UNDERSTANDING FLOW PATHWAYS, MAJOR CHEMICAL TRANSFORMATIONS AND WATER SOURCES USING HYDROCHEMICAL DATA IN A CONSTRUCTED FEN, ALBERTA CANADA.

UNDERSTANDING FLOW PATHWAYS, MAJOR CHEMICAL TRANSFORMATIONS AND WATER SOURCES USING HYDROCHEMICAL DATA IN A CONSTRUCTED FEN, ALBERTA, CANADA.

By KELLY BIAGI, B.Sc.

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TITLE: Understanding flow pathways, major chemical transformations and water sources using hydrochemical data in a constructed fen, Alberta, Canada.

AUTHOR: Kelly M. Biagi, B.Sc. - Environmental Science (Dalhousie University)

SUPERVISOR: Dr. S. K. Carey

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ABSTRACT

Bitumen extraction in the Athabasca oil sands causes significant disturbance of landscapes originally rich in wetland and forest ecosystems, which now require reclamation as mandated by the Alberta Government. However, most research to date has focused on upland-forest ecosystems with little attention on wetland-peatland ecosystems, which are considered more challenging to construct due to salinization potential from ubiquitous salts used in the oil sands extraction and treatment processes; with particular focus on elevated Na^+ due to its detrimental ecological effects. Syncrude Canada Ltd. (SCL) has constructed an upland-wetland system, the Sandhill Fen Watershed (SFW), to advance the understanding of wetland reclamation in the oil-sands region. The SFW is a highly engineered and managed system. Water is supplied from an artificial fresh water source and drainage is enhanced through a constructed surface outlet and an under-drain system intended to provide a downward hydraulic gradient to inhibit the upward movement of salts from the underlying waste material. The objective of this research is to understand the hydrochemical response of the SFW to variations in hydrological management with respect to sources, flow pathways and major chemical transformations of water as it moves throughout SFW. Through surface and pore water sampling, the electrical conductivity and major ions were measured throughout the growing season of 2013 and 2014. Results indicate that the combination of freshwater inflow, flushing of the system with the outflow pump and open underdrains in 2013 kept the overall salinity within the SFW relatively low, with most lowland sites under 1000 µS/cm. Major ion results indicate that most water throughout the SFW classified as $Ca\text{-}HCO_3$ or $Ca\text{-}SO_4$ in 2013, with higher concentrations in the uplands however Na^+ concentrations did not exceed 250 mg/L at any sampling sites. With minimal management in 2014 and consequent limited freshwater input and flushing of the system, the overall salinity of the SFW increased considerably and EC at most sites in lowlands exceeded 1000 µS/cm. Na^+, Ca^{+2}, SO_4^{-2} and HCO_3^- concentrations increased across the SFW, with higher concentrations in the uplands than the lowlands. Although most sites classified as $Ca\text{-}SO_4$, the most notable change in 2014 was the presence of several Na^+ "hotspots" along the southern hummocks in the SFW, where water samples classified as $Na\text{-}SO_4$ and Na^+ concentrations reached as high as 886 mg/L. Results provides evidence of modelled upward movement of Na^+ from underlying waste materials and subsequent seepage from hummocks with limited pump management in the SFW.

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LIST OF ABBREVIATIONS AND SYMBOLS

a	Temperature compensation factor
Alk	Alkalinity
B1	Boardwalk one
B2	Boardwalk two
B3	Boardwalk three
Ba^{+2}	Barium
Ca^{+2}	Calcium
$CaCO_3$	Calcium carbonate
CH_4	Methane
CHWE	Clark hot water extraction
Cl^-	Chloride
CO_2	Carbon dioxide
Cs^+	Cesium
CT	Composite tailings
D	Deuterium/^2H (atomic weight of 2 g/mol)
EC	Electrical conductivity (µS/cm)
EC_{25}	EC at 25ºC
EC_t	Corrected EC at temperature, *t*
EIC	Equivalent ionic conductivity
EIP	East-In-Pit
Fl^-	Fluoride
HCO_3^-	Bicarbonate
I	Illite
K	Kaolinite
K^+	Potassium
KF	King Fisher
LEL	Local evaporation line
Li^+	Lithium
LMWL	Local meteoric water line
M	Montmorillonite
MF	Mid fen
MFT	Mature fine tailings
Mg^{+2}	Magnesium
MWL	Meteoric water line
Na^+	Sodium

NaOH	Sodium hydroxide
NH_4^+	Ammonium
NO_3^-	Nitrate
OP	Outlet pond
OSPW	Oil sands process-affected water
Pf Sand	Pleistocene fluvial sand
PO_4^{-3}	Phosphate
R	Ratio of the heavy to light isotope
Rb^+	Rubidium
R_{std}	Standard isotope value
SAR	Sodium adsorption ratio
SCL	Syncrude Canada Limited
SE	Suncor Energy
SFW	Sandhill Fen Watershed
SO_4^{-2}	Sulphate
Sr^{+2}	Strontium
SRP	Soluble reactive phosphorus
t	Temperature (°C)
TR	Transition
UP	Uplands
VSMOW	Vienna standard mean ocean water
WBP	Western Boreal Plains
WSP	Water storage pond
^{16}O	Oxygen (atomic weight 16 g/mol)
^{18}O	Oxygen (atomic weight of 18 g/mol)
^{1}H	Hydrogen (atomic weight of 1 g/mol)
$\delta^{18}O$	Isotopic composition of oxygen (‰)
δD	Isotopic composition of hydrogen (‰)

CHAPTER 1: Introduction

1.1. Motivation

Some of the world's largest oil sand deposits are located in Alberta, Canada which include the Peace River Oil Sands, the Athabasca Oil Sands and the Cold Lake Oil Sands, covering approximately 140, 200 km^2 of the province. Bitumen extraction in the Athabasca oil-sands is either achieved through in-situ recovery for deeper deposits, or open-pit surface mining when the ore deposit is ~75 m or less from the ground surface. Although surface mining is only of 3% of the total minable area which is approximately 4800 km^2, it makes up the majority of current mining activities and is the most widespread form of open-pit mining in Canada (Government of Alberta, 2012a, 2012b). However, large open-pit mining processes cause significant destruction to natural landscapes originally rich in wetland ecosystems and northern Boreal forests and to date has disturbed over 700 km^2 (Government of Alberta, 2012a, 2012b; Price et al., 2010; Rooney et al., 2012; van den Heuvel et al., 1999). During the bitumen extraction process entire landscapes are removed, resulting in a permanent alteration of ecosystems (Price et al., 2010; Rooney and Bayley, 2011; Trites and Bayley, 2009a). The Government of Alberta requires companies to reclaim post-mining landscapes to an equal or greater functioning capability; with most research and reclamation to date focussed on forested ecosystems. Conversely, there has been limited reclamation of wetlands and peatlands in the oil-sands region, which are challenging to construct as they take thousands of years to develop (Price et al., 2010) and are susceptible to salinization (Renault et al., 1998; Trites and Bayley, 2009a). Syncrude Canada Limited (SCL) and Suncor Energy (SE) are the first companies to attempt wetland-peatland creation within the Athabasca oil sands region, each varying considerably in design (Daly et al., 2012; Wytrykush et al., 2012). The focus of this study is on the Sandhill Fen Watershed (SFW) which has been constructed by SCL.

In addition to major landscape and habitat alterations, many oil-sands mining and treatment processes require a significant amount of water that becomes contaminated due to the various chemicals used throughout these processes. By-products of these processes comprise of large quantities of wet tailings which encompass various contaminants including sands, silts and clays in suspension, polar organic carboxylic acids as well as major ions such as Na^+, SO_4^{-2}, HCO_3^- and Cl^-. These tailings are referred to as oil sands process-affected water (OSPW) when they can no longer be recycled within the industrial process. Most of the concern surrounding this OSPW is the high concentrations of Na^+ and naphthenic acid due to their occurrence in reclamation materials and consequent negative ecological effects (MacKinnon & Boerger, 1986). OSPW also has high chemical and biological demand, resulting in low dissolved oxygen concentrations (MacKinnon and Boerger, 1986). Current mining activities may continue for many decades as Alberta has over 170 billion barrels of proven oil reserves (Energy Resources Conservation Board, 2009), and will therefore continue to produce significant quantities of OSPW which needs sufficient and effective treatment to minimize negative environmental impacts on reclaimed landscapes.

1.2. Research objectives

Improved understanding of the engineered watersheds within the oil sands region requires quantification of how and where water and chemicals move throughout the constructed landscape particularly because of the potential for contamination from the waste materials that underlie reclaimed ecosystems. Although critical to the success of these reclamation efforts, the movement of water and solutes among different landscape units is complicated due to the highly managed and engineered aspect of the system. The objective of this research is to understand the hydrochemical response of the SFW to variations in hydrological management with respect to sources, flow pathways and major chemical transformations of water as it moves throughout SFW.

More specifically, major ion data from the SFW are used to 1) identify the chemical changes of water as it moves throughout the SFW 2) classify water types spatially and temporally in the SFW and 3) provide insight to the major water pathways within SFW. In addition, stable hydrogen and oxygen isotopes are used to supplement the major ion data and give insights to water sources in the SFW. In order to have successful wetland reclamation, knowledge of the sources, transport and resulting impacts of salts is needed, especially with respect to OSPW influence.

CHAPTER 2: Background

2.1. Oil sands open-pit mining processes and associated by-products

SCL's Mildred Lake Base Mine, the location of this study, is situated on Pleistocene glacial tills and clays that overly Cretaceous clay shale from the Clearwater formation, which is marine in origin. These materials make up the majority of the overburden removed during surface mining processes. Beneath this, lies the McMurray formation, comprising of bitumen, mineral matter and water (Lord and Isaac, 1989).

2.1.1. Overview of open-pit mining processes

The open-pit surface mining is process begins by stripping the landscape of all overburden material including vegetation, soil, glacial tills and clay and Cretaceous clay shale, which is preserved and used in future reclamation (Rooney et al., 2012; Wytrykush et al., 2012). At SCL, bitumen is separated from the sands using a process known as the Clark Hot Water Extraction (CHWE), which achieves over 90% bitumen recovery. The CHWE process involves the addition of caustic hot water (NaOH) to the oil-sand ore, which increases the pH and temperature of the ore and subsequently decreases its structural integrity, allowing bitumen recovery. Essentially, the CWHE process is effective because it simultaneously promotes formation of water-bitumen emulsions as well as increased dispersion of clays by lowering interfacial forces between the clay and water (Chalaturnyk et al., 2002). While the CHWE process effectively extracts bitumen from the sands, it consequently produces a significant amount of wet tailings comprising mostly of sands, clays, unrecovered hydrocarbons, water and other dissolved components (MacKinnon, 1989). These tailings are hydraulically transported to a settling basin where they begin to segregate and stratify, leaving particle-free water at the surface which can be removed and recycled within the plant. Coarse sand and large clay particles settle to the bottom relatively quickly, while fine clay particles stay suspended in the water and can take decades to aggregate and settle out of the water due to their slow consolidation rate. Over time, the fine tailings in the tailings water become denser, and are referred to as mature fine tailings (MFT) (MacKinnon et al., 2001). MFT form a very stable fluid structure due to the asphaltic acids that accompany the bitumen that reduce the surface and interfacial tension of water in the tailings, as well as the repulsive forces that establish between the clay particles that it strong enough to prevent the clays from aggregating (Chalaturnyk et al., 2002; MacKinnon et al., 2001). Without additional management of these tailings, MFT were predicted to exceed one billion cubic meters by 2020, presenting significant environmental issues (Chalaturnyk et al., 2002).

Extensive research has shown positive results from the addition of gypsum ($CaSO_4$•$2H_2O$) to tailings slurry. Gypsum acts as a coagulant and decreases the volume of segregated MFT by lowering the threshold at which the MFT will aggregate enough to settle in the tailings ponds. Gypsum is a readily available chemical, is easy to handle and produced similar, if not better results from other tested coagulants such as lime (MacKinnon et al., 2001). Treating oil sands tailings with gypsum decreases the effect of the asphaltic acids by increasing the surface tensions and interfacial forces between the clay and water particles and decreasing the repulsive forces between clay particles, allowing for aggregation (Everett, 1988; Hiemenz and Rajagopalan, 1997; MacKinnon et al., 2001). After treatment with gypsum the tailings is a nonsegregating mix in the ponds, referred to as composite tailings (CT), and as a result, settle more quickly and produces particle-free surface water that can be recycled for other oil sands processing activities (Chalaturnyk et al., 2002). Eventually, once all particle-free surface water has been removed from the tailings pond, the remaining sand and clay material can be used in reclamation.

2.1.2. Origin of soluble salts in the oil sands

Excessive salts are ubiquitous in oil-sands regions and consequently, reclaimed ecosystems are more susceptible to salinization, which can severely limit productivity and overall success of reclamation (Trites and Bayley, 2009a). The Clearwater formation, which overlies the oil sand deposit, is comprised of natural marine shale sediments and saline aquifers that were originally deposited in a marine environment approximately 112 – 110 Ma during the Cretaceous Period (Alberta Energy and Utilities Board, 2000; Ogg et al., 2000). During the extraction process, these marine shale sediments become exposed and can contaminate reclamation material with soluble salts, particularly with Na^+, SO_4^{-2} and Cl^- (Kessler et al., 2010; Leung et al., 2003; Lord and Isaac, 1989).

In addition to the naturally occurring saline-sodic overburden, salts can be incorporated into reclamation material from chemicals in OSPW that are added during various bitumen extraction and treatment methods such as the addition of NaOH in the CWHE process and $CaSO_4$ to initiate the formation of CT (Chalaturnyk et al., 2002; Matthews et al., 2002). Although the gypsum treatment for MFT involves large additions of Ca^{+2} (1000-1200 g/m^3)(MacKinnon et al., 2001), chemical analysis of OSPW associated with CT shows high concentrations of SO_4^{-2}, Cl^- and Na^+ (Table 2.1). High SO_4^{-2} and Cl^- concentrations result from the addition of gypsum and marine oil sand ore, respectively. At a neutral pH, SO_4^{-2} and Cl^- have the highest equivalent ionic conductivity (EIC) of all ions involved in oil sands extraction and treatment processes. EIC is a numerical value identifying an ion's relative contribution to the electrical conductivity (EC) of a solution, and therefore, SO_4^{-2} and Cl^- can be attributed to the high salinity of OSPW (MacKinnon et al., 2001; Rossum, 1975). The addition of gypsum to tailings increases the occurrence of free Ca^{+2} ion concentrations because gypsum is an acid salt, which reduces the pH of the solution and therefore decreases the precipitation of Ca^{+2} as calcite, and increases the release of free Ca^{+2} ions. High Na^{+} concentrations in OSPW is a result of cation exchange that occurs between Na^{+} on the clays and the free Ca^{+2} ions in solution (MacKinnon et al., 2001). The Na^{+} on the clays initially from the extraction processes (marine sediments and addition of NaOH from the CWHE process), are replaced by Ca^{+2} when they come in contact with CT release waters, thus releasing free Na^{+} ions into the OSPW, which can be incorporated into reclamation material. Kaolinite (K), illite (I) and montmorillonite (M) are the dominant clay components of the McMurray formation and all have high cation exchange capability when in aqueous form (M > I > K). This is the driving factor for the cation exchange of Na^{+} with Ca^{+2} on the clays in tailings ponds, resulting in saline-sodic OSPW (Chalaturnyk et al., 2002). CT will underlie many reclamation landscapes and due to the saline-sodic water that accompanies the CT, it is crucial to design ecosystems that will be resilient to this saline-sodic water and will limit salinization while providing equivalent functional capability as the pre-mining landscapes.

