to the precipitation of a calcium-magnesium carbonate mineral phase.

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Chapter 6: Biogeochemical Processes Controlling the Mobility of Major Ions and Trace Metals in Aquitard Sediments beneath an Oil Sands Tailings Pond*

*A version of this chapter has been submitted for publication.
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6.1 Introduction

Increased generation of waste materials resulting from the rapid expansion of the oil sands industry, the approaching closure of the first oil sands mining facilities, public scrutiny, and stricter regulation for environment compliance, have driven science to better understand the environmental impacts of oil sands mining activities. This includes not only aspects of remediation and reclamation (e.g. Kessler et al., 2010, Nix and Martin, 1992), but also the fate and transport of seepage from oil sands tailings ponds. Given the enormity of tailings ponds, perfect containment is not possible. There is therefore great need to better understand the fate and transport of seepage from oil sands tailings ponds en route to downstream groundwater or surface water resources.

Several researchers have studied seepage migration and evolution within OSPW-impacted sandy aquifers (e.g. Yasuda et al. (2010), Gervais and Barker (2005), Oiffer et al. (2009), Tompkins (2009)). However, an increasing number of tailings impoundments will be situated in glacial till, overlying glaciofluvial sand channels. And yet, to this date, no targeted attempts have been made to characterize the attenuation capacity, or biogeochemical evolution and end products as OSPW seepage infiltrates into glacial till prior to reaching these aquifers, thus overlooking a key component of the contaminant transport pathway. Addressing this knowledge gap is a critical step towards protecting aquatic resources.

Accordingly, the objectives of the present study are to:

1) Assess the potential for release (or attenuation) of trace elements and major ions from glacial tills when exposed to OSPW; and to

2) Identify the principal biogeochemical processes involved in controlling pore water and sediment chemistry.

6.2 Materials and Methods

6.2.1 Sediment Samples

The glacial till on site was recently characterized as having a hydraulic conductivity between $3*10^{-8}$and $4*10^{-9}$m s^{-1}, and diffusion was identified as the dominant mechanism of transport (Abolfazlzadeh, 2011). Although it is plausible that the upper till is fractured, and thus a contribution of advective transport cannot be ruled out, diffusive influx of solutes is believed to be a key process controlling the fate and migration of solute contaminants in the glacial till (§3.2.2). Detectable aqueous Mn, mg L^{-1} concentrations of dissolved Fe and tens of mg L^{-1} dissolved organic carbon in the pristine groundwater in the mid to low glacial till indicate anaerobic conditions. Radial diffusion cells (Van der Kamp, 1996) allow for representative modeling of in-situ behavior under these conditions. The cells evaluate water-sediment interactions under strictly diffusive transport, using relatively large and undisturbed sediment samples, in a controlled redox environment.

Sediment cores for this study were collected from various depths in the clay-rich till and into the underlying till-sand channel interface region (Figure 6-1), and care was taken to preserve subsurface redox conditions (site geology, and sample collection and preparation are detailed in Chapter 3 §3.1.2, §3.1.4). Two radial diffusion cells (10cm tall, 9cm diameter) were created from each 1.5m core, creating a pseudo-duplicate pair, since mineralogical variation may occur at this scale. Subsamples of the pristine core, taken adjacent to the radial diffusion cells, were retained for additional geochemical analysis.

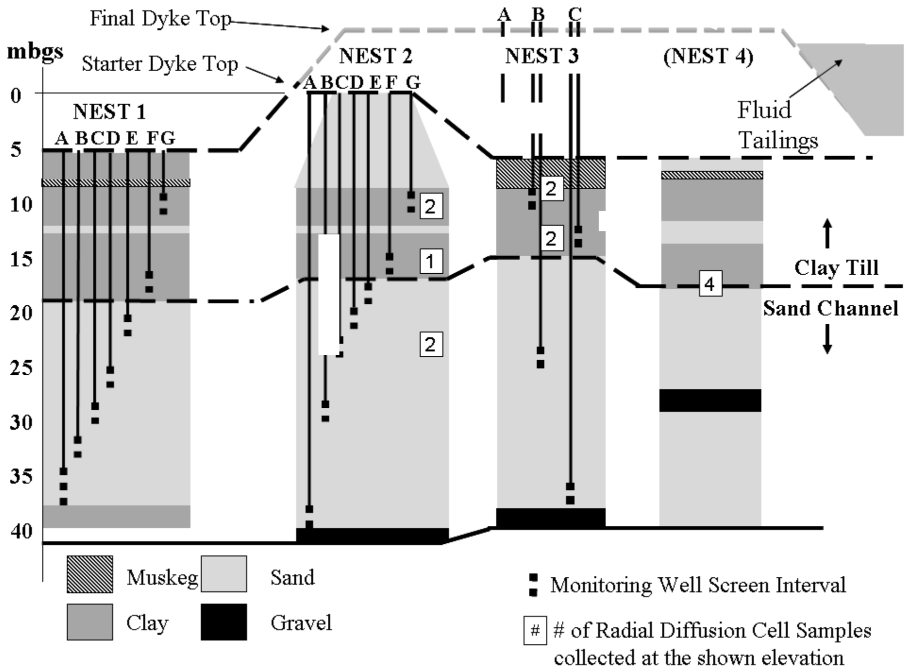

Figure 6-1 Schematic of the groundwater monitoring transect showing the distribution of radial diffusion cell sampling locations in the subsurface. The transect is positioned across the NW dyke wall. *Note: Nest 4 had data loggers initially, which are in progress of being replaced with monitoring wells.*

6.2.2 Radial Diffusion Cells

A reservoir was drilled out of the core section using a 2.2cm stainless steel auger drill bit and fitted with a water-saturated, hydrophilically-coated, 20-40micron porosity, polyethylene tube, allowing water and ions to move freely between the reservoir and sediment core, yet preventing sediment sloughing into the reservoir (Figure 6-2). All metal tools used in construction were disinfected with ethyl ether to prevent cross-contamination of microbial species from one diffusion cell to the next. Handling time was minimized to avoid atmospheric contamination of the samples (core section faces were directly exposed to the atmosphere for about 5-10minutes during reservoir drilling). Constructed cells were placed in an anaerobic glove bag (Sigma-Aldrich Canada Ltd., Canada) filled with Argon gas (4.8 purity (O_2< 5ppm and moisture < 5ppm), Praxair Services Inc., Canada). Also included were a mass balance (SI-4002, Denver Instrument, U.S.A.), portable multi-gas detector (‘Eagle’ series, RKI Instruments Inc., U.S.A.), electrical conductivity and semi-micro pH probes (Microelectrodes Inc., U.S.A. and Thermo Electron Corporation, U.S.A., respectively) and reservoir top-up fluid. Chamber gas was refreshed as needed to maintain an oxygen-free environment.

Each radial diffusion cell was subjected to several treatments: 1) the DI stage, 2) the OSPW stage, and optionally, 3) the GW stage. In the first stage, deionized (or DI) water was added to the reservoir, and the system was allowed to equilibrate. The purpose of this stage was to evaluate the natural pore fluid composition. After equilibration, judged by stabilization of electrical conductivity and pH, the reservoir fluid was withdrawn for chemical analysis and replaced with OSPW, initiating the ‘OSPW stage’. The purpose of this stage was to assess the potential for uptake or release of major ions and trace elements by the sediment-pore water system, following ingress of OSPW. After the second stage, the reservoir fluid of select cells was again withdrawn for chemical analysis, and replaced with uncontaminated groundwater collected on site, to investigate the potential for major ion or metal release into clean groundwater by OSPW-contaminated sediments (‘GW stage’). During each stage, cells were monitored for conductivity, pH and mass changes (e.g. by evaporation); reservoirs were topped up with treatment fluid as required. A set of controls was included to assess potential changes to solution chemistry by inadvertent dissolution (in deionized water) of the reservoir tubing’s hydrophilic coating. (A section of the tubing used to construct each cell was placed in DI water, in a sealed, taped vial (the latter to block sunlight) and placed alongside the cells in the anaerobic chamber for the duration of the DI stage). Equilibration periods for each stage were at least sixty days (durations and cell sizing were guided by preliminary geochemical simulations (PHREEQC (Parkhurst and Appelo, 1999)).

Reservoir contents, sampled at the conclusion of each stage, were analyzed for major ions by Ion Chromatography (Dionex ICS-2000 and Dionex 2500, see

Chapter 3 §3.3.1 for details), trace elements by Inductively Coupled Plasma Mass Spectrometry (PerkinElmer SCIEX ELAN 9000), total alkalinity (potentiometric titration, 0.02N H_2SO_4), pH, and electrical conductivity.

As described by Langmuir, 1997 (p414) "Eh measurements may be stable and meaningful in anaerobic sediments or groundwaters, when species of iron, sulfur, and manganese dominate the redox chemistry, but otherwise are of qualitative value only" (see §2.1.2 for details). Therefore, though it is acknowledged that Eh measurements may be of use in approximating the redox state of a system, in this thesis, without prior knowledge of which dominant redox species could be expected in the final system, Eh measurements were not made. Instead redox state was assessed by evaluating the presence of key aqueous species including SO_4, aqueous sulfides, NO_3, NO_2, NH_4, Mn(II) and Fe. Total iron was measured, though under the anticipated conditions of circumneutral pH and a reducing environment, is reflective of Fe(II) content. Total organic carbon (TOC) was measured in the source OSPW, but not in the equilibrated diffusion cells, as the small reservoir size constrained the number of chemical analyses that were possible. Analytical techniques used are listed in the preceding paragraph, except that TOC and combined H_2S, HS^-, and soluble metal sulfides were analyzed by Spectrophotometry (Hach Company, model DR/2400).

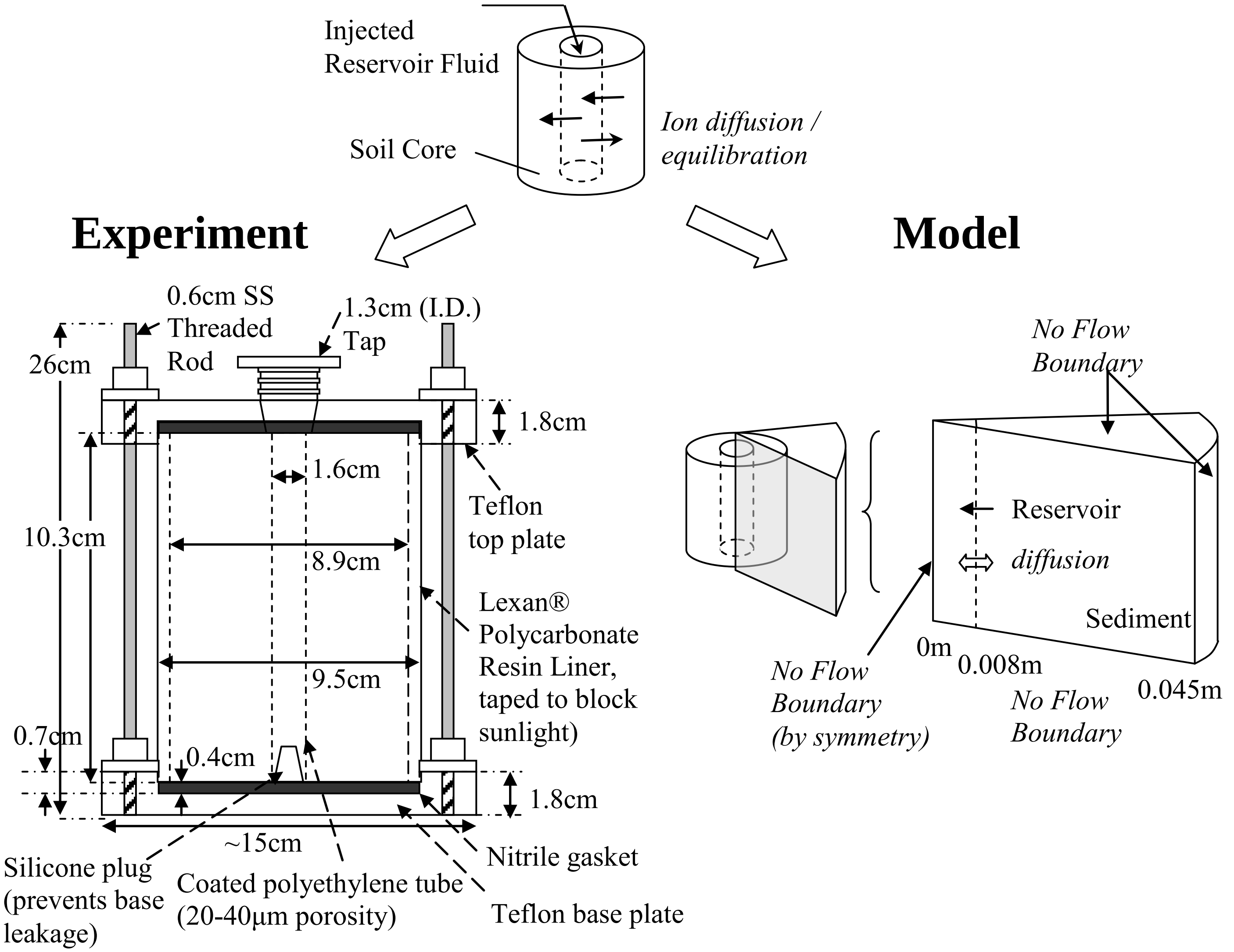

Figure 6-2 Summary of radial diffusion operation, and laboratory and reactive transport construction. The radial diffusion cell is summarized at top. The experimental cell apparatus is shown to the left (side-view) and the conceptual one dimensional model (in radial coordinates) to the right.

6.2.3 Sequential Extraction and other Solid Phase Analyses

A sequential extraction procedure was used to evaluate trace element content within different, operationally-defined sediment phases or fractions. A reagent is applied to the sediment, causing preferential release of trace metals associated with a targeted phase. By repeating the exercise with increasingly harsh reagents, trace metals associated with a series of phases may be each targeted sequentially, in principle, with minimal inadvertent dissolution of non-targeted phases. The procedure used here is based upon Tessier et al. (1979) and described by Herbert, 1997, and quantifies the concentrations of trace elements that are easily exchangeable (termed the F1 fraction), as well as those associated with poorly crystalline metal oxides, hydroxides, oxyhydroxides and hydrous oxides (herein broadly termed oxyhydroxides) (F2 fraction), well-crystallized metal oxyhydroxides (F3), organic matter and sulfides (F4), or silicates and primary minerals (F5). Treatments are summarized in Appendix B, Table B-1. Samples were prepared under oxygen-free conditions. Extract supernatants were analyzed for Fe, Mn, Ag, Al, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Sr, V, and Zn using inductively coupled plasma optical emission spectroscopy (Varian Inc. 725-ES). Pristine sediments, sampled from the same cores, though not necessarily immediately adjacent to radial diffusion cell sections, were also analyzed using petrographic, qualitative X-ray diffraction (Bruker D8 Focus Bragg-Brentano diffractometer) and scanning electron microscopy (Philips XL30) - energy dispersive spectrometry techniques.

6.2.4 Geochemical Modeling of Radial Diffusion Cells

The geochemical evolution in the radial diffusion cells was simulated using the multicomponent reactive transport program MIN3P (Mayer et al., 2002), to identify the reaction processes controlling system behavior. The conceptual model was predicated on the assumption that ion exchange, redox, and select mineral phase reactions would dominate system behavior, based upon batch sorption results, presented in Chapter 5. The following processes were included:

- Degradation of organic matter via a) aerobic respiration, b) denitrification (inhibited by oxygen presence), and c) sulfate reduction (inhibited by oxygen and nitrate presence)
  (It was assumed that dissolved organic carbon (DOC) is not rate limiting, justified by the large pool of DOC in the sediments and OSPW)

- Competitive ion exchange of Na, Ca, K, Mg, NH_4, Fe, Mn, Sr, Ba, Zn, Pb, Cd

- Precipitation-dissolution of calcite (1% initially, by mass), dolomite (4% by mass, dissolution only), mackinawite (precipitation only). Other minerals present were deemed unlikely to influence groundwater composition on the time scale of interest. (Saturation indices for all possible mineral phases were calculated using PHREEQC (Parkhurst and Appelo, 1999) and the WATEQ4F database (Ball and Nordstrom, 1991))
  (Note: Sulfate reduction and the subsequent formation of sulfides is a complex process involving the reduction of sulfate to thiosulfates, elemental sulfur, and sulfide. This series of reactions is difficult to parameterize, in particular under field conditions, Due to its higher solubility and lower degree of crystallinity, mackinawite tends to precipitate first from a supersaturated solution and is therefore most appropriate to describe sulfide solubility. It is acknowledged that mackinawite will mature over time to form more crystalline and less soluble phases, such as pyrite.)

Trace element behavior was modeled using ion exchange reactions as a surrogate for the suite of complex water-rock interaction processes expected to be involved. The inclusion of surface complexation and additional mineral reactions was only deemed necessary, if the chosen approach yields an unsatisfactory fit to observational data.

For simplicity, iron and manganese oxyhydroxides were not included within the model. Evidence presented by the data suggests that the contribution of these phases is small; therefore they have been neglected. Testing of this working assumption, through inclusion of these phases within the model, will be left to future work.

The physical structure was represented using a 2D model in radial coordinates (Henderson et al, 2009), and consisted of a fluid reservoir and fully saturated sediment core (Figure 6-2). All boundaries were impermeable and transport in the cell was governed by diffusion (free-phase diffusion coefficient: $1x10^{-9}m^2 s^{-1}$). Tortuosity in the sample was estimated, based on the approach by Millington, as a function of porosity (Millington, 1959). Porosity and (dry) bulk density values were determined empirically for each radial diffusion cell (mean values 0.24 and 1.89g cm^{-3}, respectively). Cation exchange capacities were assessed on pristine samples, taken adjacent to each cell, using both Methylene Blue (AFNOR, 1993) and Ammonium Acetate (USEPA, 1986) extractions (overall mean across till and interface samples: 6.8meq $100g^{-1}$). (Note: Methylene Blue and Ammonium Acetate methods performed best, of the four methods tested, in evaluating cation exchange capacity in sediments rich in carbonates (Chapter 4)). Effective maximum reaction rates for calcite, dolomite, nitrate reduction and sulfate reduction, were determined by calibration, to achieve the best fit to empirical observations. Inhibition constants were derived from literature values (Table 6-1).

Table 6-1
Inhibition terms (due to the presence of aqueous components) used in the specification of kinetically-controlled intra-aqueous reactions in reactive transport models

Inhibiting species	**Inhibition constant [mol L^{-1}]**
Reaction = CH_2O degradation - aerobic respiration - Monod-kinetics	
none	none
Reaction = CH_2O degradation - denitrification - Monod-kinetics	
O_2(aq)	$6.3*10^{-6}$
Reaction = CH_2O degradation - sulfate reduction - Monod-kinetics	
O_2(aq)	$3.1*10^{-5}$
NO_3^{-1}	$1.6*10^{-5}$

The model was run in two stages to mimic the laboratory experiment: the DI stage (reservoir = deionized water; sediment pore water chemistry = experimentally-determined, baseline pore fluid chemistry; reaction time = 60d) and the OSPW stage (reservoir = OSPW; sediment pore water chemistry = DI stage model (equilibrated) output; reaction time = 75-77d).

Model output (concentrations in the reservoir) was compared to laboratory observations to assess whether or not the reaction processes included were able to reproduce the final reservoir water composition. Large dissimilarities would suggest other processes (e.g. reductive dissolution of metal oxyhydroxides) need be considered.

6.3 Results

6.3.1 System Inputs: Native Pore Fluids Before OSPW Intrusion

The DI stage identifies the baseline pore fluid chemistry that will react with ingressing OSPW. In the pristine pore fluids, the major cations, in descending order of presence, were: Ca>Mg>Na>K>NH_4, with total alkalinity (dominantly HCO_3) and SO_4 the principal anions (Appendix B, Table B-2). Nitrogen was predominantly present as NH_4. Fe, Sr, Si and Mn were detected throughout the subsurface, and other elements only in select regions: Cr (upper till), V (mid till), Ni and Rb (low till), B and Mo (low till + transition zone) (Appendix B, Table B-3).

6.3.2 System Inputs: Solid Phase Geochemistry of Pristine Aquitard Sediments

Among operationally defined fractions, the easily exchangeable (F1) trace element fraction contained the lowest percentage of total extractable elements (Table 6-2), with only Ag, As, Cd, Co, Cu, Sb and V having ~10% or more of their presence in this fraction. (Note: percentages calculated as the mg kg^{-1} concentration in a particular fraction, versus the total mg kg^{-1} presence of that species in the sediment) Instead, the poorly crystalline and well crystallized Fe oxyhydroxide fractions (F2 and F3) contained a substantial portion of the total trace element content. In particular, Al, Fe and Mn F2 fractions ranged from below detection to 59%, 41 to 78% and 62 to 82%, respectively. Also with relatively high F2 presence were Sr, Ba, Cr, Ni and V. By comparison, the F3 fraction was characterized more by As, Cd, Cu, Pb, and Sb presence. Release from the organics and sulfides (F4) fraction is not supported, since only a minor portion (generally <10%) of trace elements were classified as belonging to this fraction. Moreover, the targeted phase is thought to consist of stable humic substances, which release limited quantities of trace elements, over long periods of time (Garcia-Miragaya and Sosa, 1994). Finally, a very large component of elements tended to reside within the stable primary mineral and silicate (F5) fraction; however, these elements are thought to reside in the mineral’s crystalline lattice, and are thus unreactive and immobile (Garcia-Miragaya and Sosa, 1994), and released by weathering.

Table 6-2
Percent fractions of extractable trace elements in pristine sediment samples measured by in-house sequential extraction procedure (SEP) analysis.

Sample	Fn[a]	%Ag	%Al	%As	%Ba	%Cd	%Co	%Cr	%Cu	%Fe	%Mn	%Ni	%Pb	%Sr	%V	%Zn
Upper Till	F1	42.9	0.25	9.9	4.90	16.4	11.8	5.67	13.0	0.12	1.82	7.28	7.94	4.61	12.8	5.80
	F2	bdl	52.3	14.4	62.1	11.3	13.7	22.2	21.9	68.8	75.6	25.7	20.1	57.8	20.3	15.4
	F3	57.1	1.62	31.3	7.84	24.7	16.1	8.25	18.2	5.00	4.79	9.22	21.5	4.22	10.7	5.67
	F4	bdl	0.50	10.8	3.27	8.36	11.2	8.25	11.6	0.36	1.16	6.80	8.88	1.08	12.4	9.68
	F5	bdl	45.5	33.6	21.9	39.3	47.2	55.7	35.3	25.7	16.7	51.0	41.6	32.3	43.8	63.4
Mid Till	F1	42.9	2.12	9.57	4.87	16.1	9.82	5.21	12.1	0.12	1.81	5.37	5.75	2.86	23.5	5.18
	F2	bdl	bdl	13.7	59.2	10.0	15.3	25.5	19.2	77.6	82.3	31.2	20.8	66.9	19.4	14.9
	F3	57.1	56.2	31.6	11.6	27.1	17.2	9.90	19.7	12.6	8.68	10.2	20.4	7.31	10.2	5.93
	F4	bdl	8.72	11.1	4.12	8.21	11.0	8.33	12.9	0.59	1.45	6.83	8.41	1.75	11.7	10.1
	F5	bdl	32.8	34.0	20.2	38.6	46.6	51.0	36.1	9.00	5.79	46.3	44.7	21.1	35.2	63.8
Low Till 1	F1	42.9	0.19	9.3	9.86	16.5	9.4	6.77	11.7	0.10	1.30	5.00	8.55	3.74	10.8	11.4
	F2	bdl	34.2	10.9	42.6	8.99	13.8	12.0	14.1	49.0	68.6	12.3	12.8	56.1	20.4	17.4
	F3	57.1	0.77	30.2	7.04	27.7	14.9	6.02	18.4	1.59	3.72	7.31	20.1	1.76	8.75	4.49
	F4	bdl	2.90	10.7	8.10	8.63	11.6	7.14	11.7	3.97	2.60	9.23	9.83	4.07	10.8	15.9
	F5	bdl	61.7	39.1	32.7	38.8	50.8	68.4	44.1	45.4	23.8	66.5	49.1	34.3	49.6	50.8
Low Till 2	F1	42.9	0.3	10.2	7.34	19.7	12.3	7.69	11.5	0.23	1.58	7.60	8.43	12.0	13.9	5.52
	F2	bdl	43.9	12.0	48.6	14.2	10.9	22.4	16.8	40.8	79.8	21.6	16.3	66.9	16.8	13.0
	F3	57.1	0.97	24.8	6.56	27.6	16.7	8.97	16.6	2.05	2.11	9.36	19.3	3.08	9.85	5.59
	F4	bdl	1.25	11.6	4.25	9.8	16.7	10.3	12.7	1.87	2.63	15.2	12.0	2.01	13.5	10.7
	F5	bdl	53.7	41.3	33.2	28.7	43.5	50.6	42.4	55.1	13.9	46.2	44.0	16.1	46.4	65.5
Upper Transition	F1	28.6	0.46	9.35	6.53	15.8	12.1	5.1	11.9	0.35	2.15	6.70	8.13	9.51	14.6	5.74
	F2	28.6	31.2	15.0	44.2	19.8	15.7	11.2	15.7	48.8	73.7	24.0	10.0	71.8	11.0	8.52
	F3	42.9	3.02	26.7	10.6	23.4	17.9	8.12	18.2	4.90	5.11	10.6	25.0	5.22	11.4	6.17
	F4	bdl	4.17	11.0	5.03	12.6	13.6	8.12	12.9	2.94	2.96	10.6	13.1	1.74	14.2	11.1
	F5	bdl	61.0	37.9	33.7	28.4	40.7	67.5	41.3	42.6	16.1	48.0	43.8	11.7	48.8	68.6
Lower Transition	F1	42.9	1.09	9.9	9.15	18.3	13.4	8.45	12.4	1.04	4.55	9.76	6.18	13.0	14.3	5.58
	F2	bdl	33.5	11.7	28.9	9.76	14.2	14.1	15.8	58.0	61.6	19.5	12.9	53.9	15.5	11.8
	F3	57.1	2.91	30.2	10.6	26.4	18.9	10.6	18.7	2.57	14.1	13.8	23.6	4.24	10.9	5.79
	F4	bdl	2.04	11.7	13.4	9.35	13.4	11.3	12.6	3.94	3.5	10.6	11.2	4.85	14.0	10.7
	F5	bdl	60.4	36.5	38.0	36.2	40.2	55.6	40.5	34.5	16.2	46.3	46.1	23.9	45.3	66.3

[a] Fn = Fraction

Ion exchange and mineralogical properties were assessed in earlier work, with exchangeable cations found to consist of Ca>Mg>K>NH_4>Na in decreasing abundance. X-ray Diffraction (XRD) (AGAT Laboratories, Edmonton, Canada) found the clay fraction in the till to be largely kaolinite and illite based (both 40% by mass), while notable mineral phases included calcite (1%), dolomite (5%) and pyrite (1%) (Chapter 4 §4.2.2).

Petrographic, and in-house qualitative XRD and Scanning Electron Microscopy (SEM) – Energy Dispersive Spectrometry (EDS) analyses (conducted by S. Haque at the University of British Columbia), indicated that the sediment samples were predominantly composed of single quartz grains, with much less abundant fragments of quartz aggregates, single plagioclase grains, single K-feldspar grains, and aggregates of plagioclase, K-feldspar and quartz. The samples contained moderately abundant amounts of limestone and minor amounts of other rock types, mainly chert and diorite. Minerals which occurred in minor amounts as single mineral grains included the iron oxides and hydroxides limonite, hematite, and ilmenite and iron sulfides pyrite and arsenopyrite (XRD, SEM-EDS results are summarized in Appendix B, Table B-4).

6.3.3 System Output: the Effects of Diffusive Ingress of OSPW

The introduction of OSPW into the native glacial till sediment-pore water system, resulted in the release of Ca, Mg, and K, and sequestration of F, NO_2, NO_3, SO_4, Li and Na (Figure 6-3, Appendix B, Table B-2). Phosphate was not detected in any samples. Uncharacteristically, Cl was not conservative and showed consistent evidence of release. Ammonium was released in the upper and mid till, but taken up in lower areas, while alkalinity displayed some variability, but was typically taken up. (See Appendix B, §B.1 for charge balance and control results)

Trace element behavior was more complicated (Appendix B, Table B-3), though reaction with OSPW tended to result in the release of Al, B, Ba, Mn, Pb, Si, and Sr, and uptake of Mo. Cd, Cr, Cu, Rb and V showed only sporadic release or uptake in the subsurface; in most samples tested the predicted value was below the detection limit and the observed output was itself below detection. Fe had a variable response throughout the subsurface. Ag, As, Be, Co, Cs, Ga, Ni, Se, Tl, U were not predicted from system inputs, nor observed in equilibrated samples.

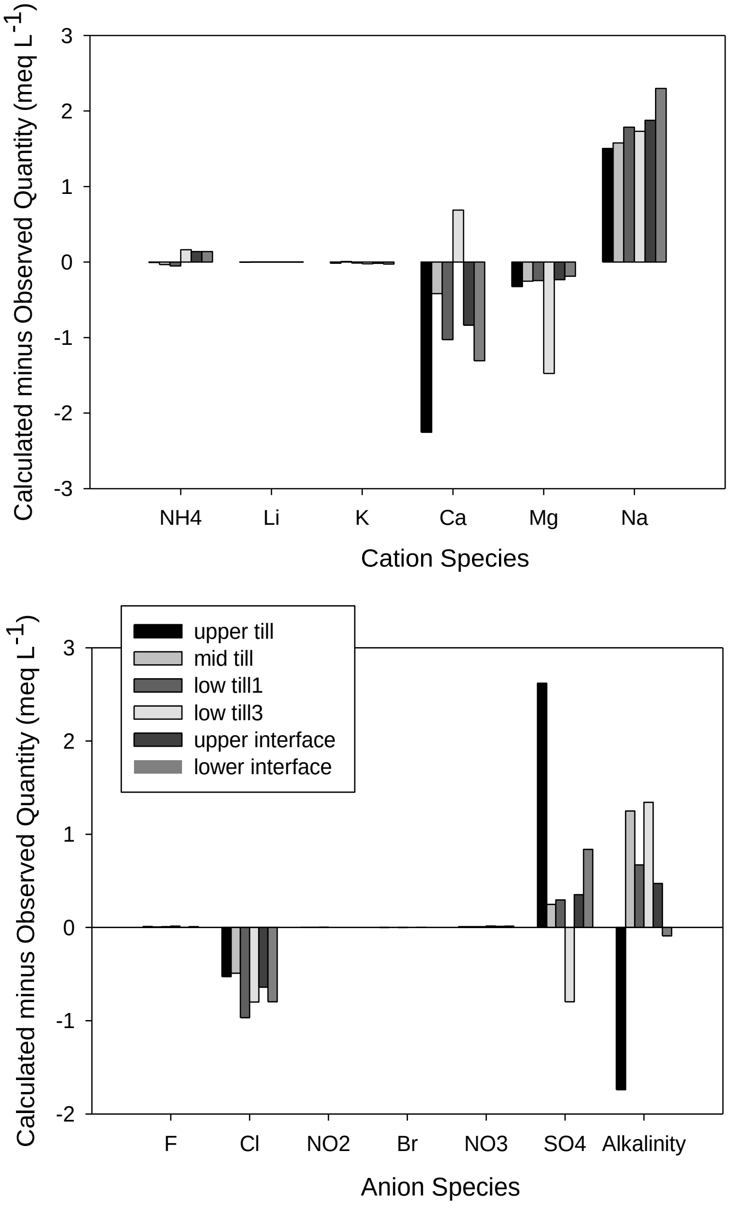

Figure 6-3 Cation (top) and anion (bottom) response following reaction between process-affected water and native till sediments and pore waters. The "calculated" quantity mixes all inputs, assuming no reactions take place. A negative (calculated minus observed) value indicates release, while a positive value indicates uptake.