2.2. Wetland reclamation in the Western Boreal Plains (WBP)

Wetlands are identified by poorly drained soils, hydrophytic vegetation and areas of land that are consistently saturated with water that promote a range of ecological and biological activities that typically found in a wet environment (National Wetlands Working Group, 1988). Wetlands can be broadly classified as either peatlands, which contain more than 40 cm of peat accumulation, or mineral wetlands where there is limited or no accumulated of peat (National Wetlands Working Group, 1988). Wetlands perform a variety of vital physical, chemical and biological ecosystem functions such flood mitigation, sediment trapping, water quality improvement, carbon sinks, high productivity and biodiversity (Kennedy & Mayer, 2002). The majority of the pre-disturbance wetlands in the Athabasca oil-sands are classified as fen peatlands, which are identified by a fluctuating water table and are minerotrophic (National Wetlands Working Group, 1997; Vitt et al., 2000). The Alberta Environmental Protection and Enhancement Act requires mining operators to reclaim disturbed landscapes from mining activities back to equal or greater pre-mining functioning capability; with most research and reclamation to date focussed on forested ecosystems (Carey, 2008; Elshorbagy et al., 2005; Price et al., 2010; Rooney et al., 2012; Trites and Bayley, 2009a). Conversely, there has been limited research on reclamation of wetland and peatland ecosystems even though wetlands covered more than half of the pre-disturbance landscape in the Athabasca oil-sands region (Rooney et al., 2012). Wetland and peatland creation presents many challenges because peatlands can take thousands of years to develop and in Alberta, the climate is characterised as dry and variable and landscapes are susceptible to salinization (Lilles et al., 2010a; Raab and Bayley, 2013; Rooney et al., 2012; Sorenson et al., 2011; Trites and Bayley, 2009a). Additionally, elements of the hydrological cycle need to be entirely re-established, due to the severity of landscape destruction, for successful hydrologic functionality in the long term (Elshorbagy et al., 2005).

2.2.1. Natural peatland formation in the WBP

Natural peatlands are widespread throughout the WBP, and have formed slowly over thousands of years as net primary production consistently exceeded decomposition rates, which results in accumulation of organic matter, carbon and thus peat (Vitt, 2006). Due to large quantity of accumulated organic matter, peatlands play a critical role in the global carbon cycle as they are a net sink for CO_2, a net source of CH_4 and have large stores of carbon (Moore et al., 1998; Price and Waddington, 2000; Vitt, 2006). Peatlands also provide many other important functions that are crucial for the entire landscape such as hydrologic regulation, biogeochemical processes, vegetation succession, and primary production and decomposition. Peatland formation is driven by the interactions between climate, hydrogeology and topography which produce the necessary allogenic and autogenic processes that exist within peatlands (Nwaishi et al., 2015; Payette, 1988). In northern regions, paludification is the dominant peat-forming process and is initiated on dry mineral soil with terrestrial vegetation that undergoes hydrological changes that cause water accumulation in low topographic areas and, over time, spreads laterally into adjacent uplands (National Wetlands Working Group, 1997; Nwaishi et al., 2015). Paludification begins in water logged areas which create anaerobic conditions and reduced decomposition of organic matter, resulting in a slow decline in tree species and subsequent forest opening, decrease in interception and low evapotranspiration losses. All of these factors provide favourable conditions for hydrophytic vegetation and peat to develop (Kennedy and Mayer, 2002; Nwaishi et al., 2015; Waddington et al., 1998). There can be large variation among peatlands as a result of complex interactions between hydrology, climate, water chemistry, geology and vegetation (Vitt, 2006), which classifies peatlands differently. Vegetation species exist within peatlands in response to the variation in hydrological conditions and associated distribution of minerals and nutrients (Price & Waddington, 2000), which is the basis for categorizing peatlands into one of the following: bogs, poor fens, moderate-rich fens and extreme rich fens. Bogs are ombrotrophic, as they are only influenced by precipitation, while fens are minerotrophic and receive water inputs from surface and groundwater in addition to precipitation (Vitt, 2006). Bogs and poor fens tend to have a pH below 5.5, limited bicarbonate alkalinity and low EC, Mg^{+2} and Ca^{+2} (Table 2.2), which result in *Sphagnum* dominated plant communities. Moderate and extreme-rich fens support large vegetation communities as a result of neutral pH conditions and higher EC, Ca^{+2} and Mg^{+2} (Table 2.2) (Chee and Vitt, 1989; Vitt, 2006; Vitt et al., 1995). Additionally, variations in water chemistry and biogeochemical processes determine the net primary production and degree of humification of peat, which subsequently influences the hydrological properties of a peatland such as water movement and storage in the long-term (Nwaishi et al., 2015).

2.2.2. Characteristics of the WBP

The landscape of the WBP comprises of various interconnected wetland-peatland and forest ecosystems and is defined by the complex relationship between its climate and geology. The climate is identified as a long-term water deficit, where evapotranspiration and evaporation exceed precipitation, as well as by seasonal and decadal wet and dry cycles (Devito et al., 2005a; Smerdon et al., 2005). The geology at depth has large heterogeneity which gives rise to its widespread variation in antecedent moisture and water storage capacity among landscapes. Hydrologic functionality in the WBP is a result of the interactions between climate, geology and connectivity between landscapes which controls their ecological and hydrological behaviour (Devito et al., 2012; Ferone and Devito, 2004). Typically wet years reduce the soil water storage which results in an increase in runoff, while dry years result in larger soil storage capacities and consequently a decrease in runoff and connectivity between landscapes (Devito et al., 2005a). Connectivity is also complex in the WBP as it is not necessarily dependant on topography alone, but on the geologic composition of the land as well (Devito et al., 2005b). The interaction of topography and geology determines antecedent moisture conditions of an ecosystem which affects its hydrologic connectivity and responses. Connectivity among landscapes is crucial for their overall functionality for example, wetlands can be an important source of water to upland forested areas during dry periods to maintain vegetation growth. Natural landscapes in the WBP have balanced interactions of climate, geology and connectivity that allows them to be sustained in an overall dry climate (Devito et al., 2012).

With a continually warming climate it is expected to become warmer and drier in the WBP region, which contains the majority of Canadian wetlands, and has the potential to increase peat temperatures and lower water tables (Rouse, 1998; Tarnocai, 2006). There is much concern surrounding this due to the potential for peatlands to become CO_2 sources due to an increase in respiration and subsequent decomposition of stored carbon, which may cause major shifts in the global carbon cycle. The most important factors that can affect the carbon budget within a peatland include vegetation community, temperature, hydrology and water chemistry (Moore et al., 1998), and understanding these interactions between these factors and how they change in response to climate change is important, but extremely challenging due to the complexity of these interactions. Contrary to this concern, model and field results show that the degree of antecedent moisture prior to climatic warming is important in a peatland to maintain or even increase its carbon sink (Waddington et al., 1998), as well as its CH_4 emissions (Strack et al., 2004). Results suggest that an increase in growing season duration may allow for vegetation to colonize in areas once occupied by pooled surface water, therefore increasing the uptake of CO_2 and highlighting potential resilience to climate change. (Waddington et al., 2014) evaluated the hydrological feedbacks that exist within peatland ecosystems, with particular focus on water table depth, due to the large control it exhibits on many ecohydrological and biogeochemical processes. Their synthesis concludes that in both wetting and drying climates scenarios, peatland ecosystems have the potential to control and regulate changes in water table depth, as there are greater negative feedback mechanisms than positive feedback mechanisms that exist within peatlands which suggests that peatlands can have resilience against water table changes induced by climate change. For example, in the predicted scenario of increased drying with climate change and possible decline in water table depth, their synthesis suggests that a negative feedback mechanisms would occur with the increased decomposition of peat from increased drying, which would result in decreased peat pore space and therefore increase the water retention and therefore resist drying in the long term (Waddington et al., 2014). However, not all positive and negative feedback mechanisms necessarily exist within every peatland and if positive feedback mechanisms exhibit greater effects within a peatland ecosystem, it may be more vulnerable to climate change.

2.2.3. Implications for fen peatland reclamation

Peat-forming wetlands have been identified as keystone ecosystems within the WBP due to the water retention and regulation functions they provide, especially during droughts when stored water is supplied to adjacent wetlands and uplands (Ferone and Devito, 2004). However, natural peatland formation and succession requires complex interactions between physical, biological and chemical factors that create optimal conditions for long-term peatland formation. Additionally, several decades are required for initiation of natural peatland formation alone, which presents many challenges for peatland construction in the oil-sands (Clymo, 1983; Nwaishi et al., 2015). Methods for fen peatland reclamation in the WBP region is currently not well understood however, it is crucial that constructed wetlands mimic the hydrologic functionality of natural systems due to their important role of effectively storing and transmitting water to adjacent forests and wetlands throughout the wet and dry climate cycles present in the WBP (Devito et al., 2012). Additionally, the design of constructed wetlands must correctly combine geologic and soil layering as well as landform shape and topography to promote the ideal antecedent moisture and water storage conditions that will enable peat formation as well as a long-term moisture surplus in a characteristically dry climate (Devito et al., 2012). Simulation modelling results suggested that a 2:1 upland to lowland ratio was effective in supplying a sufficient amount of water throughout the growing season under local drought conditions (Price et al., 2010). The current reclamation project at SCL was covered with salvaged and transferred peat with hopes to increase the initiation of peat formation however, it is unknown if transferred peat can perform the vital ecohydrological functions at the same capacity as natural peatlands. For example peat stratification properties, which control hydrologic regulatory functions, may be impaired at reclamation sites because peat is sourced from stockpiles or has been transferred. This may have an negative effect on vegetation species native to peatlands (Nwaishi et al., 2015). Due to the probability of increased temperatures in response to climate change, wetland-peatland design must incorporate adaptive mechanisms capable of moderating responses to a drying climate such as negative feedback mechanisms that can moderate changes in water table depth, which controls many important peatland ecosystem functions (Waddington et al., 2014).

Another important factor in wetland reclamation in the oil-sands region is limiting salinization of the ecosystem from the upward movement of salts, via advection and diffusion mechanisms, that exist in the mine waste materials and OSPW that underlay the SFW. Poor water quality as a result of elevated salinity may restrict vegetation growth and success as well as sufficient vegetation succession required for long-term peatland development (Nwaishi et al., 2015). Design and management of constructed ecosystems needs to limit the OSPW from interacting with soils near the surface to prevent diebacks of vegetation not tolerant to high salinity. In the long term, constructed peatland-wetland ecosystems should not only be capable of sustaining itself, but surrounding landscapes particularly in dry years. Collectively, reclaimed peatlands should be carbon- and peat-accumulating, support a vegetation assemblage representative of peatlands in the WBP, promote salt flushing to provide sufficient water quality for vegetation growth and habitat development and perform critical hydrologic regulatory functions (Daly et al., 2012; Devito et al., 2012).

2.3. Salt transport and its implication on wetland reclamation

2.3.1. Salt transport mechanisms

Salinity has a strong influence on the success of vegetation in the boreal forest and due to the ubiquitous elevated salinity associated with the oil sands region, understanding the salinity thresholds at which boreal species can survive is crucial for the overall success of reclaimed landscapes (Lilles et al., 2010b). Much of the concern surrounding salinity in reclaimed ecosystems is focussed on elevated concentrations of exchangeable Na^+ that is transported upwards from depth as a result of the combination of salt transport mechanisms including diffusion, advection, mechanical dispersion and cation exchange.

Molecular diffusion and advection are considered the two most important solute transport mechanisms in peatlands (Reeve et al., 2001). Concentration gradients drive the movement of a salts in solution through molecular diffusion (Crank, 1956), particularly in systems with a low hydraulic conductivity (Shackelford & Daniel, 1991). Advection is the movement of solutes in the direction of the bulk movement of the fluid (Schulze-Makuch, 2009). Mechanical dispersion, which describes the varying paths water containing solutes will travel within a medium, will cause mixing and dilution of various solutes as water continues to travel within an environment (Schulze-Makuch, 2009). This is usually minimized in groundwater because water movement is too slow to see the effects of mechanical dispersion (Price and Woo, 1990). Due to its high degree of heterogeneity, peat has variable physical and hydraulic properties (Chason & Siegel, 1986) and thus can enhance the effects of mechanical dispersion (Reeve et al., 2001). Peat has also been shown to have retardation effects on solute transport, and peat depth in reclaimed ecosystem may be important when considering potential contamination from elevated salinity (Rezanezhad et al., 2012a, 2012b). Many ecosystem functions in peatlands rely on solute transport, as it determines nutrient supply and dissolved organic carbon circulation (Waddington & Roulet, 1997), as well as distribution and abundance of vegetation communities (Glaser et al., 1981).

Cation exchange on clays is a commonly occurring process that affects the chemistry of the OSPW and water in reclaimed landscapes. In general, clays have an overall unbalanced negative charge at their surface, and therefore attract positively charged cations to neutralize the charge. These cations can undergo exchange with any existing cations adsorbed to the clay surface (Carroll, 1959). Exchange capacities of soils varies with clay and mineral structural and composition differences which affects the position and number of negative charges on the surface of clays. Cation exchange capacity of clays will be greater with (1) smaller grain size due to increased surface area and number of broken bonds, (2) increased organic content, and (3) increased occurrence of unsatisfied bonds at the edge of clay as a result of irregularities in the lattice structure and variation in grain size (Carroll, 1959). In more alkaline environments, such as the SFW, the primary cations involved in cation change on clays tend to be Ca^{+2}, Mg^{+2}, Na^{+} and K^{+}, with Ca^{+2} being the dominant ion involved in soil clay minerals. Divalent cations are preferred on clay surfaces over univalent cations due to their higher charge and subsequent higher electrostatic forces which form stronger bonds at the clay surface. Therefore, if a univalent cation is adsorbed to a clay particle it will be replaced subsequently released into surrounding waters if a divalent cation is present. Typically, the order of the preferred adsorbed cations on clays is: $Li^{+} < Na^{+} < K^{+} < Rb^{+} < Cs^{+}$ & $Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$ (Carroll, 1959).

Water chemistry in peatlands is dependent on a combination of the inputs, precipitation and surface/subsurface water, as well as processes such as plant uptake, microbial decomposition and mineralization and cation exchange mechanisms. These factors will affect the ecosystem functions as a result, can be an indicator of a successfully functioning peatland (Vitt et al., 1995).