6.3.4 System Output: the Effects of Diffusive Ingress of OSPW on Isotopic S and C Signatures

Constrained by the very small reservoir sample volume, few samples had sufficient amount of sulfate or carbon to permit isotopic analysis. For the samples tested, results suggest that exposure to OSPW led to an enrichment of ^{32}S, relative to ^{34}S, within the remaining SO_4 reactants. In addition, exposure to OSPW led to an enrichment of ^{12}C dissolved inorganic carbon, relative to ^{13}C, in the produced alkalinity (Table 6-3).

Table 6-3
Isotope analysis of 34/32S (sulfate) and 13/12C (dissolved inorganic carbon) in select aquitard samples

Sample ID	$\delta^{34}S$	$\delta^{13}C_{-DIC}$
Upper Till	not enough sample	-7.9
Upper Till (duplicate radial diffusion cell)	-22.5	-9.5
Low Till 3	-29.1	not enough sample
Control (Reference OSPW)	9.3	-4.0

Note: For two samples, the available sample size/concentration was insufficient for analysis
Note: Precision and accuracy as 1 sigma of (n=10) lab standards are: 0.3for $\delta^{34}S$ and 0.2 for $\delta^{13}C$.
Note: Sulfur isotopes were quantified within aqueous sulfates (inputs to the system $SO4^{2-}$ – S^{2-} redox reaction) and carbon in DIC (thus outputs of system oxidation of organic carbon reactions)

6.3.5 Changes to the Contaminated System by Future Entry of Fresh Groundwater

After equilibration with OSPW, the diffusion cell reservoir fluid was replaced with pristine groundwater (Appendix B, Table B-5), in order to examine how the OSPW-contaminated system may change, following diffusive influx of fresh groundwater in the future. The addition of groundwater resulted in the release of NH_4, Li, K, and Mg; and uptake of Ca, Na, Cl, NO_3 and SO_4 (Figure 6-4). The exception was the single mid till sample, which generally showed uptake of all species.

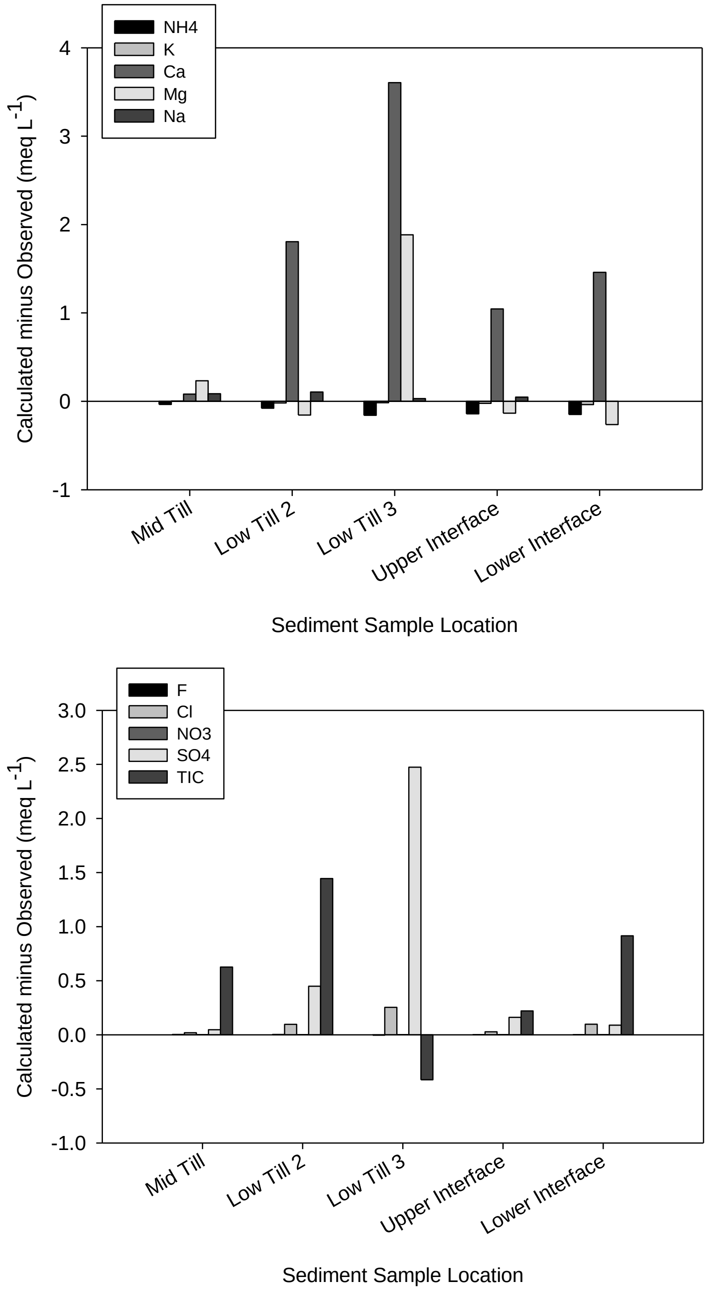

Figure 6-4 Cation (top) and anion (bottom) response of OSPW-impacted pore fluids and sediments to ingress of fresh groundwater. The “calculated” quantity mixes all inputs, assuming no reactions take place. A negative (calculated minus observed) value indicates release, while a positive value indicates uptake.

6.4 Discussion

To analyze the data, laboratory observations were compared to both a) calculated equilibrium concentrations (from mass balance calculations, given the system inputs, but assuming no reactions take place), and the b) results from the reactive transport modeling. These three values are referred to hereafter as “observed”, “calculated” and “simulated” values respectively (Figure 6-5).

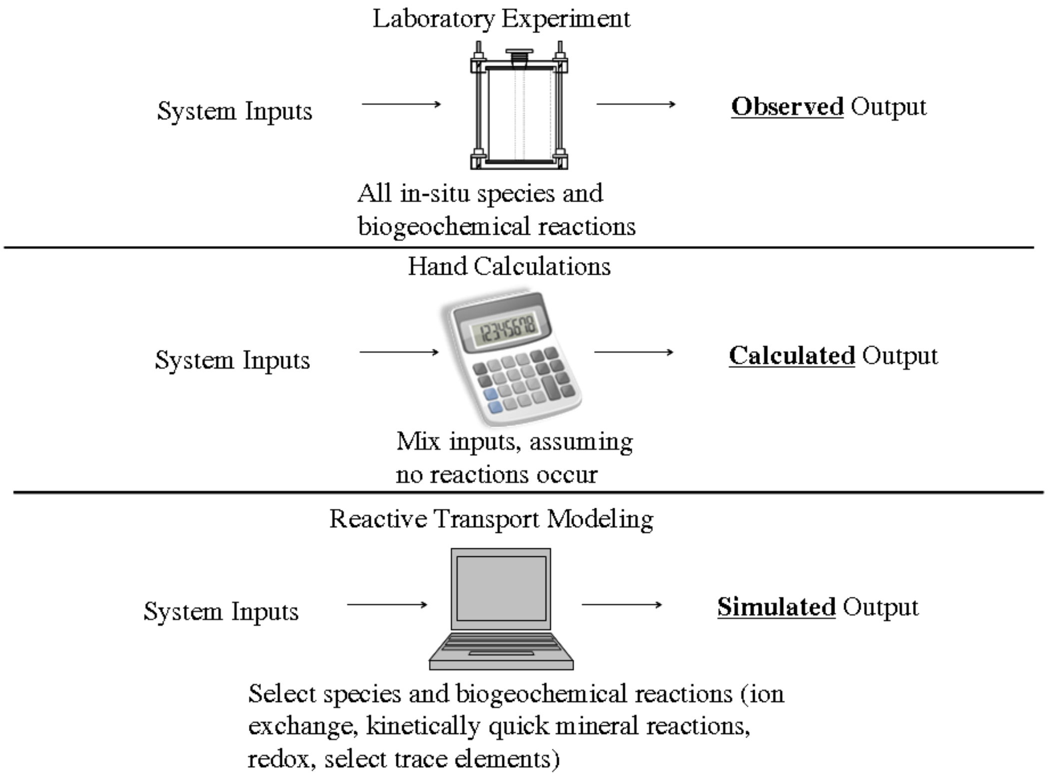

Figure 6-5 Process diagram identifying the different datasets used in the analysis of radial diffusion cell behavior.

6.4.1 Release (or Attenuation) of Major Ions by Ingress of OSPW

The radial diffusion experiment predicts that Na in the OSPW will be mitigated by ion exchange with sediment-bound Ca, Mg and K, in turn, releasing these cations into solution. Simulations closely predicted Ca, Mg, Na and K concentrations (within 11±8% relative to the initial solution), confirming that the behavior of these cations is controlled by ion exchange (Figures 6-6 and 6-7). Small discrepancies between modeled and observed results may be related to minor infidelity in modeled inputs, such as carbonate mineral presence, cation exchange capacity or calibrated mineral reaction rates. Saturation indices showed that all equilibrated solutions were oversaturated with respect to calcium and magnesium carbonates, reaffirming previous results that exchanged divalent cations may not remain in solution but rather precipitate out as a carbonate mineral phase (Chapter 5). This is also consistent with the observed decline in alkalinity. Extending these results to in-situ conditions where the limited, fixed volume of OSPW in the diffusion cell reservoir is replaced with the constant source of OSPW in the pond, it is hypothesized that Na uptake will be manifested by retardation (and not decline in concentration), while displaced Ca and Mg may appear as a 'halo' preceding the other contaminant species.

Ammonium may have been influenced both by ion exchange and reduction reactions. For example, nitrite was observed (no nitrate was present) only the upper and mid till of DI stage solutions and neither species was detected following the OSPW stage, suggesting reduction of N species may have been a contributing factor to NH_4 release at these elevations. The results of reactive transport modeling, generally showed close similarity to the observed concentrations in the glacial till (9±5% difference) implicating a dominant role for ion exchange. (It should be noted that NH_4 was predicted by the model, but not observed, in select low till and interface samples, though this discrepancy is attributed to poor performance of the IC machine for those analyses).

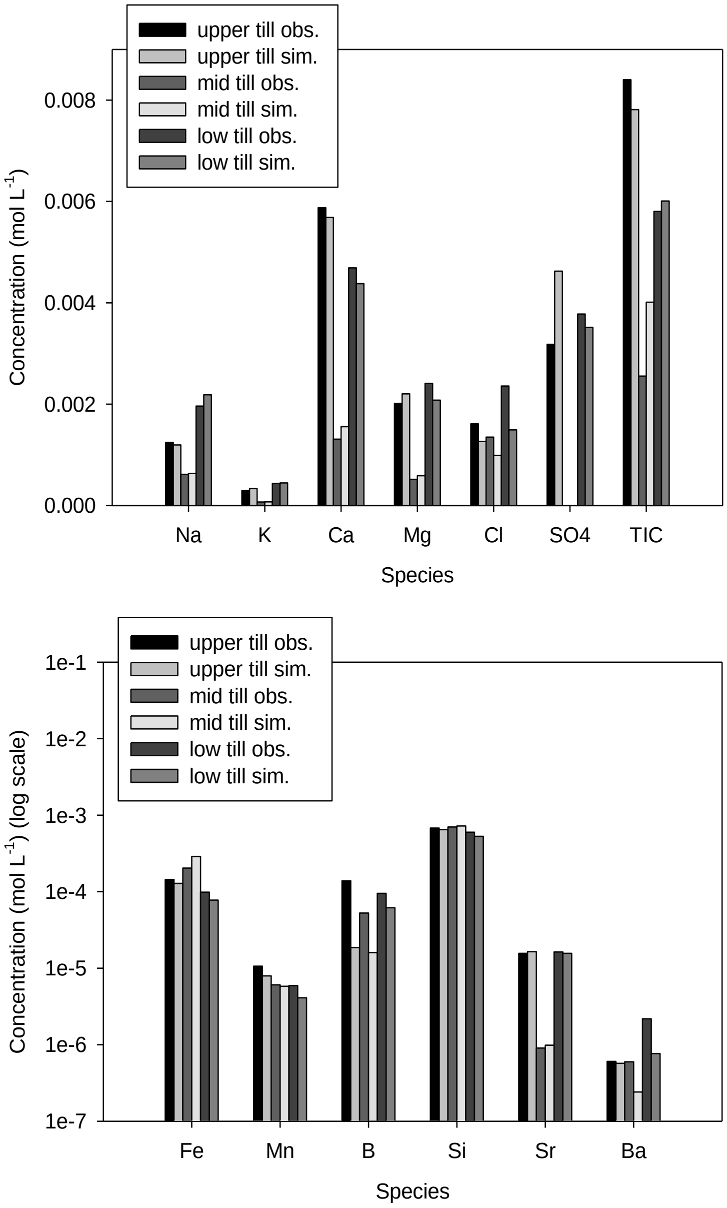

Figure 6-6 Comparing simulated to observed concentrations of major ions (top) and select trace elements (bottom), in the glacial till, following equilibration with OSPW.

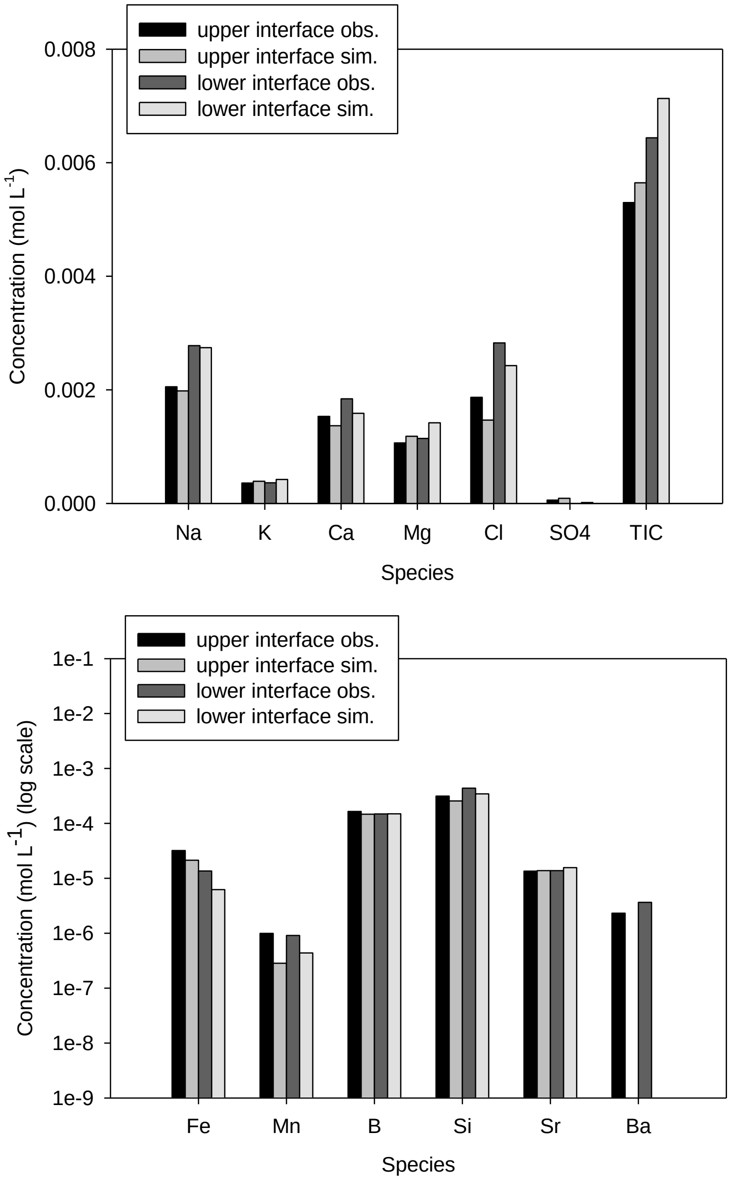

Figure 6-7 Comparing simulated to observed concentrations of major ions (top) and select trace elements (bottom), in the glacial till-sand channel transition zone, following equilibration with OSPW.