2.3.2. Consequences of elevated salinity

The progression of increasing salinity within landscapes is dependent on the interactions between the source of salt, climatic and hydrologic factors. The oil sands region in Alberta has naturally saline overburden materials, that are sufficient to create salinity problems or salinization in reclamation material (Moran et al., 1990), in addition to highly saline waste materials that underlie reclaimed ecosystems. Reclamation landscapes that tend to have ponded water will promote a consistent water table at or close to the ground surface and may be more susceptible to salinization from an increase in diffusion due to the large concentration gradient that would exist between the relatively fresh surface water and highly saline OSPW groundwater (Merrill et al., 1983). Studies examining changes in the chemistry of reclamation material as a result of the underlying saline-sodic overburden, attribute diffusion and advection as the dominant processes contributing to the increase in soluble salts in soils (Kessler et al., 2010). In these environments it has been observed that diffusion is driven by the sharp salinity gradient between the overlying reclamation material and the underlying OSPW, and advection is a result of high evapotranspiration rates and limited downward movement of water due to the low hydraulic conductivity of underlying materials (Dollhopf et al., 1980; Merrill et al., 1983; Oddie & Bailey, 1988; Sandoval & Gould, 1978). Diffusion was determined as the primary salt transport mechanism in two studies involving a soil cover over a sodic mine spoil from surface coal mining (Bailey, 2001; Merrill et al., 1983) however, other studies have documented evapotranspiration-driven advection as the dominant salt transport mechanism in soil covers overlying saline-sodic spoils from surface coal mining in Alberta (Moran et al., 1990). Although advection has the potential to transport more salts over a larger distance, soil covers in reclamation landscapes are typically elevated and promote groundwater recharge which makes advection more of a transient process during the summer months when evapotranspiration and/or evaporation are occurring (Hilderman, 2011). With either transport mechanism, the concern lies with the replacement of Na^+ with Ca^{+2} on clays and thus releasing free Na^+ ions in reclamation water (Renault et al., 1998), which can have negative effects on vegetation success.

A significant reduction in plant taxa and species richness in wetlands affected by OSPW has been observed in comparison to natural wetlands within the WBP and oil sands region (Rezanezhad et al., 2012a; Rooney & Bayley, 2011; Trites & Bayley, 2009a). Soils are considered to be saline above 4000 µS/cm, and are considered to have detrimental effects on plants (Renault et al., 1998; USDA Salinity Laboratory, 1954). However, elevated salinity is not necessarily harmful to all vegetation as it has been observed that particular species can grow stress-free when exposed to OSPW (Pouliot et al., 2012; Purdy et al., 2005; Trites and Bayley, 2009a). Certain plant species have shown considerable resilience to OSPW exposure in controlled greenhouse studies set to similar climatic conditions experienced in the oil sands region to a maximum of two years. Plants were exposed to a range of Na^+ concentrations similar to those found throughout reclaimed wetlands in the oil sands region (14 – 1800 mg/L), and many vascular and graminoid species showed no or minimal effects to the OSPW exposure, while mosses were highly effected to the treatments. However, due to the relatively short study period of these studies, up to two years, effects may have been reduced due to the retardation effects that peat has on Na^+ transport (Rezanezhad et al., 2012a, 2012b).

CHAPTER 3: Site Description and Methodology

3.1. The Sandhill Fen – climate, location and design

SCL is one of the first companies to undertake wetland creation and completed construction of their first constructed watershed in 2012, which is 52 ha and is referred to as the SFW (Figure 3.1). The SFW is a highly engineered and managed system and is located in the north-west corner of a former mining area called East-In-Pit (EIP), which was mined between 1977 and 1999 and later filled with CT. The SFW is located approximately 50 km north of Fort McMurray, Alberta (53.80N, 104.62W) and is situated within the WBP ecoregion of western Canada which has a sub-humid climate. Thirty-year climate normal data (1981-2010) from Environment Canada for Fort McMurray indicates that mean daily temperatures for January and July are -17.4°C and 17.1°C, respectively. Mean annual potential evapotranspiration (607 mm) exceeds mean annual precipitation (418.6 mm) where 316.3 mm of that precipitation falls mostly as rain between May and September (Environment Canada, 2015; Wytrykush et al., 2012).

The SFW area of EIP was filled with 35 m of CT, which is overlain by 10 m of tailings sand that acts as a structural cap, followed by 0.5 m of clay to provide mineral soil and attenuate upward migration of salts from the CT layer and lastly, 0.5 m of peat material to provide organic soil (Figure 3.1). SFW is composed of several landscape units including hummocks, vegetated swales, perched fens, a pond and a lowland fen wetland (Wytrykush et al., 2012). The clay till was placed throughout the entire watershed except for hummocks 2, 4, 5, 7 and 8. Instead, these hummocks are constructed of tailings sand and received 0.1 – 0.5 m of Pleistocene fluvial sand (Pf Sand) on top of the tailings sand cap which was compacted by a dozer that passed over the material several times (Figure 3.1). There are four important engineered components of SFW: the water storage pond (WSP), underdrains, outlet pond (OP) and SUMP (Figure 3.2). In addition to precipitation, water is supplied to SFW through the clay-lined WSP from an artificial source (Mildred Lake Reservoir) which gradually flows through a gravel dam into the lowland area of SFW. This water flows east towards the OP where drainage in enhances as the surface and near-surface water flow through a spillbox and weir, and into the SUMP. The SUMP collects the surface and near-surface water as well as the underdrain water, before it is collectively pumped out of the SFW back into EIP (Wytrykush et al., 2012). The underdrain system consists of perforated 20 cm high density polyethylene covered in a fine-screen geotextile cloth and was installed to: 1) provide an overall downward hydraulic gradient to inhibit salinization by limiting the upward diffusion of salts from deep groundwater and 2) collect any upward movement of OSPW and transport it to the SUMP. Overall, the SFW system was designed to provide water to the lowland area from the uplands, while limiting salinization through providing a supply of fresh water to the storage pond and usage of the underdrains (Wytrykush et al., 2012). Groundwater flows from the south of SFW towards the lowland areas and then to the east towards the outlet and SUMP.

3.2. Methodology

3.2.1. Naming convention of sampling sites

The lowlands and uplands within the SFW are represented in Figure 3.2 by the green and yellow areas respectively (Figure 3.2), and the boundary between these two was referred to as "transition" areas, which were not strictly bound by the lowland/upland border depicted in Figure 3.2. Starting in the western side of the SFW and moving eastward, is the WSP followed by boardwalk 1, 2 and 3, the OP and SUMP (Figure 3.2). All site labels are prefaced by "SH" to indicate that they are from the Sandhill Fen. The label for each of the surface and well samples are based on the location within the SFW which was categorized as: water storage pond (WSP), boardwalk 1 (B1), boardwalk 2 (B2), boardwalk 3 (B3), transition area (TR), uplands (UP), outlet pond (OP) and SUMP. This location label is followed by the well number which increased sequentially based on the order of installation (W#). Surface water samples have the same naming convention except that the well number (W#) was replaced by a surface water sample number (S#). For example, a pore water sample from boardwalk 3, well 2 was labelled as “SH-B3-W2”, and the second surface water sample from the transition area was labelled as “SH-TR-S2”. It should be noted, that “SH-B3-W2” was considered to be in the transition area. Also, in 2013 the only surface water samples collected within the lowland of the SFW was in between B2 and B3 and was referred to as “mid fen” which is labelled as “MF”.

3.2.2. Inflow, outflow and precipitation

Lateral inflow into the WSP was measured using Model AT868 AquaTrans Ultrasonic Flow Transmitter as well as a transducer (Rosemount) to measure the water level. Total outflow comprised of both surface flow and underdrain contributions. Once at the outlet, surface flow entered a V-notch weir, where water level was continuously measured with a transducer. The surface water then drained into the SUMP, where both surface and underdrain water collect before being pumped out of the SFW. The same model of flow transmitter was used to measure total outflow from the SUMP, including both the surface and underdrain water.

Three meteorological towers within SFW were used to measure precipitation, all equipped with a Campbell Scientific Model CS700 tipping bucket rain gauge to measure rainfall, a Campbell Scientific CS725 to measure snow water equivalent (SWE) as well as a SR50A sonic ranger to monitor snow depth. All measurements were recorded on an hourly basis with Campbell Scientific CR1000 data loggers. Data from these gauges were averaged to represent the mean inputs for the SFW. Evapotranspiration was measured at three towers using the eddy covariance method.

3.2.3. Groundwater and wetness maps

Groundwater from a network of deep wells and surface wetness maps for the SFW were provided by Dr. Carl Mendoza, University of Alberta, for 2013 and 2014. Over 50 deep piezometers (1 to 10 m) were installed throughout the SFW to represent the spatial distributions of hydraulic head at depth. Data for wetness maps was collected during a survey completed on 21 September 2013 to gather qualitative information on soil moisture saturation and presence of standing water within the SFW. In addition to deep piezometers, near surface water table fluctuations were measured using PVC slotted wells that were augured down between 0.48 – 1.02 m throughout the SFW and instrumented with Solinst Junior Edge Levelogger pressure transducers. 11 near-surface wells were installed in 2013, and 22 additional wells were installed in 2014 with transducers throughout the entire SFW including the lowlands, transition and upland areas. Transducers were programmed to take readings of water level and temperature every 15 minutes from May to October in 2013 and 2014. Manual measurements of water level were made weekly using a Solinst TLC water level tape for quality assurance and control. Levels were corrected each year for barometric pressure using a Solinst Barologger that was deployed off of B3.

Data for surface wetness maps was collected at 95 sites throughout the SFW for moisture content, depth of standing water and EC. Saturation was determined using the “squishy boot method” and visual observations which was classified into categories based on wetness. Depth of standing water was determined using a measuring tape and EC was determined using a calibrated Solinst TLC water level tape.

3.2.4. EC measurements

Continuous and discrete EC measurements of surface and pore water were taken in both 2013 and 2014. Five Solinst LTC (level, temperature, conductivity) Levelogger Junior pressure transducers, were installed in five of these wells along boardwalk three. In 2014, and a total of ten LTC transducers were installed down the major flow pathways (Figure 3.2). All transducers were calibrated with 12,800 µS/cm conductivity solution prior to deployment. Both years, transducers were programmed to take continuous measurements every 15 minutes for level, temperature and conductivity from May to October. Data was corrected for EC by removing values that corresponded to water levels greater than 1.595 m to eliminate any samples collected where the water level may not have been completely covering the sensor. Additionally, EC values less than 100 µS/cm were also removed, as they likely indicated when the Levelogger was taken out of the well for water samples.

Discrete measurements of EC were taken weekly using a YSI Professional Plus Multiparameter instrument, which sampled temperature, pH, dissolved oxygen and EC. The instrument was calibrated using 12,880 µS/cm conductivity solution approximately once per month. Each week “walkarounds” of the SFW were completed, part of which involved EC measurements at all near-surface wells as well as in any pooled surface water. These sample sites were marked on a GPS and used in conjunction with the EC values in arcGIS to map spatial variability of EC within the SFW. EC data from 2013 was supplemented with surface water EC measurements taken by the University of Alberta (methods in 2.3.2).

All EC values, both discrete and continuous were manually corrected for temperature in both 2013 and 2014 for consistency (Equation 3.1).

$$EC_t = EC_{25} / (1 + a*(t - 25)) \qquad (3.1)$$

Where EC_t is the corrected EC at temperature (µS/cm), t (ºC), EC_{25} is the EC at 25 ºC (µS/cm) and a is the temperature compensation factor which assumed to be 2% for the purpose of this study (Hayashi, 2004).

3.2.5. Major ions

A total of 23 surface and pore water samples were taken biweekly and analyzed for major ions and stable hydrogen and oxygen isotopes (Figure 3.2). Wells were purged prior to sample collection to discard of any stagnant water, and samples were collected manually using a Model 428 BioBailer and were poured into 1L amber bottles, both of which were environmentalized. Wells were capped in between sampling periods to avoid any contamination. Grab samples of surface water samples were also collected using the 1L amber bottles. Before chemical analysis, water samples were then run through 25 mm, 0.07 µM filters using vacuum suction and were stored the fridge in 60 mL, translucent HDPE bottles.

Cations (Li^+, Na^+, NH_4^+, K^+, Mg^{+2} & Ca^{+2}) and anions (Fl^-, Cl^- & SO_4^{-2}) were analyzed using a Dionex AS40 Automated Sampler at the Biogeochemistry Laboratory, University of Waterloo, and results were reported in mg/L. Additionally, a Bran & Luebbe AutoAnalyzer3 (Folio Instruments) was used for analysis of NH_4^+, NO^{-3}, alkalinity, PO_4^{-3} and soluble reactive phosphorus (SRP). HCO_3^- values were calculated by multiplying the alkalinity values by a conversion factor of 1.22. The conversion factor was determined by diving the equivalent weight of HCO_3^- (61 g/mol) by the equivalent weight of $CaCO_3$ (50 g/mol) which results in a conversion factor of 1.22 (Csuros, 1994). Major ion results were plotted onto Piper Diagrams (meq/L) using The Geochemist's Workbench Student program, to determine the various hydrochemical facies of water throughout the SFW. The water type of a sample is calculated once ions have been speciated to identify the true dominant free ions in a sample. Piper diagrams display the relative abundance of anions and cations of a sample (meq/L) in separate ternary diagrams, which are then projected onto the central field and based on where the two points intersect within the central field indicate that water type of that sample.

Additionally, the sodium adsorption ratio (SAR) for each sample was calculated (Equation 3.2) to infer the relative activity of Na^+ to Ca^{+2} and Mg^{+2}, which indicates the degree of cation exchange and the potential for soils to become saline-sodic (Robbins, 1984).

$$SAR = [Na^+] / \sqrt{([Ca^{+2}] + [Mg^{+2}])} \qquad (3.2)$$

Where cation concentrations are in mmol/L. Soils are considered saline when electrical conductivity exceeds 4000 µS/cm and sodic when SAR values are greater than 13, however some vegetation can show adverse effects at lower SAR values (USDA Salinity Laboratory, 1954). The non-parametric Mann-Whitney U analysis was used to compare the differences in major ion samples between 2013 and 2014 in the lowlands and the uplands of the SFW.

3.2.6. Stable isotopes

Stable hydrogen and oxygen isotope samples were collected simultaneously with the pore and surface water samples described above. Samples were also filtered and stored in 20 mL scintillation vials at room temperature. Stable isotope ratios for hydrogen and oxygen were determined using a Los Gatos Research DTL-100 Water Isotope Analyzer at the University of Toronto. Results of δD and $\delta^{18}O$ (‰) were plotted against a LMWL developed for SCL’s Mildred Lake Base Mine as well as isotope signatures for various source waters across SCL, all of which were previously determined (Baer, 2014). A LEL was established for the SFW by plotting a regression line through the δD-δ^{18}O relationship of surface waters within the SFW. The slope of the regression line is equivalent to the slope of the LEL. Source waters within the SFW were determined by visual comparison to the reference isotope signatures provided by Baer, 2014 of the varying signatures throughout SCL.