High concentrations of sulfate in OSPW were mitigated, with evidence that sulfate reduction has taken place. In the diffusion cells (OSPW stage), not only were concentrations of sulfate lowered, but aqueous sulfides were detected at concentrations of approximately 2mg L^{-1}. This agrees with recent observation of SO_4 attenuation in OSPW seepage from a field-scale infiltration pond on site (Abolfazlzadeh, 2011). Moreover, modeling revealed that solutions were undersaturated with respect to sulfate minerals including gypsum or anhydrite, but saturated with respect to the sulfide mineral phases FeS, FeS_2, and ZnS. This is in agreement with mineralogical data which detected pyrite and arsenopyrite, even within pristine sediments. Together, these observations are consistent with sulfate reduction and sulfide precipitation having taken place.

Select samples (post-OSPW interaction) were sent to the University of Calgary Isotope Science Lab (Calgary, Canada), to assess stable isotope fractionation among S and C species. To conserve energy, during oxidation of organic carbon, microbes preferentially break ^{12}C-^{12}C bonds, then ^{12}C-^{13}C and then ^{13}C-^{13}C; as a result, the remaining organic carbon (the reactant) will be rich in ^{13}C, while dissolved inorganic carbon (the product) will be rich in ^{12}C. This also extends to sulfur, so that microbial mediated sulfate reduction would be expected to result in enrichment of ^{34}S in the sulfate reactants, and of ^{32}S in the sulfide products. In this light, relative to OSPW, radial diffusion cells showed enrichment of ^{12}C in the produced alkalinity, indicative of biodegradation of carbon. (Constrained by a limited radial diffusion reservoir, DOC was not measured in the equilibrated cells and thus, at present, the source of degraded carbon (DOC or FOC) is not known). Sulfate signatures however, showed unexpected enrichment of ^{32}S (again, in the sulfate reactant). Evidence contradicts oxidation of pyrite as the cause, as this is in clear disagreement with the large decrease in aqueous SO_4 concentrations, and the appearance of reduced aqueous sulfides, consistently observed in all radial diffusion cells. The shift in isotope abundance may represent evolution from a typical surface water signature in this region (which the measured OSPW signature had: *J. Birks, personal communication*) towards the natural background groundwater signature, as pore waters and OSPW mix in the diffusion cell. A follow-up study has been scheduled to compare the isotopic S composition in pristine groundwater, OSPW, and OSPW-impacted groundwater at the STP, to elucidate this complex sulfur biogeochemistry.

Analysis indicates that total inorganic carbon (TIC) response is regulated by potentially competing organic carbon reduction and precipitation-dissolution reactions. Observations indicated the uptake of total inorganic carbon (TIC) across the till and interface region (with some variability in response amongst samples), except for within the upper till. Uptake is in agreement with saturation index analysis which found carbonates (e.g. $CaCO_3$, $(Ca,Mg)CO_3$, $FeCO_3$, and $MnCO_3$) to be oversaturated. This in turn, implies that precipitation of carbonates, induced by ion exchange, makes up or exceeds the addition of TIC as a result of organic carbon oxidation. By contrast, the opposite may be true in the upper till, where release was observed. Thus, it could be postulated that seepage on site may display evidence of either a) bicarbonate uptake as the contamination evolves (if carbonate precipitation is dominant), as per the retardation observed in an OSPW sand channel plume by Oiffer et al. (2009), or alternately, b) high concentrations of ingressing bicarbonate, if significant biodegradation of source OSPW occurs prior to its ingress into the subsurface.

Reactive transport simulations demonstrated good agreement with empirical observations (Figure 6-6, 6-7). According to the conceptual model, sulfur behavior was controlled by: i) reduction of sulfate by oxidation of organic carbon (practically this implies organic carbon would be acting as the electron donor, with bacteria being the catalyst) and by ii) precipitation of mackinawite. In the model, TIC was influenced by organic carbon oxidation reactions (by reduction of O_2, NO_3 or SO_4) and by carbonate mineral phase reactions. The modeled output represents TIC and SO_4 behavior quite well, though this does not preclude Fe-oxide reductive dissolution (proposed below) from having occurred. For example, similar results might be achievable with a slightly elevated SO_4 reduction rate, reductive dissolution of Fe-oxides, and Fe and excess sulfides sequestered by mackinawite, leaving excess carbonate in solution, which could itself be removed by modifying the carbon precipitation rate. This will be explored by future modeling efforts. And in support of the conceptual model used, carbonate output was constrained by Ca concentrations, which like CO_3, did match closely to observed values. In fact, modeled output for all major ions matched observations quite well, reducing the non-uniqueness of the modeled results, and building confidence that the chosen conceptual model is a plausible interpretation of system interactions.

Lastly, pH was well predicted by models (9±3% difference), suggesting carbonate reactions and ion exchange were its principal determinants.

The observed chloride concentrations exceeded both modeling predictions (~30% difference) and calculated output concentrations suggesting unaccounted-for Cl release; however, this behavior is believed to be specific to the radial diffusion cells and is not anticipated on site. Release does not appear attributable to dissolution, as chloride minerals were not reported by mineralogical analyses, nor did experimental controls demonstrate release of Cl. Interestingly, chloride release was similarly reported in radial diffusion cells by both Van der Kamp et al. (1996) and by Chang and Donahue (2007). The former, observed ~30% greater concentrations than expected, hypothesizing that contamination by cell materials may have been responsible. The latter authors postulated that in their system, ingress of high concentrations of NH_4 had displaced exchangeable Ca and Mg into the reservoir, but also resulted in the collapse of clay mineral interlayer spaces, thereby preventing divalent cation re-entry into pore spaces. A surplus of Cl then migrated into the reservoir to maintain system charge balance.

A similar explanation is tenable in the present context, if diffusive influx of Na-rich OSPW led to structural degradation or dispersion of clay sediments – a tendency often linked with high sodium adsorption ratios (SAR)(Kessler et al., 2010). A lack of field evidence supporting Cl release (Abolfazlzadeh, 2011), and the observance of such release by authors in three independent radial diffusion investigations though, suggests the effect could be method-related, and expectation of Cl release in the field may not be justified.

6.4.2 Release (or Attenuation) of Trace Elements by Ingress of OSPW

In general, in the subsurface, the distribution and mobility of trace elements are affected by changing pH values and redox conditions. Dissolution of metal oxyhydroxides can occur under acidic conditions (pH < 3; Bowers and Higgs, 1987); however, this mechanism is not anticipated in the present system, where at the tailings pond site, native pore waters are circumneutral pH and the ingressing OSPW has pH ~8.3. Alternately, release could be facilitated by reductive dissolution. Previous research within sandy aquifer sediments from the Athabasca Oil Sands region revealed that a large fraction of trace element content in the solid phase, was associated with poorly crystalline and well-crystallized Al, Mn and Fe oxyhydroxides (e.g. Haque. 2009). Thus, ingress of carbon-rich OSPW has the potential to induce both reductive dissolution of native metal oxyhydroxides and the consequent mobilization of associated trace elements, assuming the supporting bacteria consortium is present and abundant.

The present study suggests this mechanism may be important to not only aquifer sediments, but the glacial till as well, where the presence of limonite and hematite and increasingly reductive conditions brought about by OSPW ingress, establish conditions conducive to these reductive dissolution reactions. In particular, sequential extractions provide evidence that in addition to limited desorption by OSPW, trace element release may be attributable to dissimilatory reduction of amorphous/poorly crystalline metal oxyhydroxides. For most elements, <12% of the trace element content was classified as exchangeable (i.e. F1 fraction). It is anticipated that high ionic strength OSPW will desorb some quantity of these elements into solution. By contrast, a large percentage of trace elements' presence was associated with the F2 and F3 fractions (poorly crystalline and well-crystallized Fe and Mn oxyhydroxides, respectively). Again, dissolution of these minerals and release of co-precipitated trace elements may be achieved by either acidic waters (discounted here as pH is >7) or by reductive dissolution reactions.

It is well established that a variety of microbes are able to conserve energy to support growth, by coupling the anaerobic oxidation of organic compounds with the reduction of Fe(III) and Mn(IV) compounds (Lovley et al., 1990; Lovley et al., 1991; Grantham et al., 1997). Moreover, even though a variety of oxides may exist in the subsurface, microbes demonstrate a clear preference for dissimilatory reduction of amorphous/poorly crystalline to crystalline Fe oxides (Munch and Ottow 1980; Ottow 1981; Neal et al., 2003). Sequential extractions reveal that the trace elements released to the greatest extent, following OSPW ingress in the radial diffusion cells, were highly associated with the poorly crystalline metal oxyhydroxides: Al(F1=1% by mass, but F2=33%), Fe(0%, 57%), Mn(2%, 74%), Sr(8%, 62%) and Ba(7%, 48%); while several species with limited or no observed release had the greatest relative abundance in well-crystallized oxyhydroxides, for example Ag(55%), As(29%), Cd(26%) and Pb(22%). This supports the working hypothesis that dissimilatory reduction of amorphous/poorly crystalline metal oxides may be occurring.

Building upon mineralogical and sequential extraction results, geochemical modeling further implicates both ion exchange and select mineral reactions in the release (or uptake) of several trace elements. Seeking to gain a preliminary understanding of trace element behavior, the simplified conceptual model included Fe, Mn, Sr, Ba, Zn, Pb, and Cd ion exchange, as well as mackinawite ($Fe_{(1-x)}S$) precipitation. The modeled output offers a good representation of Fe, Mn, Sr and Ba (Figures 6-6, 6-7), though given the suggestive evidence that reduction dissolution of metal oxides may be taking place, it will be important to include these reactions in future iterations of the model, to assess how modeled fit changes. Silicon and boron release were also typically well-predicted by modeling, with mild Si under-representation possibly attributable to release by limited dissolution of abundant quartz, plagioclase, or feldspar; while B differences may reflect desorption of surface complexed-H_3BO_3, by competing anions such silicate or SO_4 (Goldberg 1997). On the other hand, the present modeled output offered a poorer fit for elements present at very low concentrations, indicating that other reactions such as surface complexation may be playing a role. Modeling also showed OSPW stage diffusion cells to be saturated with respect to FeS, FeS_2, ZnS, $FeCO_3$, and $MnCO_3$ mineral phases, in agreement with previously proposed reductive dissolution, sulfate reduction and sulfide precipitation reactions.

By contrast, few elements displayed evidence of being mitigated. Mo was taken up throughout the subsurface, Fe (selectively), Cr selectively in the upper and mid till and V in the mid till. In the radial diffusion simulations, MoO_4^{2-} was predicted at higher concentrations than empirically observed, which may be attributable to sorption reactions (e.g. Kaback and Runnells, 1979) or precipitation/co-precipitation into carbonate or reduced sulfur minerals, e.g. pyrite as $(Fe,Mo)S_2$, or MoS_2. Fe behavior, as discussed above, is believed to be influenced by ion exchange and reductive dissolution reactions. Although select samples ultimately showed uptake, this is likely due to subsequent precipitation of the very low solubility Fe, $FeCO_3$ and FeS phases, which act as solubility controls. Finally, not all elements were found to be relevant to the present system: Ag, As, Be, Co, Cs, Ga, Ni, Rb, Se, Tl and U were not observed within in baseline pore fluids, OSPW or in equilibrated solutions (i.e. not in aqueous system inputs or outputs).

The experimental results predict that several trace elements will be released as diffusive influx of OSPW passes through the glacial till sediments, though the question remains – to what extent? In order of increasing final concentration, the released elements consisted of Cd (detected sparsely), Pb, Ba, Mn, Sr, Al, Fe (selectively), B, Si. The percent release of the abundant elements were: Ba(34%), Mn(11%), Sr(14%), Fe(26%, where released), B(49%), and Si(13%). Therefore the present results do not support the potential for large-scale release of trace elements, in response to ingress of OSPW.

6.4.3 Impact of Future Ingress of Groundwater on Major Ions in OSPW-Contaminated Aquitards

The major ion response of OSPW-impacted sediments, when exposed to fresh groundwater, was generally consistent with previous behaviors. Simulations were not conducted and instead analysis completed by mass balance calculations of empirical data and by saturation index assessment using PHREEQC (Parkhurst and Appelo, 1999). The findings suggest that groundwater nitrate and sulfate were reduced into ammonium and sulfide. Chloride was taken up, perhaps indicative of a reversal in migration to achieve charge balance, though again, this may be specific to the laboratory model. Alkalinity was initially variable, though titrations were challenging due to a slow creep in pH during their measurement. When select cells' data were adjusted to achieve zero charge balance error, alkalinity tended to show uptake in the subsurface, in agreement with saturation indices, which revealed oversaturation with respect to Ca and Mg carbonates. It is thus postulated that incoming Ca and Na (the dominant groundwater cations) exchanged with bound Mg, K and NH_4, with additional incoming Ca consumed by precipitation into $CaCO_3$. Milliequivalent comparisons of (Ca+Na-alkalinity) versus ($Mg+K+NH_4$) were similar, supporting this possibility.

6.4.4 Extending Previous Findings

The present findings suggest that ingress of OSPW into surficial glacial till sediments induces a similar, though not identical, geochemical outcome to that previously reported in other settings in the Athabasca Oil Sands region. Using a field model of the STP, Abolfazlzadeh (2011) concluded that OSPW infiltration into the glacial till led to attenuation of Na, SO_4, alkalinity, Mo, Pb, release of Ca, Mg, Ba, Sr, and neither uptake nor release of Mn. Only Mn and Pb (here both released) are different; failure to observe Mn release (via reductive dissolution) may simply reflect the limited dataset in that study. In a study of the underlying sand channel on site, aquifer injections of OSPW led to increased concentrations of Fe, Mn, Ba, Sr, Co, Zn, which were attributed to reductive dissolution of Fe and Mn oxides and oxyhydroxides (Tompkins, 2009). At the Albian Muskeg River Mine, Yasuda et al. (2010) observed that down-gradient seepage into a surficial sand formation led to a decrease in Na and pH, and an increase in Ca and SO_4, in support of cation exchange (Na-Ca) having occurred. Monitoring an OSPW plume in a sandy aquifer on a third oil sands lease, Oiffer et al. noted retardation of HCO_3, Na and NH_4, and B, attributed to calcite precipitation, cation exchange, and surface complexation respectively. He also postulated that precipitation of carbonate minerals may act to mitigate aqueous Fe and Mn concentrations. Of interest, none of the three aquifer studies noted of the possibility for SO_4-reduction. Conditions here, including the persistence of aqueous Fe and Mn and evidence supporting sulfate reduction, may indicate more strongly reducing conditions, and accordingly account for the greater apparent release of trace metals observed here. Kelly et al. (2010) observed that Athabasca River concentrations of Ag, Cr, Hg and Ni, near oil sands tailings ponds or other development, exceeded upstream values in the winter. These findings were not repeated here, but could be attributable to site-specific tailings composition. However, by in large, the geochemical outcome of seepage through the glacial till bares similarity to that observed previously in sand channel formations, on oil sands leases in Northern Alberta.

6.4.5 Model Performance: Sensitivity to Model Inputs and Increasing Future Complexity

Sensitivity analysis was conducted to assess the sensitivity of the simulated output to changes in input parameters. The parameters tested were:

- dissolved oxygen content in deionized water: 4 versus 8mg L^{-1} (insensitive)

- carbonate mineral presence: 0.5 to 2% calcite, or 4 to 6% dolomite (insensitive)
- free-phase diffusion coefficient (10^{-8}m^2 s^{-1} to 10^{-10} m^2 s^{-1}) (mild sensitivity)
- mineral phase effective reaction rate: 10^{-7} to 10^{-14} mol L^{-1} bulk s^{-1} (mild to moderate sensitivity)
- cation exchange capacity: 50% and 150% of empirical value (mild sensitivity (mild to moderate for sodium))

6.5 Conclusions

The present study indicates that the biogeochemical processes of importance in the glacial till are similar to those previously reported in sandy aquifers, and include: ion exchange, precipitation-dissolution of mineral phases (particularly carbonates), and dissimilatory reduction of metal oxyhydroxides. However, evidence also supports the reduction of sulfate, which was not reported in those settings.

The results further indicate that the key outcomes of OSPW interaction with till sediments and pore waters include: the attenuation (likely retardation) of ingressing Na (~575mg L^{-1}), displacement and limited precipitation of pre-bound Ca and Mg (as carbonates), reductive dissolution of metal oxides, sulfate reduction and sulfide precipitation, and biodegradation of organic carbon. There was no evidence of Cl attenuation, present at high concentrations in OSPW (~375mg L^{-1}). Preliminary assessment of trace element behavior revealed that, in increasing order of final concentration, Cd (detected sparsely), Pb, Ba, Mn, Sr, Al, Fe (selectively), B, and Si were released, while few elements were attenuated, most notably, Mo. No release of Ag, As, Be, Co, Cs, Ga, Ni, Rb, Se, Tl, U was observed, despite the presence of these metals in the solid phase. The experiment also suggests that OSPW ingress will not result in the large-scale mobilization of trace elements, though confirmation will be sought by future on-site groundwater monitoring.

Consequently, in addition to naphthenic acids, a component of OSPW that has historically received a great deal of attention because it is acutely toxic to aquatic life, remediation of OSPW-impacted groundwater will also need to address high concentrations of major ions contributing to salinization, while it appears as if trace metal mobilization is of lesser importance.

6.6 Chapter 6 References

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Chapter 7: Conclusions, Engineering Significance and Recommendations for Future Work

7.1 Summary

Increasing stress is being placed upon Alberta’s water resources due to drought, population growth, and agricultural and industrial development. Compounded by the rapid expansion in oil sands operations, there is increased urgency to reduce the potentially harmful ecological impacts associated with the use and disposal of water by this industry. Of relevance, is the use of above-grade impoundments to store fine fluid tailings. These facilities present a major environmental challenge, which includes the risk of pollutants migrating beyond pond containment features and into the surrounding environment. This is being exacerbated by a developing trend of placing tailings facilities atop glacial till-mantled sand channels, which unchecked, could facilitate transport of oil sands process-affected water (OSPW) seepage into downstream ground and surface waters. In order to protect these water resources, it is critical to first understand how geochemical reactions within the overlying glacial till aquitard sediments, affect the long-term movement, persistence and chemical speciation of infiltrating contaminants. The experiments in this thesis represent the first targeted attempt to clarify the role of the glacial till in this contaminant transport pathway. The principal objectives have been to evaluate the potential for mobilization of trace elements and major cations contributing to salinization, and to characterize the key geochemical processes driving system behaviour, as tailings pond seepage migrates through, and interacts with, native aquitard sediments, en route to an underlying aquifer.

7.2 Conclusions and Engineering Significance

While several studies have investigated the fate and transport of oil sands tailings pond seepage in the past, this is the first detailed investigation of the biogeochemical reactions and reaction products following seepage into glacial till. Novel contributions herein include: assessing the potential for release (or attenuation) of trace elements and major ions from glacial till when exposed to

OSPW; and identifying the main processes controlling pore water and sediment chemistry. As well, it is the first study to characterize the cation exchange properties of surficial glacial till sediments near Fort McMurray, AB. And it is the first to conduct a detailed comparison of several widely used, yet methodologically distinct cation exchange methods, to assess their suitability with carbonate mineral-bearing glacial sediments in the Athabasca Oil Sands region.

7.2.1 Seepage into the Glacial Till

The biogeochemical processes of importance in the glacial till were found to be similar to those previously reported in sandy aquifers, and include: competitive ion exchange, and precipitation-dissolution of mineral phases (particularly carbonates), with preliminary indications of dissimilatory reduction of metal oxyhydroxides as well. However, evidence also supports the presence of sulfate reduction reactions in the glacial till, which was not reported in those settings.

Experimentation further revealed that the key outcomes of OSPW interaction with glacial till sediments and pore waters include: the attenuation (likely retardation) of ingressing Na (~575mg L^{-1}), displacement and limited precipitation of exchangeable Ca and Mg (as carbonates), reductive dissolution of metal oxides, sulfate reduction and sulfide precipitation, and the oxidation of organic carbon. There was no evidence of Cl attenuation, present at high concentrations in OSPW (~375mg L^{-1}). Preliminary assessment of trace element behavior revealed that, in increasing order of final concentration, Cd, Pb, Ba, Mn, Sr, Al, Fe (selectively), B, and Si were released, while few elements were attenuated, most notably, Mo. No release of Ag, As, Be, Co, Cs, Ga, Ni, Rb, Se, Tl, U was observed, despite the presence of these metals in the solid phase. The experiment also suggests that OSPW ingress will not result in the large-scale mobilization of trace elements, though this will be further explored by future on-site groundwater monitoring.

Consequently, in addition to the oft-cited naphthenic acids, which are the primary cause of toxicity in OSPW, remediation of OSPW-impacted groundwater will need to address high concentrations of major ions contributing to salinization, while it appears as if trace metal mobilization is of lesser importance.

7.2.2 Cation Exchange Capacity and Exchangeable Cation Measurements

Four methods were tested for cation exchange capacity (CEC) assessment (Silver Thiourea, Lithium Chloride, Ammonium Acetate, Methylene Blue), and two for exchangeable cation determination (Silver Thiourea, Lithium Chloride), in sediments known to contain several percent, by weight, of partially soluble carbonate mineral phases. For CEC, the Methylene Blue method was the most suitable for use with mildly calcareous sediments (least impacted by the presence of these carbonate minerals); while, for exchangeable cations, the LiCl method was least impacted by their presence. However, it is recommended that the relevance of a particular extractant also be considered for the field conditions at hand (e.g. matching extractant species and pH to those of anticipated contaminant waters).

This study also characterized, for the first time, the cation exchange properties of surficial glacial sediments near Fort McMurray, Alberta. The mean cation exchange capacity was found to be 4.7±2.7meq 100g-1 in the clay-rich glacial till, 0.7±0.0meq 100g-1 in the underlying sand and 4.1±2.3meq 100g-1 in the till-sand transition zone (Methylene Blue method). Exchangeable cations in decreasing abundance consisted of: Ca>Mg>K>NH_4>Na.

7.2.3 Specific Findings and their Engineering Significance

In addition to the broad conclusions presented above, a number of specific findings resulted from the research in this thesis. These observed results and their significance are listed below.

Table 7-1
Specific findings and their engineering significance

Finding	**Significance**
Methylene Blue method is suitable for determining CEC of calcareous sediments. Other extractants tested - silver thiourea, lithium chloride, and ammonium acetate - showed varying degrees of suitability with calcareous sediments.	Accurate quantification of CEC is important for evaluating contaminant transport in the subsurface. This will allow for consistent characterization of calcareous sediments of Northern AB. If other extractants are to be used for engineering measurements in these sediments, it will be important to understand their limitations and to use the proposed method improvements (Chapter 4).
For the first time, exchangeable cation composition in the glacial till near Fort McMurray was quantified (is Ca>Mg>K>NH_4>Na).	This parameter is important in understanding contaminant transport outcomes (e.g. here identifying that pore water concentrations of Ca and Mg will increase following seepage into the subsurface). Exchangeable cations are also a specifiable input parameter into contaminant (reactive) transport modeling.
For the first time, mineralogy in the glacial till was evaluated in detail and made publicly available. Clay composition ~ illite +kaolinite; Mineral phases (that react quickly) included: calcite, dolomite, reduced iron sulfides and iron oxyhydroxides.	In the context of seepage or reclamation, kaolinite and illite have a relatively low capacity (among clays) to bind potential contaminants. Knowledge of reactive mineral phases is critical for understanding the geochemistry of sediment-solution interactions (e.g. here identifying the potential for release of trace metals, through reductive dissolution of iron oxyhydroxides).
Major ion and trace element concentrations were measured in pristine glacial till pore water	Knowledge of baseline concentrations is crucial for establishing local water quality benchmarks, particularly since pristine concentrations may exceed regulated water quality guidelines (e.g. when upstream waters are naturally exposed to oil sand geological formations).

Important reactive processes to the system include ion exchange, precipitation, reductive dissolution to release trace elements and oxidation of organic carbon	This has several implications for further (in space or time) evolution of seepage: • Ion exchange and precipitation may be reversed by future ingress of fresh groundwater (although preliminary study, Radial Diffusion Cells - 'GW stage', did not support significant release of sequestered ions or elements.) • As the seepage plume encounters stronger oxidizing conditions (e.g. at the point of encountering downstream surface waters) re-precipitation of trace elements may result.
The outcome of OSPW seepage through glacial till bares similarity to that previously reported in sandy aquifers	The determination of effective techniques to remediate groundwater in these aquifers may provide guidance for future remediation in the glacial till (though hydrodynamics may limit their applicability).
Several trace elements showed potential for release, following OSPW seepage into the till (Al, B, Ba, Cd, Mn, Pb, Si, Sr), though large-scale mobilization into the underlying sand channel is not supported.	These species should be included within environmental compliance monitoring and water quality legislation (though lease-specific differences in ore mineralogy, extraction processing, etc. may necessitate future modification to this list). Although large-scale mobilization was not observed in this study, it will be critical to monitor these species' concentrations on site, to ascertain whether guidelines are exceeded and targeted remediation is warranted (e.g. through use of an appropriate reactive barrier). The presence of these metals should be considered when applying remediation treatments targeting different contaminants. E.g. in situ chemical oxidation (persulfate), is being pursued for naphthenic acid treatment in the underlying, OSPW-impacted aquifer on site. Introduction of a strong oxidizing agent may impact the mobility or toxicity of trace elements.
High concentrations of Cl, Na and potentially HCO_3 will enter the sand channel	High concentrations of these species are expected to: • impact the efficacy of persulfate treatment (Cl and HCO_3 act as scavengers), • result in pore water chemistry that is adverse to aquatic and vegetative life,

Incoming Na will be retarded by ion exchange, resulting in displacement then limited precipitation of pre-bound Ca and Mg (as carbonates). Reductive dissolution of metal oxides, sulfate reduction and sulfide precipitation will further modify seepage waters.	● necessitate that remediation strategies address not only naphthenic acids but salinity as well. Oil sands operators are required to reclaim disturbed land to a "capability equivalent to, or better than, that which existed prior to disturbance” (Kessler, 2010). Reclamation options include wet and dry landscapes – the former consists of capping a layer of tailings with OSPW and/or fresh water. Ongoing research into the ecological viability of these end pit lakes should include lakes populated specifically with evolved seepage waters, which have a modified composition compared to source OSPW. Ca and Mg are detrimental to bitumen extraction and recovery, lowering bitumen adhesion to air bubbles but increasing it to sediment particles, neutralizing surfactants, and coagulating sediment fines (Allen, 2008a). The release of divalent cations by exchange with Na-rich OSPW seepage, could contribute to a long-term reduction in the efficiency of bitumen extraction, as the seepage waters become part of the inventory of recycled water. Elevated concentrations of Ca and Mg, silica, carbonates and iron oxides may contribute to scale formation in extraction machinery, while total dissolved solids, chloride, bicarbonate and ammonium contribute to corrosivity (Allen, 2008a). Thus capture and recycle of OSPW-seepage waters, which are rich in these species, could impact operations, necessitating pre-treatment of waters prior to their re-use.

7.3 Avenues for Future Research

The results from this thesis have identified several important avenues of follow-up research - pertaining either to method development, extensions of the present work, or remediation of OSPW-impacted systems.

7.3.1 Future Research: Method Development

1) Though exchangeable cation extraction using lithium chloride was less susceptible to the confounding influence of carbonate minerals than silver thiourea extraction, both methods were affected. Modified or alternate extraction methods should be explored for use with calcareous sediments (e.g. a potentially novel application could be to use Methylene Blue, which performed well in CEC tests, to quantify exchangeable cations).

2) Future work should compare several of the most commonly used, or potentially suitable, laboratory methods for assessing aqueous geochemistry in low permeable sediments. For example, comparing a leach test (with extremely low flow rate), with radial diffusion cells, with a single or double reservoir column test. This would include evaluating qualitative and quantitative parameters – including ease of set-up, magnitude of observed geochemical changes, cost of set-up, etc.

3) Future work should compare several methods for characterizing pore fluid geochemistry in low permeable sediments. In particular, it would be valuable to compare radial diffusion cells (in this thesis, the 'DI stage' of the experiment), ultra-high centrifugation, pore water squeezing, etc. with actual groundwater field results from the same geologic formation.

7.3.2 Future Research: Extensions of the Present Work

4) It may be worthwhile, to conduct a column study experiment using NaCl (ionic strength ~0.04M, pH ~8.3), in attempt to quantify the cation exchange capacity of the field sediments using as representative a leachate/extractant solution as possible (since Na and Cl are dominant ions in OSPW). This would also offer a further means to evaluate the CEC determined by each of the 4 methods used in this thesis. In a related

manner, it would be valuable to extend Methylene Blue testing, to assess whether or not the method is insensitive to a broader range of calcite concentrations, e.g. testing Methylene Blue performance in kaolin standards spiked with 1, 5, 10, 25wt% calcite.

5) A separate initiative, already underway, will evaluate thesis-derived, laboratory-scale research, against observations at the field scale; specifically, in comparison to study of OSPW seepage into the glacial till from a field scale model of the STP (the Infiltration Pond), and also to 6 years of groundwater monitoring data of actual seepage taking place at the STP. If results do not agree, how do we revise our conceptual understanding?

6) The radial diffusion study could be extended to include different operators also having tailings ponds atop glacial till (e.g. Shell Jackpine Mine (AEUB and CEAA, 2004) and Imperial Oil-ExxonMobil Kearl Oil Sands external tailings areas (Government of Alberta, 2005; AEUB and CEAA, 2007)). Introducing variability to system inputs such as site-specific tailings composition and glacial till mineralogy, would allow for the present understanding to be further broadened.

7) Now that geochemical processes are better understood, and conceptual models exist to explain radial diffusion data, it may be valuable to extend the scope of the reactive transport model. A logical step would be to utilize initial MIN3P (Mayer et al., 2002) results and parameter values, supplemented with empirical data from field samples, to create a MIN3P model of the Infiltration Pond, or perhaps even to create a 1D model of STP seepage, using groundwater monitoring observations. (The latter may require that simplifying assumptions be made, such as the subsurface clay is competent (without fissures), with average thickness of 5-10m, etc.) Such larger scale models would help to establish a preliminary, semi-

quantitative understanding regarding what concentrations of ions might seep into the underlying aquifer.