CHAPTER 4: Results

4.1. Climate

Results from this study include data collected during 2013 and 2014 with most focus during the summer and fall months (May – October). Average climate data for Fort McMurray from 2013 – 2014 are summarized in Table 4.1. Average air temperature at the SFW was warmer in 2013 than 2014 with average daily air temperatures of 9.2°C and 8.5°C respectively from April – October, which are both lower than the climate normal of 10.4°C for the same period (Table 4.1). Convective storms make up the majority of rainfall events and as a result, are high intensity and short-lived. Average cumulative rainfall from April to October at the SFW in 2013 exceeded rainfall in 2014, amounting to 366 mm and 306 mm, respectively both of which exceed the climate normal of 318 mm (Table 4.1). Timing of rainfall varies substantially between the two years, as 86% of rainfall occurred during the mid-summer months in 2013 and only 36% of the rainfall in 2014 occurred during those same months. Snowfall was also greater in 2013 than 2014, with average SWE values of 160 mm and 62 mm, respectively.

4.2. Hydrology

4.2.1. Hydrologic management of the SFW

Management of inflow and outflow pumping regimes varied substantially between the two years, with 2013 exhibiting frequent and inconsistent management of both pumps, while pumps in 2014 remained off and were only active during short, controlled events. Inflow events in 2013 were not frequent, but lasted for several weeks at a time. A total of 809 mm of water was delivered into the WSP in 2013, exceeding the annual precipitation for that year almost two-fold. Outflow pumping events in the early months of summer in 2013 were longer in duration that lasted several days, while in the late summer had a shorter duration typically lasting no longer than a few hours (Figure 4.1). In total, 883 mm of water was pumped out of the SFW in 2013. Comparatively, inflow pumping was isolated to one event in 2014 (May 19-20), and only provided a total of 14 mm. The inflow pumps then remained off for the remainder of 2014. Similarly, the outflow pumps remained largely off in 2014 with the exception of short and controlled drainage events, totaling 18.2 mm (Figure 4.1). The underdrains were open in 2013 and contributed over 90% of the total outflow in the SFW while in 2014, were closed as much as possible and surface water dominated most of the outflow waters.

4.2.2. Water table and groundwater

Inconsistent pumping activity resulted in a highly variable water table in 2013 with the most rapid water table responses observed in the lowland area of the SFW (Figure 4.2). Precipitation, snowmelt and runoff events controlled the water table responses in 2014, which exhibited an increase in the spring, followed by a slow decline as the SFW dried throughout the summer as a result of evaporation (Figure 4.3). Although it was attempted to remove disturbances from the data as a result of removing Leveloggers for water samples, spikes are still present the EC data as the sensor was likely restabilising after purging or being removed from the well (Figure 4.3). In 2013, standing water increased towards the B1 area due to 1) continuous input of fresh water into the WSP which moved through the gravel leaky dam into the B1 area and 2) the underdrains which influenced water table depth by limiting pooled water from the induced the downward movement of water. The latter resulted in an increase of standing water towards the inlet around B1, and a decrease towards B2 and B3 in 2013 (Figure 4.4).

Once closed in 2014, standing water increased at B2 and B3 as downward hydraulic gradients were removed and lateral flow was dominant, and decreased at B1 over the summer as water supply to SFW was off (Figure 4.5). In May 2014, much of the lowlands were hydrologically connected via surface water. Hummock 2 was connected to B1 which was entirely surrounded by pooled water and slightly extended into B2. A large pool of standing water was observed in the transition area, but did not connect to the lowlands (Figure 4.5). Pooled surface water was most extensive in June 2014 across the SFW, as it extended outwards from all boardwalks significantly and was connected from B1 through to the OP. In addition, pooled water in the transition areas were connected to pooled surface water that surrounded B2 and B3. The SFW began to dry throughout July and pooled water decreased and became disconnected across the lowlands at B2 as well as from the transition areas. Water level in the WSP decreased and wetness around hummock 2 also became less pronounced. The SFW had the least amount of standing water in August and pooled areas that surrounded B1 and B3 decreased considerably and B2 and transition areas became mostly dry. The water level in the WSP also continued to decrease and hummock 2 became disconnected from B1 (Figure 4.5).

Deep piezometers indicate similar groundwater movement in 2013 (Figure 4.6) and 2014 (Figure 4.7), with hydraulic heads showing a general movement of groundwater originating from south of SFW in EIP, and moving northeast through SFW and exiting in the east at the outlet.

4.3. Hydrochemistry of the SFW

Different pumping regimes between the summers of 2013 and 2014 resulted in notable differences in water chemistry. Results below outline the changes in EC and major ion concentrations throughout each summer and highlights the important differences between the summers of 2013 and 2014 as a result of the different management regimes at SFW.

4.3.1. Temporal hydrochemical variation

4.3.1.1. Electrical conductivity

Water level was highly variable among all sampling sites in 2013 and both pumping and rainfall events caused marked responses in water level and EC. Water levels increased at all sites in response to three large rainfall events of 68.3 mm from 8 - 9 June 2013, 30.7 mm from 4 – 13 July 2013 and 37.8 mm on 28 July 2013. The most noticeable response occurred as a result of a long outflow pumping event from 20 July 2013 to 8 August 2013, where EC decreased at all sites along B3 (Figure 4.2). Although outflow pumping continued after 8 August 2013, individual responses to each pumping event were not evident in the EC or water level data because outflow pumping was in short intervals of a few hours (Figure 4.1 & 4.2). The cumulative effect of various rainfall events throughout August and September caused water levels to increase after the large pumping event which ended 8 August 2013. EC was variable, but relatively low throughout the SFW in 2013, with the average EC at most sites in the lowland area below 1000 µS/cm. There is elevated EC around hummock 2 and in the transition and upland areas with EC exceeding 3000 µS/cm (Figure 4.8).

Unlike 2013, water level steadily declined among all sites in the SFW from May to September in 2014. Two large rain events in September amounting to 33.2 mm which fell over a span of nine days from 30 August – 7 September 2014 and 28.3 mm which fell on 26 September 2014, caused an increase in water levels at all sites. Evidence of controlled outflow events, which were all four hours or less, were not observed in the data. EC typically increased with a decline in water level as the SFW dried over the 2014 summer (Figure 4.3), which was dissimilar to the variable pattern observed in 2013. Average EC values increased from 2013 to 2014, exceeding 1000 µS/cm at many of the lowland sites. The elevated EC in the transition and upland areas extended further into the transition and lowland area where EC mostly exceeded 3000 µS/cm (Figure 4.8).

4.3.1.2. Major ions

Major ion concentrations at most sampling locations were lower in 2013 in the lowlands and transition/uplands (Figure 4.9). Although standard deviations do show considerable variability among site averages, particularly with Na^+ and Ca^{+2} which are the ions of most concern (Table 4.2), the dominant ions at all sites showed little change throughout the summer of 2013, except at the WSP, OP and SUMP that changed in response to inflow and outflow pumping (Figure 4.10). The WSP was dominant in Ca^{+2} throughout the summer, while the dominant anion shifted from SO_4^{-2} to HCO_3^- when the inflow pump was on (Figure 4.10a). Average Na^+ and Ca^{+2} concentrations in the WSP in 2013 were 46 ± 49 mg/L and 57 ± 25 mg/L, respectively (Table 4.2). Although standard deviations indicate variable concentrations at the WSP, Ca^{+2} remained the dominant ion and absolute Na^+ and Ca^{+2} concentrations did not exceed 100 mg/L (Figure 4.11). An increase in both Na^+ and Ca^{+2} and consequent shift to Na^+ dominant in October was the only drastic change in ion chemistry at the WSP, likely the combined effect of decreased freshwater input and evapo-concentration. The MF surface and near-surface well sites on the boardwalks did not show changes in response to pumping, but were variable throughout the summer. Na^+ and Ca^{+2} concentrations at the MF were below 100 mg/L except for an isolated sample on 16 Jul 2013 when concentrations increased to 246 mg/L and 146 mg/L respectively (Figure 4.11), which was in between inflow and outflow events. Sampling sites on B3 were dominant in SO_4^{-2}, while sites closer to the WSP were HCO_3^- dominant (Figure 4.10b). Average Na^+ and Ca^{+2} concentrations were similar but variable in the MF surface samples of 61 ± 60 mg/L and 66 ± 29 mg/L respectively, but Ca^{+2} remained the dominant cation throughout the summer of 2013 (Figure 4.10b). The only major change observed in the lowland wells was at well B1-W3 where Na^+ concentrations increased from 22 mg/L in July to 159 mg/L in August. Dominant ions were more variable in response to outflow pumping at the OP in 2013, and average Na^+ and Ca^{+2} concentrations were 119 ± 122 mg/L and 90 ± 50 mg/L respectively. Ca^{+2} was the dominant cation when the outflow pump was active, which shifted to Na^+ dominant as pumping events decreased later in the summer. The dominant anion shifted from SO_4^{-2} to HCO_3^- as the summer progressed (Figure 4.10c). Na^+ concentrations in the SUMP in 2013 showed the most variability, with an average concentrations of 355 ± 225 mg/L, while Ca^{+2} was considerably less variable with an average concentration of 103 ± 27 mg/L. These concentrations also changed in response to outflow pumping, but remained mostly dominant in Na^+ throughout 2013, while the dominant anion was more variable (Figure 4.10d). During the winter months, from November 2012 to March 2013, the outflow pump was off, water was stagnant and the Na^+ concentrations were consistently above 500 mg/L (Figure 4.11). Once pumping activity began in the spring and continued throughout the summer and fall, the average Na^+ concentration in the SUMP decreased to an average of 246 mg/L from April to October 2013. Ca^{+2} concentrations fluctuated with pump activity, but remained relatively consistent in comparison to Na^+ (Figure 4.11).

In general, major ion concentrations increased in both the lowlands and uplands of the SFW from 2013 to 2014, with the most noticeable increase in the range and distribution of Na^+ concentrations in both the lowlands and transition/uplands (Figure 4.9). All pumps were off for the duration of the sampling period from May to October 2014, and most sites had consistent dominant ions (Figure 4.12), as well as showed less variability in average concentrations (Table 4.3). Excluding the OP and SUMP, all sampling sites displayed an overall increase in Na^+ and Ca^{+2} concentrations throughout the summer of 2014 (Figure 4.13), similarly to the increase in EC in response drying throughout the summer within the SFW. SO_4^{-2} was consistently the dominant anion throughout the SFW, whereas the dominant cation was Ca^{+2} at most sites except at the inlet and outlet, B1, B2-S1 and sites that lie along the border of the southern hummocks, all of which were Na^+ dominant (Figure 4.12). Ion concentrations also increased in the OP from 2013 to 2014, but a decrease or similar concentrations were observed in the SUMP between the two field seasons (Figure 4.9). Both the OP and SUMP had elevated Na^+ concentrations early in the summer of 2014 until the outflow pump was on (and underdrains closed in the SUMP), where Na^+ concentrations decreased considerably (4.12a). After the drastic decrease in the SUMP, Na^+ remained low, while Ca^{+2} slightly increased (Figure 4.13). The average Na^+ concentrations in the SUMP decreased from 623 ± 100 mg/L to 165 ± 51 mg/L once the underdrains were closed on 20 May 2014 (Table 4.3).

A simple non-parametric statistical test showed a significant difference in Na^+, Ca^{+2}, SO_4^{-2} and HCO_3^- concentrations in the lowlands from 2013 to 2014 (Table 4.4). There was insufficient data collected in the uplands during 2013 to run a statistical test however, the hydrochemical changes in the uplands from 2013 to 2014 did not appear to be as significant in comparison to the lowlands.

4.3.2. *Spatial hydrochemical variation*

4.3.2.1. Electrical conductivity

The freshwater pumped into the WSP from Mildred Lake was estimated to have an EC of approximately 500 µS/cm (Wytrykush et al., 2012). The EC gradually increased from the WSP and across the SFW towards the SUMP, where the average EC was 2570 µS/cm. In 2013, much of the lowland areas of SFW were below 1000 µS/cm, with few locations exceeding 1000 µS/cm (Figure 4.8). Elevated EC is evident along the border of the southern hummocks including 2, 7 and 8. The upland area did not benefit from the freshwater supplied to SFW, and EC ranged between

2000 - 4000 µS/cm (BCG, 2014). From 2013 to 2014, the EC of the WSP increased and had an average of 1337 µS/cm, as no freshwater was being brought in. EC in the lowlands as well as the transition and upland areas also increased from 2013 to 2014, and ranged between 1000 – 3000 µS/cm and 3000 – 5000 µS/cm, respectively (Figure 4.8). Elevated EC was still evident along the border of hummocks 2, 7 and 8 and has increased from 2013 to 2014. The SUMP was the only location where EC decreased from an average of 3157 µS/cm to 1456 µS/cm between 2013 and 2014, as the underdrains were closed in May 2014.

4.3.2.2. Major ions

Na^+ exhibits the most notable increase from 2013 to 2014 across SFW. Excluding the WSP, OP and SUMP, in 2013 Na^+ concentrations ranged from 20 – 246 mg/L in the lowland area, and 190 – 632 mg/L in the transition and upland areas and in 2014, ranged from 20 – 613 mg/L in the lowlands and 3.5 – 886 mg/L in the transition and upland areas (Figure 4.9). In 2013, the SUMP and OP have some of the highest Na^+ concentrations and were highly variable with averages and standard deviations of 119 ± 122 mg/L and 355 ± 225 mg/L respectively (Figure 4.14), while most other sites within SFW did not exceed Na^+ concentrations of 100 mg/L. Once the outflow pumps were off and underdrains closed in 2014, the OP and SUMP no longer had the highest average Na^+ concentrations, which decreased to 228 ± 127 and 165 ± 51 mg/L respectively, whereas B1 and the transition areas along the border of the hummocks in the south fen exhibited the highest Na^+ concentrations (Figure 4.14). Unlike the other major ions, Na^+ exhibited considerable increase only in specific "hotspot" areas across SFW from 2013 to 2014, whereas the other ions have generally increased evenly across the upland and transitional areas (Figures 4.15 – 4.17). These "hotspots" included B1-S1, B1-W3, TR-S1, TR-S2 and TR-W2 which had average Na^+ concentrations of 352 ± 123 mg/L, 441 ± 110 mg/L, 521 ± 247 mg/L, 470 ± 181 mg/L and 347 ±

84 mg/L, respectively. Although values at these sites were variable, the dominant ions were consistently Na^+ and SO_4^{-2} throughout the summer of 2014. The lowest Na^+ concentrations were observed at TR-W3 with an average concentration of 8 ± 3.5 mg/L.

Although Ca^{+2}, SO_4^{-2} and HCO_3^- also exhibited spatial variation and increased from 2013 to 2014, the distribution of their concentrations were more consistent throughout the SFW with no noticeable areas experiencing an extreme increase in 2014 (Figures 4.15 - 4.17). In general, the Ca^{+2}, SO_4^{-2} and HCO_3^- concentrations were highest in the transition and upland areas whereas the lowland-wetland areas exhibit lower concentrations. Excluding the WSP, OP and SUMP, in 2013 Ca^{+2}, SO_4^{-2} and HCO_3^- concentrations ranged from 34 – 505 mg/L, 30 – 1610 mg/L and 22 – 348 mg/L respectively in the lowland area, and 268 – 632 mg/L, 672 – 1895 mg/L and 166 – 377 mg/L respectively in the transition/upland areas. In 2014, Ca^{+2}, SO_4^{-2} and HCO_3^- concentrations slightly increased and ranged from 46 – 584 mg/L, 92 – 1687 mg/L and 84 – 602 mg/L respectively in the lowland area, and 45 – 688 mg/L, 75 – 2213 mg/L and 63 – 830 mg/L respectively in the transition/upland areas (Figure 4.9).