8) Previous work and this thesis have together explored the fate and transport of OSPW seepage through surficial glacial till or saturated sand aquifers; however, no targeted attempts have investigated seepage evolution through the upper unsaturated portion of sandy aquifers. It is reasonable to expect this zone could be geochemically distinct from the saturated zone, with a different response to incoming seepage.

9) Future work could evaluate the potential for tailings pond seepage into the subsurface to generate Greenhouse or other gas emissions, such as CO_2(g), CH_4(g), H_2S(g) or NH_3(g) (Prakash et al., 2012). Research could include contaminant pathway assessment – would gas emissions generated at depth be largely contained by overlying saturated till sediments? Alternately, due to the closed loop circuit of process impacted waters on site, if contaminated aquifer waters were captured and deposited within a tailings pond, would gases then be released?

10) Future work should characterize the native microbial communities before and after OSPW seepage into native sediments. For example identification of, or changes to iron reducing or sulphate reducing bacteria populations could supplement geochemical understanding of system behaviours.

11) Tompkins (2009) proposed that the ingress of OSPW induced reduction reactions in the aquifer underlying STP; however, there was no evidence of oxidation of the dominant source of dissolved organic carbon, naphthenic acids, creating uncertainty as to the identity of the electron donor. Thus future studies could investigate the role of organics during OSPW seepage. For example, if reduction reactions are occurring, is it

through oxidation of organic carbon? If so, which source – unrecovered bitumen? residual naphtha? Organics in the sediments themselves?

12) Minerals identified in pristine surficial sediments, that have the potential to equilibrate quickly included calcite, dolomite, iron oxyhydroxides and iron sulfides. It would be valuable to conduct a more detailed quantification of these phases in surficial sediments in the Athabasca Oil Sands region, since they have the ability to influence pore water chemistry. (For example, the calcite quantification following the method of Barker and Chatten, 1982)

13) Conduct a detailed comparison of the isotopic C and S composition in pristine pore water, OSPW, and OSPW-impacted pore water, to elucidate the biochemistry of sulfur behavior. This could be expanded to also include examination of the mineralogical phases (e.g. ZnS, FeS) and aqueous phases (e.g. HS^-) present, post-OSPW seepage.

14) The research community is putting an increasing amount of attention towards delineating between natural and anthropogenic signatures of potential contaminant species in the Oil Sands region. Novel measurement of Pb and Zn (or Fe) isotopic signatures (Gammon, 2012) as a potential means of tracing OSPW seepage should be explored, given that both were observed to have been released during the radial diffusion experiment.

15) Peters et al. (2007) noted that the toxicity of naphthenic acids (NAs) can be worsened or lessened through interaction between naphthenic acids and the dominant ions in the process water solution. In support the authors referenced a study in which increasing salinity caused unexpected biological changes to young yellow perch which reduced NA uptake and hence mitigated its toxicity. Peters et al. also noted though, that to date, no research had addressed whether salinity-NA interactions might result in

greater toxicity, for example higher mortality rates of yellow perch – in particular, in the case of hardened waters. The present research showed increased hardness of pore waters following seepage. Ultimately these waters will be recycled as part of the closed circuit system on site, and further, will one day require remediation such as in wet pond reclamation scenarios. Thus an important unknown, is how evolved seepage waters, with increased hardness compared to OSPW, will impact the biological impact of NA toxicity on aquatic species.

16) Prediction of long-term groundwater effects on geotechnical stability has been identified as a shortcoming with current state of groundwater science knowledge (McKenna and O'Kane, 2009). The present research indicates that high concentrations of inorganics will seep into the glacial till, and potentially thereafter the underlying sand channel. An important question will be: given that a significant portion of the dyke walls rest atop these formations, how will seepage impact the geotechnical stability of the supporting subsurface?

7.3.3 Future Research: Remediation

17) Future work should investigate potential treatment methods to remediate high concentrations of major ions or trace elements here shown to result from OSPW seepage through the till. This could include comparison of methods such as electrodialysis, nanofiltration, reverse osmosis and adsorbents, which were recently identified as being potentially suitable to reduce salinity or trace metal content in OSPW (Allen, 2008b). Another option to explore would be a technology such as a reactive barrier. Larger scope (and more practical) investigation, should assess how one of the aforementioned technologies might be incorporated within an integrated remediation scheme that also deals with other contaminants, such as naphthenic acids. For example, Canadian Natural Resources Ltd. is

developing an extensive water treatment scheme, using a combination of techniques to treat basal aquifer and OSPW waters (Romero and Loganathan, 2012).

In addition, desalinization of OSPW or basal waters, will still result in a contaminant by-product – heavily concentrated salts. Future research will need to explore disposal options of these concentrated salts, for example, deep injection into the underground? Use as road salt? This in turn will require characterization of the final composition and purity of salts following treatment.

18) Microorganism sensitivity to salinity can limit success of biological treatment of waste waters (Allen, 2008b). It would be valuable to examine whether or not desalinization of OSPW-impacted sediments and pore waters, as pre-treatment, improves the efficacy of subsequent natural attenuation of naphthenic acids.

19) Future work should investigate how the use of In Situ Chemical Oxidants (ISCOs), such as persulfate, which is proposed for treating naphthenic acids in the OSPW-impacted sand channel, underlying the STP, will alter the local inorganic geochemistry. Research questions include:
    - will the applied oxidants, oxidize reduced Fe, S, minerals, releasing these elements or their co-precipitates (e.g. Mo, As) into solution?
    - Or, in general, how will ion and trace metal speciation change following persulfate application?

7.4 Recommendations

Recommendations are included below, in increasing scope, from lessons learned during the laboratory experiments, to recommendations for future industry-wide practice.

A) Although the Methylene Blue and Lithium Chloride (LiCl) cation exchange extractants performed best in calcareous sediments, no method was without shortcomings. Improvements to the methods, which are proposed in detail in Chapter 4, include that i) LiCl extraction should be modified to consist of at least three rinses of approximately 1mol L^{-1} solution, (though evidence by Papanicolaou (1976) suggests that even this may be insufficient to achieve complete extraction), and ii) Methylene Blue samples must be fully dispersed before testing, for example by using a chemical dispersant as well as 20-30minutes of sonication.

B) As evidenced in this thesis, different cation exchange capacity methods yield different values, and it is often not clear which answer is best. For consistency, it may be useful to develop a single standard operating procedure for quantifying the cation exchange capacity in the Oil Sands region, for example, using the Methylene Blue Index test (e.g. AFNOR, 1993).

C) The radial diffusion cell apparatus would be improved through the following:
  - creating a much larger reservoir (should result in larger or more easily distinguishable concentration changes, and would permit measurement of more chemical species)
  - measuring additional parameters including dissolved organic carbon, dissolved oxygen, redox potential (Eh), etc.
  - use of resazurin in the glove bag (to provide quality assurance that the local environment is oxygen-devoid)
  - running longer term reactions, e.g. 120-365days, since mineralogical reactions will still be occurring at these time scales
  - subjecting the cells not to one, but repeated injections of reservoir fluid (e.g. OSPW). This should provide a better representation of long term seepage from the source pond, and may also identify an

upper limit ability for sediments to adsorb contaminants (as modeled in Chang and Donahue, 2007).

D) Enhancements to the MIN3P (Mayer et al. 2002) reactive transport modeling:

    - Future iterations of the radial diffusion model could be advanced by empirically measuring and simulating a greater number of redox variables (e.g. N_2(aq), HS(aq) and CH_4(aq)), though this would require redesigning the cells to include a larger reservoir so that sufficient samples exist to accommodate all of these tests. The conceptual model could also be complicated to include oxyhydroxide dissolution reactions, while future inclusion of ion-specific diffusion rates within MIN3P (in development), might offer insight into select species transport (e.g. Cl migration).

E) The intended approach of the broader research venture, of which this thesis is only one part, had been to assess aqueous (inorganic) geochemistry, along with collaborative solid phase geochemistry and microbiology of both pristine sediments and of the same samples, post-interaction with OSPW. In the present work, the ‘before’ and ‘after’ sediment samples, were taken up to a meter apart, and though from the same core, mineralogical variability at this scale confounded the before and after comparison. Also, several methods for characterizing the microbial communities were attempted, though unexpectedly, none successful. Nevertheless, the approach of combining aqueous and solid phase geochemistry with microbiology is highly recommended where possible, since the three are expected to be highly associated with one another in actual field settings.

F) If economically feasible, it would be valuable to characterize the extent of fracturing in the clay till aquitard. This could be accomplished at the time that sediment cores are recovered in the field, using borehole imaging or logging. This information would allow for appropriate design of laboratory or computer modeling representations of field conditions.

G) Canada's Oil Sands Innovation Alliance (COSIA) is an association of oil sands producers, which seeks to accelerate resolution of the industry's environmental challenges through collaboration, knowledge sharing, etc. Given this mandate, it seems natural that research such as this thesis be made publicly available, for example via hyperlink posted on the COSIA web site.

7.5 Chapter 7 References

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Appendix A: Detailed Methods for Cation Exchange Experiments

A.1 Lithium Chloride

Exchangeable cations were characterized using a modification of the Lithium Chloride method proposed by Husz (2001). An undried sediment sample was mixed with deionized water (18.2MΩ cm 0.7μScm^{-1} Barnstead), to create a saturated paste (Rhoades, 1982). Ten grams (or instead 20g) of the resultant paste was mixed with 25mL of 0.4mol L^{-1} LiCl and the slurry shaken for 2 hours (Model BB Burrell Wrist-Action ® Laboratory Shaker, Burrell Scientific Inc., U.S.A.,10° amplitude, 400±20 oscillations minute^{-1}). The mixture was then centrifuged at 4150 rpm for 14 minutes (Heraeus Multifuge ® 3 L-R, Kendro Laboratory Products, Germany), and the supernatant decanted into a sealable glass container. A second addition of 25mL of 0.4mol L^{-1} LiCl was added to the remaining solid phase, the contents re-formed into a slurry using a glass stirring rod, and again shaken for 2 hours, then centrifuged for 14 minutes. Preliminary experiments revealed that exchangeable cation values were lower than observed CEC values from other methods – which was also reported by Husz (2001). Therefore, as a modification to the method, a third 25mL LiCl mixing step was performed, in the same manner as rinse number two, under the hypothesis that perhaps two rinses with a weak exchanger was insufficient for displacing all pre-bound cations. The supernatants were combined and filtered (0.2μm, 30mm nylon syringe filter, National Scientific Company, Ireland). Exchangeable cations were quantified by Ion Chromatography (described in Chapter 3). Filtered supernatants were also analyzed at 100x dilution, for easily displaceable aluminum and trace elements, by Inductively Coupled Plasma Mass Spectrometry (PerkinElmer SCIEX ELAN 9000). Exchangeable cations were summed to estimate the cation exchange capacity.

A.2 Sodium Acetate-Ammonium Acetate

USEPA method 9081 was used to estimate the cation exchange capacity (USEPA, 1986). Briefly, 33mL of 1.0N Sodium Acetate (pH 8.2) and 4g (or instead 8g) of undried sediment were combined in a 50mL plastic centrifuge vial, and mixed into a slurry using a glass stirring rod. The vial was then shaken for 5 minutes (Model BB Burrell Wrist-Action ® Laboratory Shaker, Burrell Scientific Inc., U.S.A.,10° amplitude, 400±20 oscillations minute^{-1}), and centrifuged (Heraeus Multifuge 3L-R, Kendro Laboratory Products, Germany) for 14 minutes, and the supernatant discarded. This process was conducted four times, to saturate the binding sites with sodium. The sample was then rinsed in similar manner, three times, using 2-propanol Optima (Fisher Scientific, U.S.A.) to remove free phase ions. Lastly, the sample mixed three more times, in similar manner, using 1N Ammonium Acetate (pH 7), and the supernatant retained, and filtered (0.2μm, 30mm nylon syringe filter, National Scientific Company, Ireland). The concentration of displaced sodium was quantified by Ion Chromatography and used to estimate the cation exchange capacity of the sediment.

A.3 Methylene Blue

The Methylene Blue procedure was based upon the Association Francaise de Normalization (AFNOR) Methylene Blue Index test (method NF P 94-068). The quantity of test sample is dictated by the clay content: clayey sediments (including kaolin standards) were tested using both 22.5g and 45g samples and sandy sediments using 45g and 90g samples.

A mixer (model# 936-2SA, Hamilton Beach Co., a division of Scovill Inc., U.S.A.) was used at ‘low’ speed to uniformly disperse the sediment sample and 500mL deionized water (18.2MΩ cm 0.7μScm^{-1} Barnstead) into suspension (~1 minute). For very hard, clayey samples, samples were first mixed at ‘low’ speed for ~1 minute, then at ‘medium’ setting for approximately another minute. Remaining sediment clumps, if present, were broken up as finely as possible, using a glass stirring rod. The slurried mixture was poured into a 1.5L glass beaker. Methylene blue solution was prepared using deionized water and Methylene Blue powder, certified by the BSC (M9140-25G, Sigma-Aldrich Co., China). Unit doses of 0.01N Methylene Blue were titrated into the slurry. When testing the first replicate of a sediment sample, Methylene Blue was added in 2mL increments. For subsequent replicate testing, once the titration endpoint was approximately known, a single initial dose of Methylene Blue was first applied (~25% of the total estimated amount required) and the solution stirred for approximately 30 minutes. Following this first dose, Methylene Blue was added in 2mL increments for most samples, except those with very large exchange capacities (i.e. highly ‘clayey’ samples), where 3mL increments were chosen so that the test wouldn’t be prohibitively long. The solution was stirred for approximately 1 minute after each addition (1.5inch magnetic stir bar, at 600rpm (CERAMAG Midi magnetic stir plate, KIA WORKS, U.S.A.)). Following each addition of titrant, a glass stirring rod was used to apply one drop of the slurry onto filter paper (Whatman 40 Ashless circles, 110mm diameter, Fisher Scientific, Canada). The procedure continued until the deposited drop develops a light blue halo around the area of the blue stain. Then, the drop test was repeated every minute, for 4 more minutes. If blue halo consistently remained, the test was complete. Otherwise the next unit dose of Methylene Blue was added. (Typically, one more dose was added following the ascertained endpoint, to ensure a brighter halo resulted and hence the endpoint had been correctly assessed.)

The Methylene Blue value, V_b, is given by

$$V_b = V*0.01*100/W \qquad \text{(A.1)}$$

where V is the volume, and 0.01 the concentration, of Methylene Blue added (in cm^3 and gcm^{-3} respectively). W is the dry mass of the sediment sample. V_b is the quantity (g) of Methylene Blue adsorbed per 100g of sediments constituting the slurry.

A.4 Silver Thiourea (AgTU) (Dohrmann 2006)

To begin, 7.6g of thiourea (certified ACS crystalline, Fisher Scientific, Germany) and 700mL of deionized water (18.2MΩ cm 0.7μS cm^{-1} Barnstead) were added into a 1L glass beaker (containing a 1cm magnetic stir bar) and sonicated for several minutes (Branson 3200, Branson Ultrasonics Corporation, U.S.A.). Next, 1.6985g $AgNO_3$ (ACS Pur, Fisher Scientific, Canada) was dissolved within 150mL deionized water. The silver solution was then added very slowly to the thiourea solution, stirring the entire time ((CERAMAG Midi magnetic stir plate, KIA WORKS, U.S.A.), 120-240rpm). One hundred milliliters of Ammonium Acetate solution (1M, pH7) was added to this solution, and the contents topped up to 1L, using deionized water. It should be noted that although buffered Ammonium Acetate (pH7) is added during stock solution creation, the solution as a whole is not buffered to a particular pH (in this experiment, the stock solution was pH 6.8). Silver Thiourea solutions were used within 48-72hr of preparation.