4.3.3. SFW source waters from stable isotope analysis

Stable isotopes of water samples from the SFW in 2014 were plotted along a LMWL previously developed for SCL's Mildred Lake Base Mine as well as compared to the isotope signatures of various source waters from a site-wide isotope study at SCL (Table 4.5) (Baer, 2014). Isotope samples showed similarities to Mildred Lake, OSPW, SFW groundwater, SFW SUMP water and BCG groundwater samples. Surface water and pore water samples in pooled areas of SFW followed a LEL developed for SFW (Equation 4.1).

$$\delta D = 4.9(\delta^{18}O) - 56.8‰ \qquad (4.1)$$

Pore water samples that were the most isotopically depleted, plot along the LMWL in between the isotopic signatures for snow and Mildred Lake which include TR-W3, TR-W8 and TR-W13 (Figure 4.18). The isotopic signatures for the SFW groundwater were widely distributed and plot in between the isotopic signatures for Mildred Lake and rainfall. Many samples also plot along the LMWL and display a similar distribution to SFW groundwater samples which include TR-W5, TR-W2, TR-W4, UP-W4, UP-W5, B3-W2 and B3-W4. Additionally, the water chemistry at these sites have similar Na^{+} and Ca^{+2} concentrations. B1-S1 and B1-W3 were isotopically similar to OSPW, and TR-S1 and TR-S2 were isotopically similar to SUMP water (Figure 4.18). On average, surface water samples were the most isotopically enriched and plot along the LEL including B2-S1, B3-S1 and OP-S1. However, some wells that were located in areas of persistent standing water throughout the summer also plot along the LEL such as B2-W7, B3-W3 and TR-W9. It is important to note that the most isotopically depleted sites correspond with the highest Ca^{+2} and lowest Na^{+} concentrations. Additionally, sites that are isotopically enriched tend to correspond with the highest Na^{+} concentrations.

CHAPTER 5: Discussion

Wetland-peatland reclamation in the oil sands region presents many hydrological and ecological challenges, as it involves complete reconstruction of the ecosystem with no benchmarks or previous knowledge of such methods. The ecology of these constructed systems will be greatly influenced by the presence of elevated salts and salinity, and therefore reclaimed wetlands need effective design and management to limit any potential for salinization of the ecosystem. It is crucial to understand salt movement and accumulation in these reclaimed systems to ensure the reclaimed wetland is capable of performing all necessary functions at equal capacity to the pre-disturbed landscape, and if not, the reasons why. In the SFW, this involves identifying the effects of variations in water management, as they were implemented in large part to minimize salinization.

The critical difference to highlight between the summers of 2013 and 2014 is the variation in pump management. In 2013, SFW was highly managed with inconsistent activity of the inflow and outflow pumps. Additionally, the underdrains were open and draining into the SUMP, which provided an induced downward hydraulic gradient and limited any upward movement of OSPW. As a result of the high degree of management in 2013, SFW water tables were not typical of a natural fen and were primarily controlled by the pumps as indicated by the highly variable water level throughout the summer (Figure 4.1). In 2014, both the inflow and outflow pumps were off and the underdrains were closed, which resulted in limited flushing of the system and eliminated the induced downward hydraulic gradient provided by the underdrains. At this point, the SFW was more similar to a natural fen in terms of water level, which showed a steady decline during the summer months (Figure 4.2).

5.1. Effect of management

The CT and mine waste materials that underlie the SFW create a strong concentration and salinity gradient with surface materials, providing the means for significant upward diffusion of salts (Fraser et al., 2001). However, with the combination of inflow supply of freshwater, open underdrains to collect any upward diffusion of salts from depth, and frequent activity of outflow of SUMP water in 2013, the overall salinity was minimized as evident from the relatively low EC (Figure 4.8) and Na^+ concentrations (Figure 4.14) across the SFW. However due to increased pump activity, ion concentrations among sites were variable (Figure 4.11), which may pose as a risk to vegetation that cannot adapt to continuously changing osmotic pressures. The upland and some transition areas have elevated EC compared to the lowlands because they do not benefit from the freshwater input. The underdrains can only be emptied when the outflow pump is on, which was frequent in 2013, and effectively limited upward movement of OSPW by continuously draining into the SUMP, where waters have elevated EC and Na^+ concentrations (Figure 4.11). Piper diagrams indicate that in 2013, SFW water classified as either $Ca\text{-}HCO_3$ or $Ca\text{-}SO_4$ (Figure 4.10) with SAR values at all sampling locations mostly below 1.5, indicating little Na^+ influence (Table 4.2). Sites closer to the WSP were HCO_3^- dominant from the freshwater contribution, while sites closer to the outlet are SO_4^{-2} dominant. This was expected knowing the source and treatment of overburden and peat materials. Only the OP, SUMP and B1-W3 had an average water type $Na\text{-}SO_4$ in 2013 (Figure 5.1), which also corresponds to higher SAR values at these locations of 2.7, 7.9 and 2.2, respectively (Table 4.2). The OP gathers all the surface and near surface water, resulting in higher ion concentrations, including Na^+. Underdrain water makes up the majority of water in the SUMP and thus accounts for the high Na^+ content and SAR values. On the other hand, B1-W3 is located within the main lowland area of the SFW and may be early evidence of OSPW that has reached the surface (Figure 4.14). B1-W3 only had two water samples taken in July and October of 2013, which classified as Ca-HCO_3 and Na-SO_4, respectively (Figure 4.10b). Starting in mid-August of 2013, the outflow pump was largely off which prevented drainage from underdrains and consequently eliminated the vertically enforced hydraulic gradient, allowing for upward transport of OSPW and presumably resulted in the transition of water type observed at B1-W3. Water chemistry from B1-W3 shows a substantial increase in Na^+ concentration and SAR as well as a shift in water classification from July to October, which suggests evidence of the first and only observed Na^+ "hotspot" within the SFW in 2013. B1-W3 was likely influenced from the elevated EC observed surrounding hummocks 2 and 7.

5.2. Effects of limited management

The overall salinity and ion concentrations throughout the SFW show an increase from 2013 to 2014 as a result of dramatically reduced inflow and outflow pump activity. The underdrains were closed almost all of the summer, which eliminated the induced downward hydraulic gradient. Other than the few short and controlled drainage events, water in the SFW was not consistently flushed, resulting in accumulation of ions and elevated EC throughout the SFW. Additionally, unlike ion concentrations in 2013 that were variable as a result of pump activity (Figure 4.11), ions gradually increased throughout the summer of 2014 as a result of accumulation and evapo-concentration (Figure 4.13). More noticeably was the increased presence of high Na^+ concentrations in certain "hotspots" along the edges of the hummocks in the south of the lowlands (Figure 4.14), presumably as a result of upward transport of OSPW interacting with the surface. Sites that classified as Na-SO_4 dominant were identified as potential Na^+ "hotspots" and include the WSP, B1-S1, B1-W3, B2-S1, TR-W2, TR-S1 and TR-S2. Other than these "hotspots", most sites were Ca-SO_4 dominant (Figure 5.1) with average SAR values ranging from 0.1 - 2.8, indicating little Na^+ influence.

In 2014, the OP and SUMP also classified as Na-SO4 dominant and exhibited elevated Na^+ concentrations and SAR values, however this likely due to their position at the outlet of the SFW where water accumulates. The SUMP showed a drastic change in water chemistry after the underdrains were closed on 23 May 2014, where the average SAR shifted from 15.1 to 3.3. There is a distinct decrease in Na^+ concentrations in the SUMP once the underdrains were closed. The OP had a relatively low average SAR compared to other Na^+ "hotspot" locations, and was likely concentrated with ions as its water was continuously evaporated over the summer. Although the water at WSP, B2-S1 and TR-W2 all identify as Na-SO_4, they all have relatively low average SAR values (3.6, 3.2 and 3.8, respectively) as well as similar Na^+ and Ca^{+2} concentrations, indicating that these locations are likely not directly influenced by OSPW (Leung et al., 2003) as the other Na^+ "hotspot" locations have considerably higher Na^+ than Ca^{+2}. B2-S1 and TR-W2 are likely Na^+ dominant because they were hydrologically connected via surface water to other Na^+ "hotspots" for the majority of the summer of 2014. Additionally, continuous drying at these sites over the summer concentrates ions in surface water (Trites and Bayley, 2009a). The WSP, has a heavily compacted clay liner which prevents interaction with groundwater, so evaporation and subsequent concentration of ions in water is likely the cause of its Na-SO_4 water type. The remaining sites, B1-S1, B1-W3, TR-S1 and TR-S2, were Na-SO_4 dominant throughout the entire summer, unlike the sites mentioned above. They also have higher average SAR values of 6.7, 6.9, 5.6 and 6.5 respectively, suggesting seepage locations along hummocks, creating the high Na^+ "hotspots". B1-S1 and B1-W3 were likely influenced by seepage and subsequent advection of OSPW from both hummocks 2 and 7, while TR-S1 and TR-S2 were likely influenced by hummocks 7 and 8, respectively, as these areas were hydrologically connected through ponded surface water, which persisted for most of the summer and fall (Figure 4.5).

SFW groundwater movement and flow was modelled under various potential boundary conditions, including salt flushing as a result of controlled pumping (BGC, 2015). With limited outflow of water through the SUMP, model results indicate that as groundwater moved in through the south boundary of the SFW, transport was primarily horizontally through the tailings sand cap until it reached the hummocks where it seeped into the lowland area of SFW. The model results indicate elevated salt concentrations at these seepage locations, particularity south of the lowland area. Unlike the majority of the SFW area, a fine- to course-grained Pleistocene fluvial sand (Pf Sand) was placed on top the tailings sand cap on hummocks 2, 4, 5, 7 and 8 with reported horizontal (Kh) and vertical (Kv) hydraulic conductivities of 2.5 x 10^{-4} m/s, 2.5 x 10^{-5} m/s, respectively for the Pf sand and 5.0 x 10^{-6} and 3.6 x 10^{-7}, respectively for the tailings sands cap. The clay till has considerably lower hydraulic conductivities of 1.0 x 10^{-7} m/s for both Kh and Kv (BGC, 2015). The higher hydraulic conductivity of the Pf Sand material placed on the hummocks, potentially provides a preferential flow path for any upward transport of OSPW to enter the lowland areas of the SFW.

The presence of the Na^+ "hotspots" within the SFW in both 2013 and 2014, provides evidence of the modelled upwards groundwater movement and subsequent seepage from the southern hummocks (#2, 7 and 8) with a decrease in pump activity. In the late summer of 2013 at B1-W3, located slightly north of hummock 7, Na^+ concentration and EC increased considerably where seepage of OSPW from depth was predicted from modelling likely because of the decreased pump activity and subsequent reduced water drainage from the underdrains during that time. Additionally, EC was elevated around both hummock 2 and 7 area, which could be a reflection of seepage and subsequent diffusion of OSPW from the hummocks. Elevated surface water EC values in the transition and upland areas are presumed to be amplified from seepage and subsequent diffusion of OSPW from the east side of hummock 7. With minimal management in 2014, multiple Na^+ "hotspots" were evident throughout the summer at the seepage locations identified by the numerical groundwater modelling. Results confirm that hummocks 2, 7 and 8 had Na^+ "hotspots" likely due to their southern location within the SFW, where groundwater movement from the south originates. Overall, OSPW likely diffuses slowly upwards from the CT layer that underlies the fen, which is then transported via advection as it moves horizontally in the tailings sand cap and through the Pf sand and consequently reaches the surface at the seepage locations, where salts are transported via diffusion through the relatively stagnant surface waters. Additionally, there is likely some slow diffusion of salts occurring through the clay layer and into the peat across the SFW, as the induced downward hydraulic gradient was eliminated, and likely contributes to the slight overall increase in Na^+ at all sites. Although hummocks 4 and 5 comprised of similar soil materials as 2, 7 and 8, OSPW seepage was not observed as groundwater movement is towards the east once it reaches lowland areas of SFW. Due to the reduced surface and pore water sampling in 2013, it is unknown if other Na^+ "hotspots" existed within the SFW, but since a considerable increase in the Na^+ concentration at B1 was observed shortly after the underdrains stopped draining continuously in August 2013, is it possible that other "hotspots" began to develop at that time as well. If so, these other "hotspots" likely developed along the east side of hummock 7 where pooled surface water was observed in 2013.

Statistical analysis shows a significant difference in ion concentrations within the lowlands between 2013 and 2014, which is attributed to the limited pump activity between years. Although no significant difference was shown statically for the transition/uplands between 2013 and 2014, they were still likely influenced by pump activity due to the presence of Na^+ "hotspots" that developed in the transition/upland areas.

5.3. SFW source waters

Most of the hydrogen and oxygen isotope ratios of sites in SFW plot along the LMWL and are bound by the isotopic values for rainfall and Mildred Lake, which are the primary water sources for the SFW. These sites also plot within the isotopic range for SFW groundwater provided by Baer, 2014 (Figure 4.18) and is likely a mix of precipitation, Mildred Lake water and SFW water, which is reflected in their water chemistry where all of these sites have similar Na^+ and Ca^{+2} concentrations and low SAR values.

Pore water samples that plot outside of the range of SFW groundwater isotope signatures either: (1) plot along to LEL developed for SFW or (2) are increasingly depleted and shifted towards the isotopic ratios for snow. Both pore and surface water from sites in areas of pooled water will be isotopically enriched compared to groundwater samples as lighter water isotopes are preferentially evaporated, therefore enriching the surface water with heavier isotopes that plot along the LEL (Craig, 1961; Smerdon et al., 2005). This is the case for all of the surface water samples including the WSP, B1-S1, B1-W3, B2-S1, B2-W7, B3-S1, B3-W3, B3-W4, OP, TR-S1 and TR-S2 which were all in pooled water areas for the majority, or all of the summer in 2014. TR-S1 and TR-S2 are isotopically similar to the SFW SUMP which suggests that TR-S1 and TR-S2 are a combination of OSPW and other fen water and therefore a Na^+ "hotspot". The B1-S1 and B1-W3 isotopic signatures are most similar to the OSPW and CT water which not only supports that these locations are Na+ "hotspots", but also suggests that these waters are a more direct source of OSPW from the CT zone. Results also indicate that the WSP, B2-S1, TR-W2 and OP locations are not Na^+ “hotspots”, as their isotopic signatures are not similar to OSPW, CT water or the SUMP.

TR-W3, TR-W8 and TR-W13 are the most isotopically depleted samples and all plot along the LMWL. Their proximity between the rainfall and snow isotopic signatures suggests that water at these locations are only meteorically sourced, are not influenced by enrichment from evaporation (Gue et al., 2015; Smerdon et al., 2005) and do not have any interaction with other waters within the SFW including saline-sodic groundwater. This is confirmed from the extremely low Na^+ and high Ca^{+2} concentrations and low average SAR values of 0.1, 0.8 and 1.2, respectively. These three sites are located either in close proximity, or on small tailings sand islands within the SFW, therefore similar areas throughout the SFW may also be isolated from other fen waters and the pore water chemistry is strictly influenced by rain and snow water that interacts with chemical species within the tailings sand.

5.4. Naturally saline wetlands as analogues for reclamation

Due to the likelihood that many reclaimed wetlands in the oil sands region will be saline as a result of by-products from mining and treatment processes, studies suggest that naturally saline wetlands in the WBP should be used as benchmarks for wetland reclamation design (Purdy et al., 2005; Trites and Bayley, 2009a; Wells and Price, 2015). Currently, much of the framework for assessing success of reclaimed wetlands is based off of indicator species for open-water marshes, which may be inappropriate for wetland-peatlands as they provide unique functions that permit development of vegetation associated with advanced succession (Nwaishi et al., 2015). Although rare within the WBP, naturally saline wetlands exist where saline groundwater discharges at the surface (Trites and Bayley, 2009a; Wells and Price, 2015). These saline wetlands support many vegetation species rare to freshwater wetlands that dominant the WBP region as a result of high

EC values, and more specifically elevated Na^+, Cl^- and SO_4^{-2} concentrations (Purdy et al., 2005; Rooney and Bayley, 2011; Timoney and Lee, 2001; Trites and Bayley, 2009a). Although reclaimed wetlands are dominated by Na^+, the absolute EC, Na^+ and Cl^- concentrations can be considerably higher in natural saline wetlands, with reported values ranging from 600 - 31000 µS/cm (Trites and Bayley, 2009a, 2009b), 195 – 25680 mg/L and 1785 – 56249 mg/L, respectively (Purdy et al., 2005; Stewart and Lemay, 2011; Trites and Bayley, 2009a, 2009b; Wells and Price, 2015). Elevated salinities in wetland and peatland ecosystems, especially high in Na^+, support different vegetation and phytoplankton communities that are not commonly found in freshwater wetlands (Leung et al., 2003; Rooney and Bayley, 2011; Trites and Bayley, 2009a). However, freshwater fens in the Boreal forest exhibit considerably lower cation concentrations and EC values which may not be realistic and achievable giving the high salinity of reclamation materials. Average reported Na^+ and Ca^{+2} concentrations in freshwater moderate-rich fens range between 2.2 – 6.9 mg/L and 9.8 – 22.1 mg/L, respectively with average EC values between 67.5 – 91 µS/cm (Chee and Vitt, 1989; Vitt and Chee, 1990; Vitt et al., 1995). Values reported for Na^+ and Ca^{+2} concentrations in extreme-rich fens ranged from 0.6 – 7.1 mg/L and 22.4 – 67.7 mg/L, respectively with average EC values ranging from 180 – 214 µS/cm (Vitt and Chee, 1990; Vitt et al., 1995). Comparatively, Na^+ and Ca^{+2} concentrations at the SFW in 2014 ranged from 3.5 – 886 mg/L and 10.3 – 668 mg/L, respectively with EC values ranging from 288 – 5092 µS/cm. Although salinities at the SFW are not as high as some of the reported values for saline wetlands, the distribution of Na^+, Ca^{+2} and EC in the SFW better matches that of saline wetlands than values reported for freshwater wetlands, as these values were considerably lower and were rarely seen at the SFW even in 2013 when the overall salinity was lower. Therefore, it may be more feasible to design reclaimed wetlands in the oil sands region similarly to naturally occurring saline wetlands in the

WBP, particularly if salinity with reclaimed wetlands is expected to increase over the first few years after construction. Additionally, studies have observed significant retardation of Na^+ transport in peat due to sorption and diffusion mechanisms which may prolong time before effects of high Na^+ are observed in vegetation.

Natural saline wetlands have adapted to high salinities with salt-tolerant vegetation communities in areas of elevated EC and Na^+ concentrations. Certain vegetation species that have been shown to survive in OSPW at lower salinities (Purdy et al., 2005; Trites and Bayley, 2009a) have also been shown to maintain the potential to form organic matter and thus peat (Trites and Bayley, 2009b) and suggest that elevated salinity does not reduce the potential for reclaimed landscapes to accumulate organic matter if certain salt-tolerant plants are present and favourable environmental conditions are met such as persistent wet conditions and higher water levels. Although some studies indicate a lower species richness in saline ecosystems (Rooney and Bayley, 2011; Trites and Bayley, 2009a), other studies suggest that saline landscapes may have higher species richness at a larger scale (Purdy et al., 2005). Collectively, these aspects of saline landscapes may provide evidence that naturally saline wetlands can act as an analogue for success of reclaimed wetlands in the oil sands region.

5.5. Potential hydrochemical changes in the long-term

Climate is one of the primary controls on the hydrology within the WBP and is classified as a long-term deficit with seasonal and decadal wetting and drying cycles (Devito et al., 2012). Wetlands typically have a low water storage capacity, allowing runoff and connectivity during a wetting cycle. This allows systems to flush salts and redistribute nutrients in natural systems (Devito et al., 2012). Although a wetting cycle may increase ponded water and dilute salts, an increase in pooled water in the lowlands of the fen might increase the concentration gradient between the surface waters and deep OSPW, resulting in an increased movement of salts towards the surface. Additionally, evaporative-driven advection of water from depth may increase as well due to the increase in evaporation as a result of the pooled water (Merrill et al., 1983). Simulated wet conditions at the SFW indicate that hydraulic heads rose by 1 – 2 m resulting in significant standing water that connects the lowlands to the uplands (BGC, 2015). Increasing evapotranspiration as the SFW vegetation develops decreases this connectivity over time, but is still highly saturated. Model results suggest that water management via the pumps may be required to prevent flooding (BGC, 2015). An increase in rainfall may provide some flushing potential for the transition and uplands areas, especially because the peat laid in the SFW is likely disturbed from transfer and not yet compacted from decomposition, resulting in large pores and increased drainage (Waddington et al., 2014). However, an increase in rainfall may also increase standing water in the lowlands. Therefore, wet climate cycles experienced at the SFW may require management of outflow to limit excessive evaporation and to prevent the potential for the SFW to progress to a marsh wetland.

With a continuously warming climate, northern peatlands are expected to experience a greater water deficit (Rouse, 1998; Tarnocai, 2006) and therefore the SFW may become vulnerable to drought conditions in the long-term (Clair, 1998) as it is unfavourable for peatlands to develop in a dry climate (Devito et al., 2012; Waddington et al., 1998). Under a 2 x CO_2 climate change scenario, modelled results estimate that water tables in northern Canadian peatlands will decrease by an average of 14 cm (Roulet et al., 1992), which will affect many peatland ecosystem functions (Nwaishi et al., 2015). However, modelling of this scenario in northern peatlands has shown the potential for recolonization of vegetation in areas where surface water has dried if adequate antecedent moisture conditions exist (Waddington et al., 1998). Dry climate conditions were modelled at the SFW and predicts that standing water will still exists in much of the lowlands and uplands, but to a lesser extent and with reduced surface water connectively between the lowlands and uplands (BGC, 2015). Due to the volume of standing water predicted within the SFW with a warming climate, recolonization of vegetation in areas of surface water that dry may occur in response to a decline in the water table. However, afforestation may occur as a result of a large decline in water table depth, which is favourable for the growth of many tree species and may draw down the water table further (Waddington et al., 2014). Under these conditions, the SFW may slowly transition to more of a forested system. There are many other scenarios that may apply to the SFW with a decreasing water table in response to climate change, but effects of water table drawdown may be difficult to predict in the SFW as constructed wetland ecosystems are relatively new within the oil sands region. With regards to salinity, a drier climate may concentrate salts within the SFW resulting in enhanced adverse effects on vegetation, especially with elevated Na^+ concentrations. If environmental conditions become drier with a warming climate, it may delay the time expected for the SFW to become self-sustaining, especially as vegetation continues to develop and thus further reducing standing water.

CHAPTER 6: Summary and Conclusions

This study has identified the changes in hydrochemical behaviour of a constructed watershed under different management regimes. It is crucial to understand how and where water moves within a highly engineered and managed system and subsequent salt distribution, particularly with respect to Na^+, to ensure ecological success of the reclaimed watershed. Results indicate that changes in pump management between 2013 and 2014 had a strong control on the SFW water chemistry. With the combination of consistent inflow of freshwater and continuous flushing of the system with the outflow pump and open underdrains in 2013, water level, EC and ion concentrations were highly variable. However, the overall salinity of the SFW was relatively low, and most sites throughout the lowland did not exceed 1000 µS/cm. Although the uplands were slightly more saline as they are not influenced by the freshwater input, Na^+ concentrations did not exceed 250 mg/L and most water throughout the SFW classified as $Ca\text{-}HCO_3$ or $Ca\text{-}SO_4$. In comparison, closed underdrains and minimal pump activity in 2014 resulted in limited freshwater input and flushing of the system, and the overall salinity of the SFW increased considerably with much of the lowlands exceeding 1000 µS/cm. EC and ion concentrations also increased and were variable in 2014, but as a result of evapo-concentration and ions gradually increased as the surface and near-surface water steadily declined throughout the summer. The most notable change with limited pump and underdrain activity in 2014 was the prevalence of specific sites along the edges of the southern hummocks in the SFW that exhibited a large increase of Na^+, where waters classified as $Na\text{-}SO_4$ and Na^+ concentrations reached a maximum of 886 mg/L. On the other hand, Ca^{+2}, SO_4^{-2} and HCO_3^- increased relatively evenly throughout the SFW from 2013 to 2014. These Na^+ "hotspots" reflect locations where saline groundwater has moved upwards and interacted with the surface. Although some evidence of this was observed in 2013, with the underdrains closed for the duration of the summer in 2014 and with limited inflow and outflow upward transport of OSPW was facilitated and subsequent development of the Na^+ “hotspots”, resulting in substantial accumulation of Na^+ over the summer. Stable isotope results in 2014 confirm these observations, as the isotope signatures of water at these “hotspots” were most similar to OSPW, SUMP and CT water, while most other sampling sites were isotopically similar to SFW groundwater. The presence of these Na^+ “hotspots” supports modelled results that predicted seepage of OSPW from depth out from the hummocks, where the clay layer was absent, after diffusing upwards from the CT and transported horizontally in the 10 m sand cap layer that underlies the SFW.

Monitoring of hydrochemistry within SFW system is essential to ensure success of the ecosystem in the long-term, particularly until the watershed can provide non-saline groundwater inputs, which may take several years. It will be important to identify the degree of Na^+ accumulation in the “hotspots” and how that seepage water is moving throughout the SFW. It is recommended that the pumps remain off, to promote similar water level patters characteristic of natural fens that gradually declines throughout the summer, as well as promote peat-accumulating conditions by having a more stable water table. However, periodical and controlled input of freshwater and outflow of SFW water may be required to minimize the accumulation of salts, especially in the “hotspot” sites, and their transport throughout the SFW. Additionally, sampling different wells and surface water sites along the southern hummocks in the upcoming field seasons may identify other seepage locations. Data from the 2015 field season will provide insight to the effectiveness of controlled pumping events with the intent to provide some flushing of the system to limit salt accumulation.

Currently, a second wetland creation project, King Fisher (KF) is underway at SCL, and is adjacent to the SFW. KF is a 64 ha watershed and unlike the SFW, it is designed to allow natural water flow throughout the watershed without engineered systems present. This system is designed more similar to the system constructed by SE, the Suncor Pilot fen, where there is no managed water supply and the system is designed to have self-sustaining hydrology. Comparing the hydrochemical responses of the contrasting designs of these watersheds will improve the understanding of the connections and fluxes between the upland-lowland and surface-groundwater units and will therefore provide critical insight to design features required in constructed watersheds to support a sustainable ecosystem, especially in a highly saline region.

The ubiquitous salinity in oil sands reclamation presents many challenges in constructing self-sustaining wetlands that provide the necessary hydrological and ecological functions required for wetland success. Understanding the sources, flow pathways and fate of solutes within a highly engineered and managed system is crucial for the success of future reclamation design. Although there is much to learn about wetland design and construction, results presented in this study provides necessary information for the building blocks of future wetland creation in the oil sands region.

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TABLES

Table 2.1. Reported water chemistry values for various oil sands process waters at SCL.

Variable	**CT**	**CT**	**OSPW**	**CT**	**Seepage Pond***	**MFT MLSB**
Na$^+$ (mg/L)	878	1100	690-1020	783 - 965	410	444 - 452
Ca^{+2} (mg/L)	-	87	8.2-18	48.2 – 52	11.3	14.7 - 18.6
Cl$^-$ (mg/L)	59.4	550	375-970	384 – 476	113	108 – 198
SO$_4^{-2}$ (mg/L)	3000	1500	26-370	988 – 1223	96.6	209 - 463
EC (µS/cm)	2270	4600	2750-4800	-	-	-
Reference	Renault, 1998	Renault, 1999	Zubot, 2010	Leung et al., 2003	Leung et al., 2003	Leung et al., 2003

* Seepage runoff from the sand dykes at Mildred Lake Settling Basin (MLSB), the main tailings pond.

Table 2.2. Reported water chemistry values for bogs, poor, moderate- and extreme-rich fens in the Boreal Plains (Chee and Vitt, 1989; Purdy et al., 2005; Stewart and Lemay, 2011; Trites and Bayley, 2009a; Vitt and Chee, 1990; Vitt et al., 1995; Wells and Price, 2015).

	Bog	Poor Fen	Moderate-Rich Fen	Extreme-Rich Fen	Saline Fen	Sandhill Fen
pH	3.5 - 4.5	3.5 - 5.44	5.93 - 7.5	6.82 - 8.5	8.07 - 8.7	5.4 - 8.9
EC (µS/cm)	36 - 69	14.7 - 60	67.5 - 91	180 - 214	600 - 31000	288 - 5092
Na+ (mg/L)	1.5 - 1.6	0.34 - 1.88	2.2 - 6.9	0.6 - 7.1	195 - 25680	3.5 - 886
Ca+2 (mg/L)	3 - 4.3	1.4 - 5.9	9.8 - 22.1	22.4 - 67.7	61 - 534	10.3 - 668
Mg+2 (mg/L)	0.7 - 1.4	3.1 - 3.8	5.3 - 4.6	0.3 - 7.8	-	-

Table 4.1. Monthly climate averages in Fort McMurray for air temperature (Ta) and rainfall (R) from 2013 – 2014 reported by Environment Canada, 2015. Monthly climate normal (CN) data (1981 – 2010) with standard deviations for air temperature. Average and total values for April – October.

Month	**Ta (ºC)**			**R (mm)**		
	2013	**2014**	**CN**	**2013**	**2014**	**CN**
April	-1.0	0.6	3.4 ± 2.6	13.7	15.6	9.3
May	12.7	7.9	9.9 ± 1.8	4.7	82.9	33.5
June	16.1	15.3	14.6 ± 1.0	165.9	69.7	73.3
July	16.9	19	17.1 ± 1.0	87.1	55.7	80.7
August	17.6	17	15.4 ± 1.8	3.9	36.3	57.1
September	13.4	9.4	9.4 ± 1.8	35	62.8	45.0
October	3.6	5.2	2.8 ± 1.8	21.1	30.3	18.8
Average	11.3	10.6	10.4	47.3	50.5	45.4
Total	-	-	-	331	353	318

Table 4.2 Summary table of average SFW major ion chemistry for 2013 with standard deviations.