To prepare samples, 48mL of AgTU solution and 2g (or instead 4g) of sediment are added to a centrifuge vial and mixed into a slurry using a glass stirring rod. [Kaolin standards were instead tested at 3g and 6g, because a lower CEC was expected]. A blank was prepared consisting only of 50.0mL of AgTU solution – this was processed along with sediment sample vials to assess AgTU losses to the system. Vials were then agitated for 2 hours, using a wrist-action shaker (Model BB Burrell Wrist-Action ® Laboratory Shaker, Burrell Scientific Inc., U.S.A., 10° amplitude, 400±20 oscillations minute^{-1}), then centrifuged at 4150rpm for 12minutes (Heraeus Multifuge 3L-R, Kendro Laboratory Products, Germany). The supernatant was then passed through 0.45μm cellulose acetate filter (GE Water and Process Technologies, U.S.A.) into a 250mL volumetric flask filled with 25mL of 0.5M HNO_3 (for chemical stabilization). The filter was next rinsed with deionized water, to limit any unwanted AgTU reactions. In the next rinse, 45mL deionized water were added to the remaining sediment, and mixed into a slurry using a glass stir rod. Vials were shaken for 10minutes, then centrifuged for 12minutes, and as before, the supernatant filtered into the volumetric flask. In the final rinse, 25mL deionized water was added to the remaining sediment, which was then dispersed using a glass stirring rod, then centrifuged, and the supernatant filtered and added to the flask. The flask was then filled to its volumetric line, using deionized water. The resulting solution was analyzed for exchanged major cations by Ion Chromatography and for change in silver content and therefore cation exchange capacity by Inductively Coupled Plasma Mass Spectrometry.

A.5 Data Corrections

Several data corrections were explored. Because undried sediments were used in experiments, all calculated results were corrected for water content. Both AgTU and LiCl results were corrected for trace presence of major ion species in the stock solutions. Both were also corrected for (estimated) pore fluid contents – using water content and the pore fluid composition, determined by ultra-high speed centrifuging of native sediment samples that were adjacent in the soil core to the tested samples. It is acknowledged that dilution of undried sediment during LiCl saturated extract formation would not only dilute pre-existing pore fluids, but these fluids would re-equilibrate with the exchange sites. Thus such pore fluid corrections are not perfect, but perhaps the best possible under the circumstances.

In principle, extracts could be analyzed for anion content, as a means of identifying, and by subtraction, correcting for, the presence of confounding mineral phases - in accordance with Appelo (1996). While possible if the offending minerals were, for example, sulfate-based, they were instead carbonate-based. Quantifying aqueous carbonate content is not trivial. Alkalinity titrations are not suitable since non-carbonate species can contribute to alkalinity. Furthermore, carbonate species are not be measurable in Ion Chromatography systems such as ours, which use a carbonate-bicarbonate eluent. Thus, such a correction was not realizable in the present study.

In the AgTU method, fluid-only controls allow one to assess non-sorptive losses to the system. A CEC value, corrected for such losses may be calculated as this silver mass in fluid-only controls minus the final mass in a particular sediment sample. However, in the present experiments, the fluid-only silver masses were unexpectedly low, preventing such a correction.

A.6 Locations from which Cation Exchange Sediment Samples were Collected

Table A-1
Sample source locations

Sample ID	Sediment Sampling Location
Mid Till	Monitoring well 2B, 9.1-10.7mbgs[b]
Low Till1	Monitoring Well 2B, 15.2-16.8mbgs
Low Till2	Monitoring Well 3B, 9.1-9.8mbgs
Upper Transition	Monitoring Well 4B, 11.0-12.2mbgs
Lower Transition	Monitoring Well 4B, 12.2-13.7mbgs
Sand Channel	Monitoring Well 2B, 22.3-23.5mbgs

[a] mbgs = meters below ground surface
Note: Monitoring wells 2B, 3B and 4B were positioned in linear fashion, with 3B approximately 100m east of 2B, and 4B 100m east of 3B.

A.7 Appendix A References

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Appendix B: Radial Diffusion Cell Study – Additional Information

B.1 Radial Diffusion Cells: Charge Balance and Experimental Controls

Charge balance errors were <10% for all cells, suggesting all major species were accounted for. The exceptions were the two mid till samples (sample 1: 40% (DI stage), sample 2: $\leq$ 13% (all stages)). The former reflects an alkalinity titration error. Thus, alkalinity was estimated for that cell, assuming a charge balance of zero.

Experimental controls revealed negligible release of major ions by dissolution of the hydrophilic reservoir coating in deionized water (<0.4mg L^{-1} for Ca, <0.2mg L^{-1} for K, Na). Negligible release of trace elements was likewise observed. The only exceptions were Al, Ba, Pb, and Zn, where the mass released in controls$\geq$10% of the final, baseline pore fluid mass; thus initial pore fluid concentrations of these four species are not precisely known. Corrections were made, for all species, in mass balance calculations.

B.2 Additional Information

Table B-1
Experimental details of the sequential extraction procedure (based upon Tessier et al. (1979) and described by Herbert, 1997).

Fraction	Extraction	Fraction extracted
1	10 mL 1 M $MgCl_2$ (pH 7); 1 hr continuous agitation (20 ˚C).	Exchangeable
2	25 mL 0.25 M $NH_2OH{\cdot}HCl$ + 0.25 M HCl; 30 min. in water basin at 50±1 °C, occasional agitation.	Poorly crystalline metal oxides
3	20 mL 0.20 M $NH_2OH{\cdot}HCl$ + 25% CH_3COOH (pH 2.0); 18 hr in water basin at 90±2 °C, occasional agitation.	Well crystallized metal oxides
4	10 mL 30% H_2O_2 in 0.05 M HNO_3 (pH 2.0); 5 hr in water basin at 85 ±2°C, intermittent agitation. After cooling, 5 mL 3.2 M CH_3COONH_4 in 20% (v/v) HNO_3 + 5 mL deionized water; continuous agitation for 30 min. at 20 °C.	Organically bound + sulfide-bound
5	Hot dissolution in 15 mL aqua regia (HNO_3+HCl; volumetric ratio of 1:3 respectively); 1 hr.	Silicates and primary minerals (i.e. residual)

Table B-2

Major ion pore fluid concentrations and response following exposure of radial diffusion cells to oil sands process-affected water (OSPW) [units: mg L^{-1}]

	Equilibrated-60d^a					Equilibrated-60d				
Sample Location	**Pore Fluid**	**Added OSPW**	**Predicted**	**Observed**	**P value^b**	**Pore Fluid**	**Added OSPW**	**Predicted**	**Observed**	**P value^b**
	Ammonium					Fluoride				
upper till	1.70	<0.14	1.24	1.37	0.13	0.43	2.15	0.51	0.33	0.04
mid till	4.92	<0.14	4.20	4.82	0.32	0.23	2.07	0.36	0.26	0.14
low till 1	6.57	<0.14	5.12	6.07	0.48	0.22	2.15	0.37	0.20	0.05
low till 3	3.75	<0.14	2.93	<0.14	0.48	0.34	1.99	0.55	0.28	0.05
upper interface	3.06	<0.14	2.51	<0.14	0.00	0.58	1.99	0.69	0.66	0.10
lower interface	3.46	<0.14	2.49	<0.14	0.00	0.64	1.99	0.75	0.59	0.10
	Lithium					Chloride				
upper till	0.15	0.16	0.12	0.13	0.28	6.24	367.9	38.5	57.2	0.06
mid till	0.01	0.16	0.02	<0.01	0.13	3.68	336.9	30.5	47.8	0.00
low till 1	0.05	0.16	0.05	0.04	0.00	8.51	367.9	41.1	75.4	0.03
low till 3	0.33	0.15	0.28	0.27	0.00	24.1	305.9	62.1	90.4	0.03
upper interface	0.18	0.15	0.16	0.16	0.08	13.0	305.9	43.5	66.2	0.00
lower interface	0.18	0.15	0.15	0.14	0.08	38.2	305.9	71.9	100.2	0.00
	Potassium					Nitrite				
upper till	13.7	10.0	10.9	11.6	0.30	0.13	<0.08	0.10	<0.08	0.08
mid till	2.49	10.1	2.96	2.69	0.36	0.08	<0.08	0.07	<0.08	0.50
low till 1	7.62	10.0	6.91	7.42	0.02	0.14	<0.08	0.12	<0.08	0.42
low till 3	38.4	10.2	31.4	32.2	0.02	<0.08	<0.08	0	<0.08	0.42
upper interface	14.9	10.2	13.3	14.0	0.01	<0.08	<0.08	0	<0.08	-
lower interface	16.2	10.2	13.1	14.2	0.01	<0.08	<0.08	0	<0.08	-
	Calcium					Bromide				
upper till	260.3	8.83	190.4	235.6	0.00	<0.09	0.81	<0.09	0.10	0.80
mid till	50.9	8.47	44.1	52.5	0.10	<0.09	1.19	0.11	0.10	0.68
low till 1	111.0	8.83	87.4	108.0	0.38	<0.09	0.81	0.07	0.15	0.90
low till 3	467.0	8.10	365.5	351.8	0.38	0.28	1.57	0.42	0.33	0.90
upper interface	53.5	8.10	44.6	61.4	0.00	0.15	1.57	0.28	0.15	0.04
lower interface	64.6	8.10	47.6	73.8	0.00	0.43	1.57	0.53	0.44	0.04

Sample Location	Equilibrated-60d[a]					Equilibrated-60d				
	Pore Fluid	Added OSPW	Predicted	Observed	P value[b]	Pore Fluid	Added OSPW	Predicted	Observed	P value[b]
	Magnesium					Nitrate				
upper till	61.2	4.49	45.0	49.0	0.24	<0.11	6.34	0.59	<0.11	0.01
mid till	10.7	4.39	9.45	12.5	0.02	<0.11	6.67	0.54	<0.11	0.07
low till 1	17.6	4.49	14.1	17.1	0.21	<0.11	6.34	0.59	<0.11	0.00
low till 3	142.1	4.28	111.4	129.3	0.21	<0.11	7.00	0.96	<0.11	0.00
upper interface	27.6	4.28	23.0	25.9	0.05	<0.11	7.00	0.74	<0.11	0.00
lower interface	34.6	4.28	25.5	27.8	0.05	<0.11	7.00	1.00	0.08	0.00
	Sodium					Phosphate				
upper till	14.0	573.5	63.2	28.6	0.00	<0.22	<0.22	0	<0.22	-
mid till	4.38	578.5	50.4	14.2	0.00	<0.22	<0.22	0	<0.22	-
low till 1	11.4	573.5	62.7	21.6	0.02	<0.22	<0.22	0	<0.22	-
low till 3	52.8	583.5	122.0	82.2	0.02	<0.22	<0.22	0	<0.22	-
upper interface	34.7	583.5	90.4	47.2	0.00	<0.22	<0.22	0	<0.22	-
lower interface	46.0	583.5	116.7	63.9	0.00	<0.22	<0.22	0	<0.22	-
	Alkalinity					Sulfate				
upper till	390.1	522.0	333.4	420.4	0.07	573.9	151.4	431.4	305.6	0.14
mid till	172.5[c]	523.1	190.3	127.8	0.16	<0.15	147.1	11.9	<0.15	0.05
low till 1	357.5	522.0	328.8	295.3	0.43	0.00	151.4	14.2	<0.15	0.78
low till 3	293.2	524.3	303.1	235.9	0.43	1295	142.9	1030	1068	0.78
upper interface	283.0	524.3	288.8	265.2	0.31	8.79	142.9	22.4	5.54	0.01
lower interface	333.1	524.3	317.7	322.2	0.31	27.7	142.9	40.5	0.21	0.01

[a] More precisely, equilibration was 63-66d for pore fluid assessment and 75-77d after introduction of OSPW.

[b] Because of sample size (n=2 except in low till where n=3), significance of paired t-test was set to α = 0.10. Statistically significant values are underlined.

[c] Titration of one replicate was noted to be inaccurate, and instead its value estimated to achieve a near zero charge balance.

Notes:

1. The average of duplicate radial diffusion cells is shown except for the low till where inter-cell variability was high (low till 1 and 3 are the relative extremes of that region's data).
2. Mass balance calculations accounted for sampling losses and possible release by hydrophilically-coated POREX® tubing. Evaporative loss and deionized water top-ups were accounted for in the water balance, though it was assumed that no dissolved ions were lost to evaporation (Van der Kamp et al., 1996) nor added in top-ups.

Table B-3
Trace element pore fluid concentrations and response following exposure of radial diffusion cells to oil sands process-affected water (OSPW)[units: mg L^{-1}]

	Equilibrated-60d					Equilibrated-60d				
Sample Location	**Pore Fluid**[a]	**Added OSPW**	**Predicted**	**Observed**	**P Value**[b]	**Pore Fluid**[a]	**Added OSPW**	**Predicted**	**Observed**	**P Value**[b]
	Silver					Molybdenum				
upper till	<0.005	<0.005	0	<0.005	-	<0.002	0.261	0.024	0.002	0.00
mid till	<0.005	<0.005	0	<0.005	-	<0.002	0.261	0.021	0.003	0.06
low till 1	<0.005	<0.005	0	<0.005	-	<0.002	0.261	0.025	0.005	0.05
low till 3	<0.005	<0.005	0	<0.005	-	0.006	0.262	0.041	0.007	0.05
upper interface	<0.005	<0.005	0	<0.005	-	0.012	0.262	0.038	0.021	0.01
lower interface	<0.005	<0.005	0	<0.005	-	0.006	0.262	0.041	0.003	0.01
	Aluminum					Manganese				
upper till	*0.164*[a]	2.25	0.42	0.91	0.86	0.660	0.097	0.489	0.584	0.21
mid till	*-0.796*	1.38	0.21	0.84	0.70	0.312	0.086	0.282	0.332	0.16
low till 1	*-0.230*	2.25	0.03	<0.5	0.36	0.228	0.097	0.186	0.228	1.00
low till 3	*-0.449*	<0.5	0.46	<0.5	0.36	0.908	0.076	0.733	0.638	1.00
upper interface	*-4.747*	<0.5	0.18	1.56	0.21	*0.035*[a]	0.076	0.049	0.055	0.44
lower interface	*-5.358*	<0.5	0.01	0.50	0.21	0.054	0.076	0.049	0.050	0.44
	Arsenic					Nickel				
upper till	<0.005	<0.005	0	<0.005	-	<0.015	<0.015	0.000	<0.015	-
mid till	<0.005	<0.005	0	<0.005	-	<0.015	<0.015	0.000	<0.015	-
low till 1	<0.005	<0.005	0	<0.005	-	<0.015	<0.015	0.000	<0.015	0.51
low till 3	<0.005	<0.005	0	<0.005	-	0.018	<0.015	0.014	0.018	0.51
upper interface	<0.005	<0.005	0	<0.005	-	<0.015	<0.015	0.000	<0.015	0.10
lower interface	<0.005	<0.005	0	<0.005	-	<0.015	<0.015	0.000	<0.015	0.10
	Boron					Lead				
upper till	<0.5	0.40	0.05	1.50	0.01	0.011	0.073	0.012	0.063	0.52
mid till	<0.5	1.25	0.11	0.82	0.59	<0.01	0.041	0.003	0.054	0.43
low till 1	<0.5	0.40	0.06	1.34	0.46	<0.01	0.073	0.007	0.013	0.83
low till 3	0.95	2.10	1.03	0.80		0.033	<0.01	0.026	0.011	0.83
upper interface	1.75	2.10	1.65	1.78	0.47	*-0.02*[a]	<0.01	0.012	0.070	0.05
lower interface	1.84	2.10	1.63	1.60	0.47	*-0.06*	<0.01	0.000	0.036	0.05
	Barium					Rubidium				
upper till	0.085	0.048	0.067	0.083	0.23	<0.005	0.013	0.001	<0.005	0.01
mid till	*0.022*[a]	0.041	0.050	0.082	0.02	<0.005	0.013	0.001	<0.005	0.02