Site	**Na (mg/L)**	**K (mg/L)**	**Mg (mg/L)**	**Ca (mg/L)**	**Cl (mg/L)**	**SO4-2 (mg/L)**	**HCO3- (mg/L)**	**EC (µS/cm)**	**SAR**	**Water Type**
B1W1	21.1	1.3	9.8	44.1	31.1	43.4	100.0		0.7	Ca-HCO3
B1W2	19.6	1.4	9.8	40.2	26.3	36.1	108.6		0.7	Ca-HCO3
B1W3	90.6 ± 97	2.7 ± 1.6	16.6 ± 8.2	73.5 ± 40	73.6 ± 42	172.7 ± 177	173.9 ± 103		2.2 ± 2.1	Na-SO4
B1W4	36.4 ± 21	1.6 ± 0.2	16.3 ± 8	66.9 ± 32	36.4 ± 9	72.3 ± 40	130.5 ± 43		1.0 ± 0.3	Ca-HCO3
B2W1	40.2	2.5	23.0	109.6	22.9	208.1	157.4		0.9	Ca-SO4
B2W4	46.7 ± 32	2.7 ± 2	23.0 ± 13	84.9 ± 53	33.4 ± 23	101.2 ± 71	192.4 ± 200		1.2 ± 0.7	Ca-HCO3
B2W6	60.6	3.2	22.1	65.9	41.7	97.5	109.3		1.5	Ca-HCO3
B3W1	86.5 ± 87	3.5 ± 1	70.3 ± 72	236.0 ± 166	72.1 ± 72	608.4 ± 539	185.4 ± 144	1952.0	1.2 ± 0.7	Ca-SO4
B3W2	86.7 ± 5	2.6 ± 0.1	64.6 ± 6.4	287.1 ± 27	87.7 ± 24	736.7 ± 91	271.5 ± 149	2222.0	1.2 ± 0.01	Ca-SO4
B3W3	40.0 ± 20	3.3 ± 1.6	34.5 ± 27	153.5 ± 127	23.8 ± 1.7	358.2 ± 350	216.6 ± 160	1361.0	0.8 ± 0.1	Ca-SO4
B3W4	79.0	5.8	108.8	503.6	16.0	1609.9	103.7	2745.0	0.8	Ca-SO4
B3W5	24.5	1.8	11.4	49.7	31.0	62.0	61.0	1752.0	0.8	Ca-SO4
MF	60.6 ± 60	3.2 ± 4.4	22.1 ± 29	65.9 ± 29	41.7 ± 14	97.5 ± 53	109 ± 43		1.5 ± 0.8	Ca-HCO3
OPS1	119.1 ± 122	4.8 ± 3	21.6 ± 13	90.2 ± 50	75.7 ± 80	184.8 ± 133	174.0 ± 173		2.7 ± 2.5	Na-SO4
UP	189.9	4.2	153.5	632.3	132.0	1894.7	246.4		1.8	Ca-SO4
V	354.9 ± 225	8.2 ± 3.3	27.2 ± 6.4	102.5 ± 27	223.4 ± 135	427.3 ± 202	422.3 ± 248	2567.0	7.9 ± 5.2	Na-SO4
WSP	46.3 ± 49	2.2 ± 1.4	15.0 ± 6.7	57.4 ± 25	38.5 ± 27	82.9 ± 81	82.5 ± 47		1.3 ± 1	Ca-SO4

*Sites without standard deviations only had one sample taken in 2013. EC data was not collected at all sites in 2013.

Table 4.3. Summary of average hydrochemistry across SFW in 2014 with standard deviations.

Site	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	SO4-2 (mg/L)	HCO3- (mg/L)	EC (µS/cm)	SAR	Water Type
B1S1	352.8 ± 123	5.6 ± 1.4	36.9 ± 5.4	144.7 ± 22	226.7 ± 68	583.4 ± 125	374.5 ± 82	2144	6.7 ± 1.9	Na-SO4
B1W3	441.1 ± 110	3.7 ± 1.9	51.7 ± 7.8	221.4 ± 45	324.0 ± 118	734.1 ± 112	492.2 ± 112	2816	6.9 ± 1.5	Na-SO4
B2S1	163.9 ± 78	3.4 ± 1.9	39.0 ± 12	131.8 ± 29	98.8 ± 32	337.5 ± 74	285.9 ± 110	1457	3.2 ± 1.5	Na-SO4
B2W7	122.8 ± 23	2.6 ± 0.4	73.1 ± 15	267.6 ± 51	81.8 ± 14	867.9 ± 165	230.4 ± 74	2056	1.7 ± 0.2	Ca-SO4
B3S1	108.1 ± 37	2.6 ± 1.5	33.7 ± 12	124.4 ± 35	76.9 ± 24	312.5 ± 93	220.4 ± 65	1476	2.2 ± 0.5	Ca-SO4
B3W2	278.1 ± 78	4.7 ± 1.4	121.2 ± 12	528.8 ± 75	252.1 ± 55	1549.9 ± 191	416.2 ± 139	3838	2.8 ± 0.6	Ca-SO4
B3W3	99.8 ± 20	1.9 ± 1.3	35.3 ± 7.3	140.4 ± 30	78.5 ± 15	358.0 ± 58	224.5 ± 78	1632	1.95 ± 0.3	Ca-SO4
B3W4	126.2 ± 84	6.0 ± 1.8	83.1 ± 29	358.2 ± 169	53.0 ± 37	1144.7 ± 598	128.6 ± 45	2389	1.91 ± 1.7	Ca-SO4
OPS1	228.1 ± 127	5.4 ± 3	36.2 ± 6.1	136.2 ± 23	149.7 ± 53	411.2 ± 91	344.5 ± 107	1489	4.5 ± 2.7	Na-SO4
TRS1	521.4 ± 247	8.5 ± 3	88.2 ± 5	475.3 ± 147	435.7 ± 162	1597.0 ± 425	311.4 ± 98	3659	5.6 ± 2	Na-SO4
TRS2	469.9 ± 181	11.6 ± 2	59.2 ± 5	308.6 ± 65	290.5 ± 110	1073.0 ± 170	518.3 ± 71	3275	6.5 ± 3	Na-SO4
TRW13	122.4 ± 5	3.5 ± 1.2	127.3 ± 1.2	562.5 ± 16	55.5 ± 18	1591.9 ± 56	476.8 ± 105	3058	1.2 ± 0.05	Ca-SO4
TRW2	347.2 ± 84	4.3 ± 1.5	125.4 ± 15	414.0 ± 52	487.0 ± 93	1091.8 ± 180	432.1 ± 95	3794	3.8 ± 0.8	Na-SO4
TRW3	8.4 ± 3.5	9.8 ± 2	29.4 ± 22	465.4 ± 195	4.6 ± 2	1069.4 ± 465	181.6 ± 74	2037	0.1 ± 0.05	Ca-SO4
TRW4	144.4 ± 97	4.2 ± 1	63.0 ± 34	212.1 ± 112	192.1 ± 160	384.6 ± 371	442.6 ± 279	2356	2.2 ± 1	Ca-HCO3
TRW5	248.5 ± 73	4.2 ± 2	117.1 ± 7	514.3 ± 26	267.9 ± 82	1358.7 ± 43	458.5 ±113	3444	2.6 ± 0.8	Ca-SO4
TRW8	72.0 ± 62	8.6 ± 3.5	66.5 ± 29	602.9 ± 71	17.0 ± 21	1498.8 ± 211	353.3 ± 28	2685	0.8 ± 0.8	Ca-SO4
TRW9	70.6 ± 28	2.7 ± 0.8	69.5 ± 25	345.7 ± 118	29.0 ± 12	1006.0 ± 380	197.6 ± 71	2242	0.9 ± 0.2	Ca-SO4
UPW1	185.3	5.1	141.5	600.3	190.0	1650.8	395.3	2700	1.77	Ca-SO4
UPW4	69.9 ± 83	9.0 ± 8	42.5 ± 40	137.3 ± 82	70.4 ± 96	170.4 ± 152	328.6 ± 282	1148	1.2 ± 1.1	Ca-HCO3
UPW5	101.7 ± 11	4.1 ± 3	68.2 ± 7	253.2 ± 10	64.5 ± 32	563.2 ± 19	386.3 ± 109	1815	1.5 ± 0.1	Ca-SO4
WSP	157.1 ± 76	3.0 ± 0.9	27.2 ± 8	92.6 ± 22	115 ± 51	357.2 ± 138	135.6 ± 23	1337	3.6 ± 1.2	Na-SO4
SUMP Open	623 ± 100	11.3 ± 1.2	27.3 ± 7.4	93.4 ± 33	343 ± 76	599.7 ± 76	697 ± 89	3156.7	15.1 ± 4	Na-HCO3
SUMP Closed	164.5 ± 51	4 ± 0.5	32.4 ± 8	124.6 ± 29	132.5 ± 41	366 ± 103	301.1 ± 69	1475.7	3.3 ± 0.9	Na-SO4

*SUMP open indicates water chemistry when underdrains were open and draining into the SUMP and SUMP closed indicates data once underdrains were closed.

Table 4.4. Non-parametric Mann-Whitney U test comparison for major ions in the lowlands and transition/uplands between 2013 and 2014.

Lowlands									
	Na (mg/L)	**Ca (mg/L)**	**SO4 (mg/L)**	**HCO3 (mg/L)**	**K (mg/L)**	**Mg (mg/L)**	**Cl (mg/L)**	**Alk (mg/L)**	**SAR**
U	201.5	349	221	405	739	349	288	405	276
n1 (2013)	42	42	42	42	42	42	42	42	42
n2 (2014)	60	60	60	60	60	60	60	60	60
Average Rank 1	26.3	29.8	26.8	31.1	39.1	29.8	28.4	31.1	28.1
Average Rank 2	69.1	66.7	68.8	65.8	60.1	66.7	67.7	65.8	67.9
z	-7.2	-6.2	-7.07	-5.8	-3.5	-6.2	-6.6	-5.8	-6.7
p (two-tailed)	< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.0004	< 0.0001	< 0.0001	< 0.0001	< 0.0001
p (one-tailed)	< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.0002	< 0.0001	< 0.0001	< 0.0001	< 0.0001

Table 4.5. Average isotope signatures for SFW supplemented with SCL source water isotope signatures from Baer, 2014.

Sample ID	**$\delta^{18}O$ (‰)**	**δD (‰)**
TRW8	-20.0	-156.8
TRW13	-19.3	-154.1
TRW3	-17.5	-136.6
TRW5	-17.4	-140.0
TRW2	-16.9	-137.7
TRW4	-16.7	-133.2
UPW5	-16.5	-131.7
B3W2	-16.2	-133.9
UPW4	-15.9	-124.6
TRS2	-15.4	-131.3
TRS1	-15.3	-128.5
B3W4	-15.1	-128.3
TRW9	-15.0	-128.4
B1W3	-13.8	-120.1
B1S1	-13.0	-118.7
B2W7	-12.5	-117.3
WSP	-12.2	-115.2
B3S1	-11.9	-117.4
B3W3	-11.8	-115.7
OPS1	-11.1	-112.7
B2S1	-10.6	-108.9

Site (Baer, 2014)	**$\delta^{18}O$ (‰)**	**δD (‰)**
Snow	-26.4	-204.7
McMurray Formation	-20.5	-152.0
Clearwater Formation	-19.3	-147.0
Deep Shale	-18.4	-158.9
Mildred Lake	-17.7	-142.7
Rainfall	-15.3	-126.0
SFW SUMP	-15.3	-130.6
SFW GW[1]	-14.9	-126.7
CT[2]	-12.9	-118.0
Surface PAW	-12.9	-113.6
West in Pit	-12.5	-115.8

[1] SFW GW isotope samples taken from groundwater wells in the 10m tailings sands cap.
[2] CT isotope samples taken from BGC wells in the 35m composite tailings layer.

FIGURES

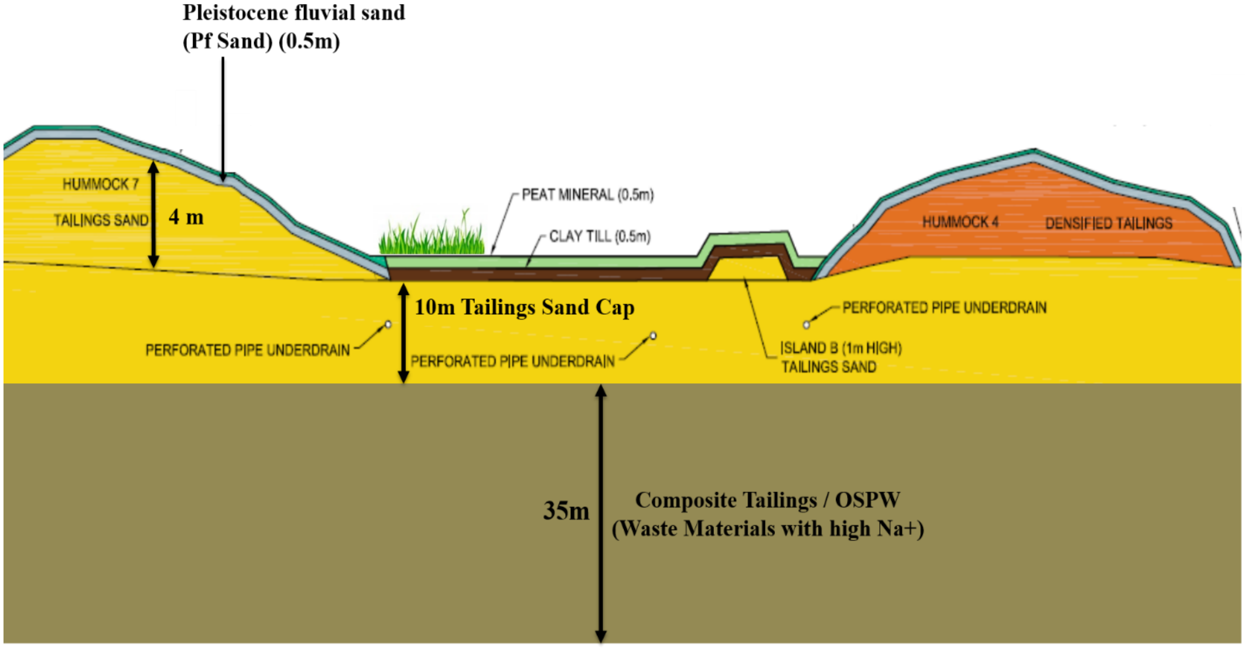

Figure 3.1. Cross section of the SFW looking east to illustrate construction materials. It should be noted that this diagram is not to scale.