Sample Location	Equilibrated-60d Pore Fluid[a]	 Added OSPW	 Predicted	 Observed	 P Value[b]	Equilibrated-60d Pore Fluid[a]	 Added OSPW	 Predicted	 Observed	 P Value[b]
low till 1	0.337	0.048	0.267	0.353	0.18	<0.005	0.013	0.001	<0.005	0.64
low till 3	*-0.002*	0.034	0.044	0.049	0.18	0.013	0.013	0.012	0.022	0.64
upper interface	*0.057*	0.034	0.193	0.318	0.02	<0.005	0.013	0.001	<0.005	0.83
lower interface	*0.296*	0.034	0.369	0.501	0.02	<0.005	0.013	0.002	0.006	0.83
	Beryllium					Selenium				
upper till	<0.005	<0.005	0	<0.005	-	<0.02	<0.02	0	<0.02	-
mid till	<0.005	<0.005	0	<0.005	-	<0.02	<0.02	0	<0.02	-
low till 1	<0.005	<0.005	0	<0.005	-	<0.02	<0.02	0	<0.02	-
low till 3	<0.005	<0.005	0	<0.005	-	<0.02	<0.02	0	<0.02	-
upper interface	<0.005	<0.005	0	<0.005	-	<0.02	<0.02	0	<0.02	-
lower interface	<0.005	<0.005	0	<0.005	-	<0.02	<0.02	0	<0.02	-
	Cadmium					Silicon				
upper till	<0.005	<0.005	0.000	0.006	0.07	22.7	<3	16.6	19.0	0.43
mid till	<0.005	<0.005	0.000	0.006	0.50	24.3	<3	20.7	19.7	0.57
low till 1	<0.005	<0.005	0.000	<0.005	0.42	29.1	<3	22.8	23.9	0.11
low till 3	<0.005	<0.005	0	<0.005	0.42	10.0	<3	7.77	9.37	0.11
upper interface	<0.005	<0.005	0	<0.005	-	9.34	<3	7.64	8.82	0.05
lower interface	<0.005	<0.005	0	<0.005	-	14.0	<3	10.1	12.3	0.05
	Cobalt					Strontium				
upper till	<0.005	<0.005	0	<0.005	-	1.57	0.22	1.17	1.37	0.061
mid till	<0.005	<0.005	0	<0.005	-	0.07	0.21	0.08	0.08	0.55
low till 1	<0.005	<0.005	0	<0.005	-	0.26	0.22	0.23	0.29	0.24
low till 3	<0.005	<0.005	0	<0.005	-	3.71	0.20	2.93	2.93	0.24
upper interface	<0.005	<0.005	0	<0.005	-	1.12	0.20	0.97	1.18	0.01
lower interface	<0.005	<0.005	0	<0.005	-	1.30	0.20	1.02	1.21	0.01
	Chromium					Thallium				
upper till	0.036	0.045	0.030	0.021	0.49	<0.005	<0.005	0	<0.005	-
mid till	0.030	0.033	0.019	<0.02	0.50	<0.005	<0.005	0	<0.005	-
low till 1[a]	*-0.005*	0.045	0.004	<0.02	0.42	<0.005	<0.005	0	<0.005	-
low till 3	<0.02	<0.02	0	<0.02	0.42	<0.005	<0.005	0	<0.005	-
upper interface	<0.02	<0.02	0	<0.02	-	<0.005	<0.005	0	<0.005	-
lower interface	<0.02	<0.02	0	<0.02	-	<0.005	<0.005	0	<0.005	-

	Equilibrated-60d					Equilibrated-60d				
Sample Location	**Pore Fluid**[a]	**Added OSPW**	**Predicted**	**Observed**	**P Value**[b]	**Pore Fluid**[a]	**Added OSPW**	**Predicted**	**Observed**	**P Value**[b]
	Cesium					Uranium				
upper till	<0.005	<0.005	0	<0.005	-	<0.005	0.005	0.000	<0.005	0.00
mid till	<0.005	<0.005	0	<0.005	-	<0.005	0.005	0.000	<0.005	0.47
low till 1	<0.005	<0.005	0	<0.005	-	<0.005	0.005	0.000	<0.005	0.30
low till 3	<0.005	<0.005	0	<0.005	-	<0.005	<0.005	0.000	<0.005	0.30
upper interface	<0.005	<0.005	0	<0.005	-	<0.005	<0.005	0.000	<0.005	0.10
lower interface	<0.005	<0.005	0	<0.005	-	<0.005	<0.005	0.000	<0.005	0.10
	Copper					Vanadium				
upper till	<1	<1	0	<1	-	<0.005	<0.005	0	<0.005	-
mid till	<1	<1	0.00	1.27	0.50	0.022	<0.005	0.019	0.017	-
low till 1	<1	<1	0	<1	-	<0.005	<0.005	0	<0.005	-
low till 3	<1	<1	0	<1	-	<0.005	<0.005	0	<0.005	-
upper interface	<1	<1	0.00	<1	0.39	<0.005	<0.005	0	<0.005	-
lower interface	<1	<1	0	<1	0.39	<0.005	<0.005	0	<0.005	-
	Iron					Zinc				
upper till	10.30	1.44	7.60	8.06	0.76	<0.1	<0.1	0.001	0.867	0.04
mid till	*14.08*[a]	0.87	12.63	11.35	0.40	*-16.3*[a]	0.181	0.420	0.259	0.49
low till 1	13.63	1.44	10.82	11.19	0.68	<0.1	<0.1	0.003	0.866	0.87
low till 3	8.02	<0.3	6.26	3.86	0.68	*-20.1*	0.262	0.477	<0.1	0.87
upper interface	1.92	<0.3	1.57	1.79	0.74	*-42.1*	0.262	0.502	0.239	0.08
lower interface	*1.75*	<0.3	1.82	0.76	0.74	*-70.2*	0.262	0.323	<0.1	0.08
	Gallium									
upper till	<0.005	<0.005	0	<0.005	-					
mid till	<0.005	<0.005	0	<0.005	-					
low till 1	<0.005	<0.005	0	<0.005	-					
low till 3	<0.005	<0.005	0	<0.005	-					
upper interface	<0.005	<0.005	0	<0.005	-					
lower interface	<0.005	<0.005	0	<0.005	-					

[a] If the release by POREX® tubing was greater than 10% of the back-calculated pore fluid mass, it was deemed the pore fluid concentration are not reliable (darkened cells with italics).

[b] Because of sample size (n=2 except in low till where n=3), significance of paired t-test was set to $\alpha = 0.10$. Statistically significant values are underlined

Table B-4
Mineralogy of aquitard samples by X-ray diffraction and scanning electron microscopy (SEM) – energy dispersive spectrometry (EDS)

Sample ID	**qtz**	**dol**	**cal**	**clin**	**musc**	**orth**	**alb**	**pyr**	**kaol**	**titan**
Upper Till	✓	✓	✓	✓	✓	✓	✓		✓	✓
Mid Till	✓	✓	✓	✓	✓	✓	✓			
Low Till 1	✓	✓	✓	✓	✓	✓		✓		
Low Till 2	✓	✓		✓	✓	✓	✓		✓	
Upper Transition	✓	✓	✓	✓	✓	✓	✓	✓		
Lower Transition	✓	✓	✓	✓	✓	✓				

Note: qtz = quartz, dol = dolomite, cal = calcite, clin = clinochlore, musc = muscovite, orth = orthoclase, alb = albite, pyr = pyrite, kaol = kaolinite, titan = titanite
All samples had a dominance of quartz, with lesser amounts of the other minerals.

Table B-5
Inorganic composition of solutions used in laboratory radial diffusion cells or models

Aqueous Species	**Units**	**Deionized water concentration (DI stage Input)**	**OSPW[c] concentration (OSPW stage Input)**	**Groundwater[f] concentration (GW stage Input)**
Na^{+1}	mol L^{-1}	$1.0x10^{-10}$	$2.46x10^{-2}$	$1.84x10^{-3}$
K^{+1}	mol L^{-1}	$1.0x10^{-10}$	$2.76\ x10^{-4}$	$6.35x10^{-5}$
Ca^{+2}	mol L^{-1}	$1.0x10^{-10}$	$2.09\ x10^{-4}$	$1.23x10^{-3}$
Mg^{+2}	mol L^{-1}	$1.0x10^{-10}$	$1.89x10^{-4}$	$1.06x10^{-3}$
Fe^{+2}	mol L^{-1}	$1.0x10^{-10}$	$6.45x10^{-6}$	$7.97x10^{-6}$
Mn^{+2}	mol L^{-1}	$1.0x10^{-10}$	$1.29x10^{-6}$	below detection
Cl^{-1}	mol L^{-1}	$1.0x10^{-10}$	$9.93x10^{-3}$	$5.45x10^{-4}$
pH	unitless	5.5[a]	8.18	8.30
O_2	mol L^{-1}	1.25d-4[b]	$1.0x10^{-10}$[d]	not measured
NO_3^{-1}	mol L^{-1}	$1.0x10^{-10}$	$1.01x10^{-4}$	$4.59x10^{-6}$
NH_4^{+1}	mol L^{-1}	$1.0x10^{-10}$	$1.0x10^{-10}$	below detection
SO_4^{-2}	mol L^{-1}	$1.0x10^{-10}$	$1.53x10^{-3}$	$2.94x10^{-4}$
inorganic carbon	mol L^{-1}	$3.0x10^{-4}$ (as pCO_2)	$1.03x10^{-2}$	$6.35x10^{-3}$
Zn^{+2}	mol L^{-1}	$1.0x10^{-10}$	$2.13x10^{-6}$	below detection
H_3BO_3	mol L^{-1}	$1.0x10^{-10}$	$1.76x10^{-4}$	below detection
Al^{+3}	mol L^{-1}	$1.0x10^{-10}$	$3.83x10^{-5}$	$1.90\ x10^{-5}$
H_4SiO_4	mol L^{-1}	$1.0x10^{-10}$	$5.75x10^{-5}$	below detection
$Cr(OH)^{2+}$	mol L^{-1}	$1.0x10^{-10}$	$2.18x10^{-7}$	$3.59\ x10^{-7}$
Sr^{+2}	mol L^{-1}	$1.0x10^{-10}$	$2.56x10^{-6}$	$3.41\ x10^{-6}$
Ba^{+2}	mol L^{-1}	$1.0x10^{-10}$	$3.49x10^{-7}$	$4.56\ x10^{-7}$
Pb^{+2}	mol L^{-1}	$1.0x10^{-10}$	$2.47x10^{-7}$	$9.03\ x10^{-8}$
Cd^{+2}	mol L^{-1}	$1.0x10^{-10}$	$1.43x10^{-8}$	below detection
MoO_4^{-2}	mol L^{-1}	$1.0x10^{-10}$	$2.70x10^{-6}$	below detection
CH_2O	mol L^{-1}	$1.0x10^{-10}$	$2.33x10^{-3}$[e]	not measured

[a] deionized water was assumed to be equilibrated with the atmosphere
[b] dissolved oxygen was not measured in deionized water and estimated to be at half saturation, i.e. 4mg L^{-1}
[c] Average of duplicate analysis
[d] dissolved oxygen assumed negligible in process water given the high total organic carbon loading
[e] measured as 70mg L^{-1} total organic carbon
[f] sampled from Nest 1, sand channel well 1B

B.3 Appendix B References

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Appendix C: Reactive Transport Software Review

C.1 Review of Reactive Transport Software Suitable for Simulating the Radial Diffusion Cell System

An extensive collection of software packages exists for simulating geochemical behaviors, presenting the novel user with a daunting task of identifying the most appropriate program for a particular application. Early reactive transport models coupled transport behavior with only equilibrium reactions, such as ion exchange or aqueous complexation, with advanced successors later adding kinetically-driven reactions such as mineral phase dissolution-precipitation reactions (Mayer et al., 1999). However, these simple distinctions have been largely removed and programs today are capable of representing increasingly complex conceptual models in 3 dimensional (3D) simulations. Several applications exist that may be well-suited to modeling the geochemical fate and transport of oil sands process-affected water (OSPW) through clay-rich sediments. A comprehensive review is beyond the scope of this document; however, key features of some of the most common programs are presented below.

PHREEQC V2 (Parkhurst and Appelo, 1999) is widely used, enables easy calculation of solution speciation and saturation indices and permits inverse modeling applications. The user may include a wide variety of reaction types, including, for example, those governing the equilibrium compositions of solid solutions. PHREEQC however, does not permit representation of variably saturated media, and requires each kinetically-driven reaction to be user-defined in the input or database file using Basic statements. PHREEQC itself is limited to 1D transport modeling, although this may be circumvented through careful model creation if the system has favourable symmetry (e.g. Chang, 2005).

Alternately, PHAST (Parkhurst et al., 2004) incorporates the flow and transport functionality of HST3D, along with PHREEQC, to offer multi-component reactive transport modeling in 3 dimensions. Because PHREEQC is embedded within this application, PHAST maintains the former's ability to model equilibrium and kinetic reactions. The application is able to model saturated conditions within laboratory to regional scale scenarios; however, it is not suited for modeling multiphase flow, or density-dependent flow due to variable concentrations or temperatures. Further limitations include flow and transport of a gas phase (although it does allow solutions to equilibrate with a multi-component gas phase), or flow in the unsaturated zone. The model is also not suited for representing high ionic strength solutions (>1molal) although this factor does not impact representation of OSPW at the study site (the South Tailings Pond), whose ionic strength is closer to 0.04.

The multi-component reactive transport model MIN3P (Mayer et al., 2002) is similarly able to include a wide variety of geochemical equilibrium and kinetically controlled reactions. Key further advantages include the ability to model behavior in variably saturated media, and in one, two or three spatial dimensions (including 2D in radial coordinates (Henderson et al., 2009)). MIN3P also allows for greater specificity in depicting dissolution-precipitation reactions - either as occurring directly on the mineral surface, or involving micro-scale transport through a mineral surface coating. However, a drawback to the program is that unlike PHREEQC or PHAST it is not publicly available.

Another multi-component reactive transport program is CrunchFlow (Steefel, 2009). The features of this application include: modeling in up to 3 spatial dimensions, variable density flow in fully saturated media, and kinetically controlled dissolution-precipitation or biologically-mediated reactions. Modifications being pursued include the addition of thermal coupling to flow. Like PHREEQC and PHAST the application is free and publicly available. An advantage to both MIN3P and Crunchflow is that they permit parallel reaction pathways affecting the same species. However, this program appears to be the least "polished" of those reviewed: for example, with the kinetic database currently under-populated regarding mineral phases, aqueous kinetic data links and formats requiring improvements, etc.

A fourth widely used geochemical program that may be used to model reactive transport is Geochemical Workbench (Bethke and Yeakel, 2009). Similar to the others, Geochemical Workbench has the capacity to include equilibrium and disequilibrium reactions such as reduction-oxidation or precipitation-dissolution reactions, or microbial growth and metabolism. It also offers special features, enabling the inclusion of heat transfer within flow and transport calculations and simple approximations for evolving permeability in response to porosity and mineral composition changes. Transport may be simulated in one or two dimensions, with 1D transport, conveniently, supporting a radial dimension. An important drawback however, is that Geochemical Workbench is a commercial product, costing thousands of dollars.

Amongst these four software packages, the two best suited for modeling the present geochemical scenario are believed to be MIN3P and PHREEQC/PHAST.

C.2 Appendix C References

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