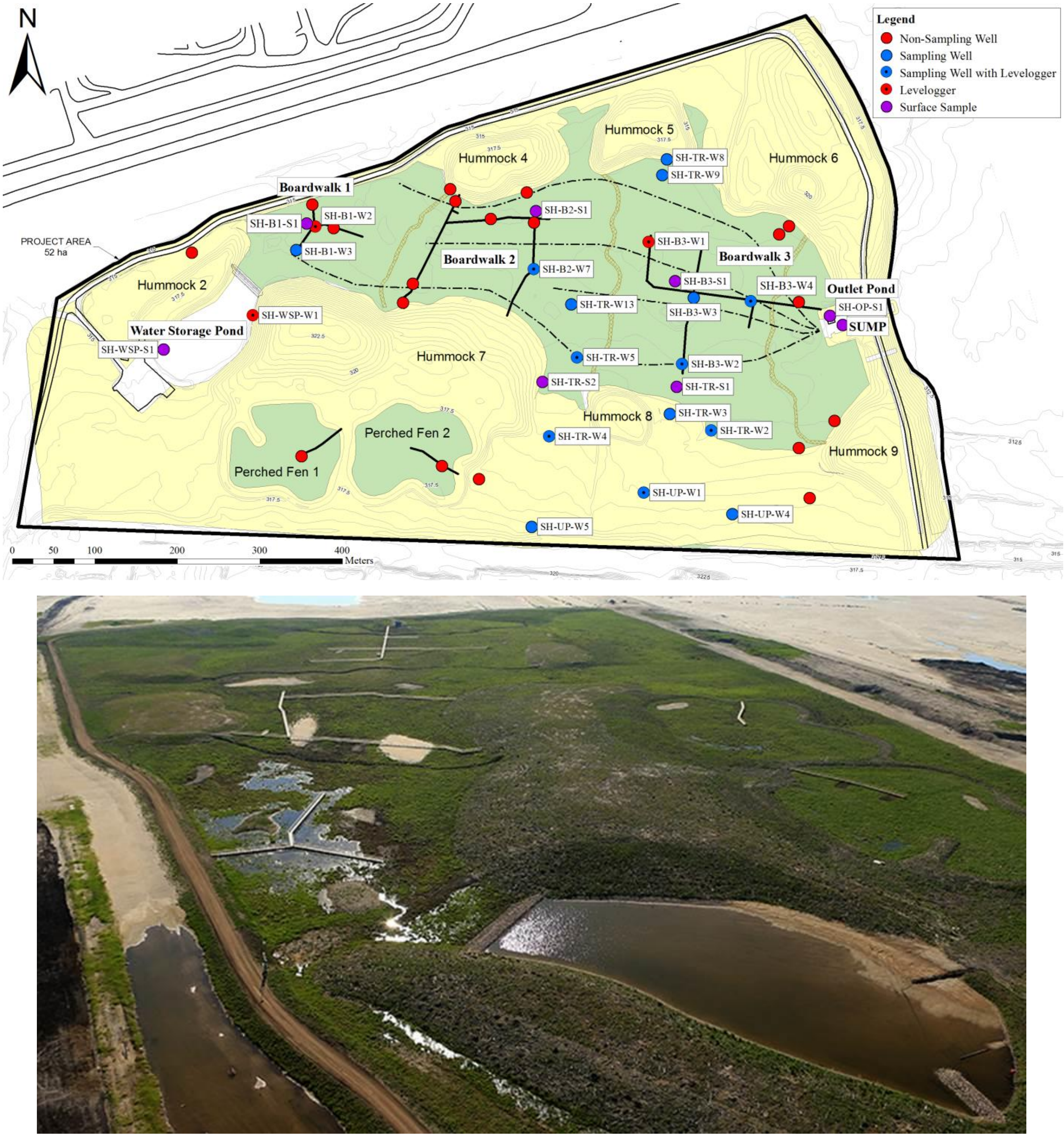

Figure 3.2. Design and well locations of the SFW. Dashed lines indicate the underdrains. Yellow and green areas represent the lowland/wetland and uplands, respectively. Named sites include all sampling locations in 2014 (top). Aerial photograph of the SFW, positioned looking east from the WSP.

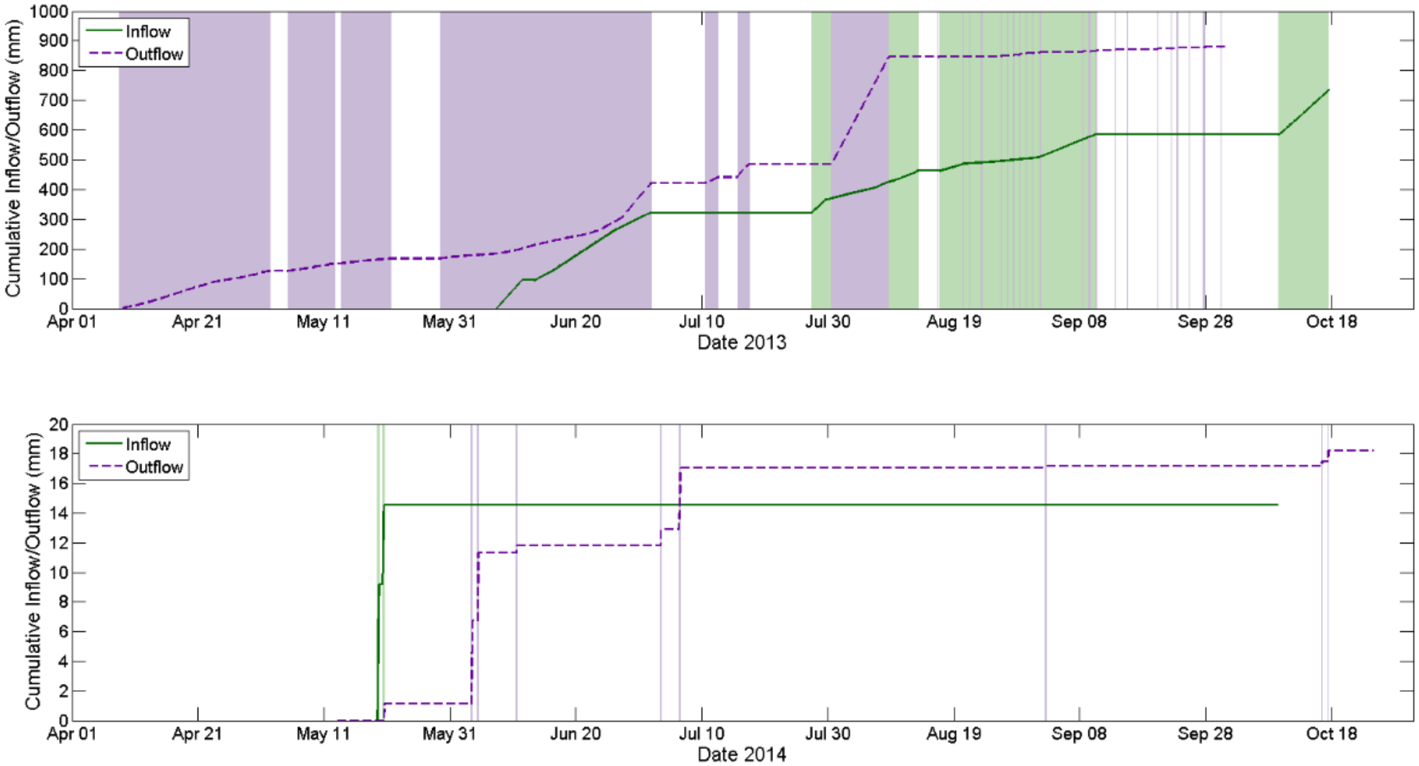

Figure 4.1. Cumulative inflow and outflow within the SFW for 2013 (top) and 2014 (bottom). Green and purple areas indicate the duration the inflow and outflow pumps were on, respectively as recorded by the Flow Transmitter.

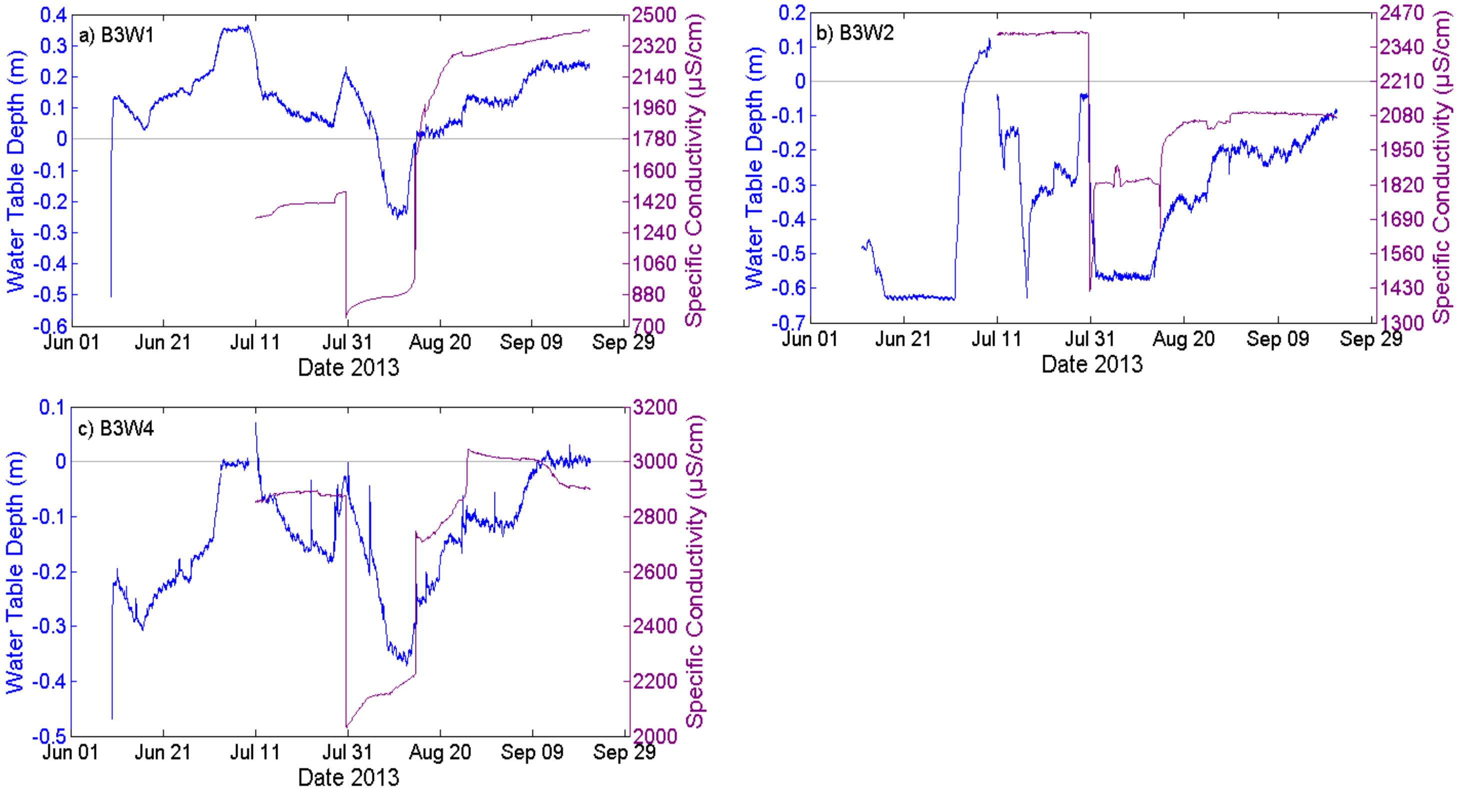

Figure 4.2. Water table depth and specific conductivity during May – September 2013. Grey horizontal line indicated the ground surface.

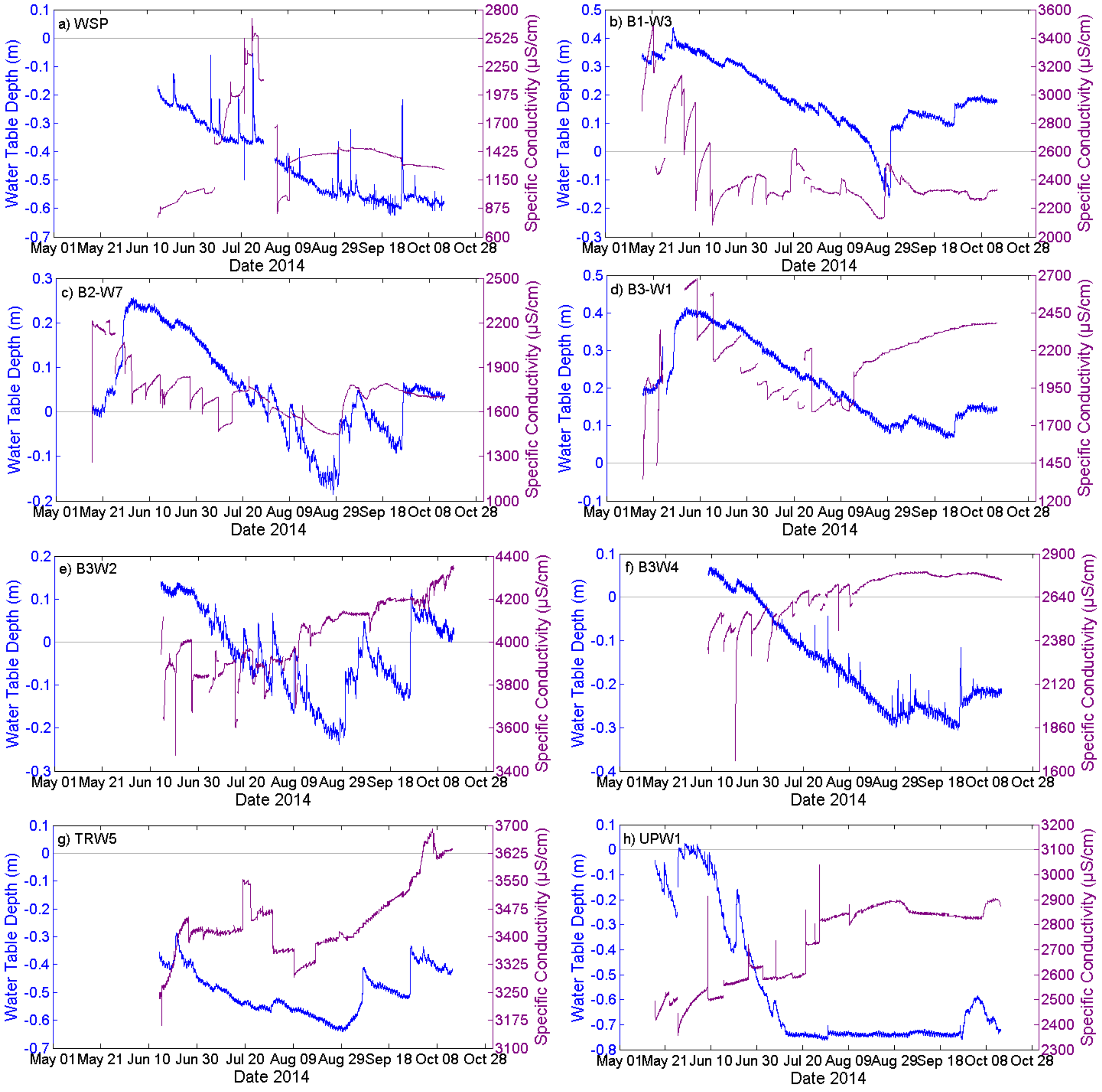

Figure 4.3. Water table depth and specific conductivity during May – October 2014. The grey horizontal line indicates the ground surface.

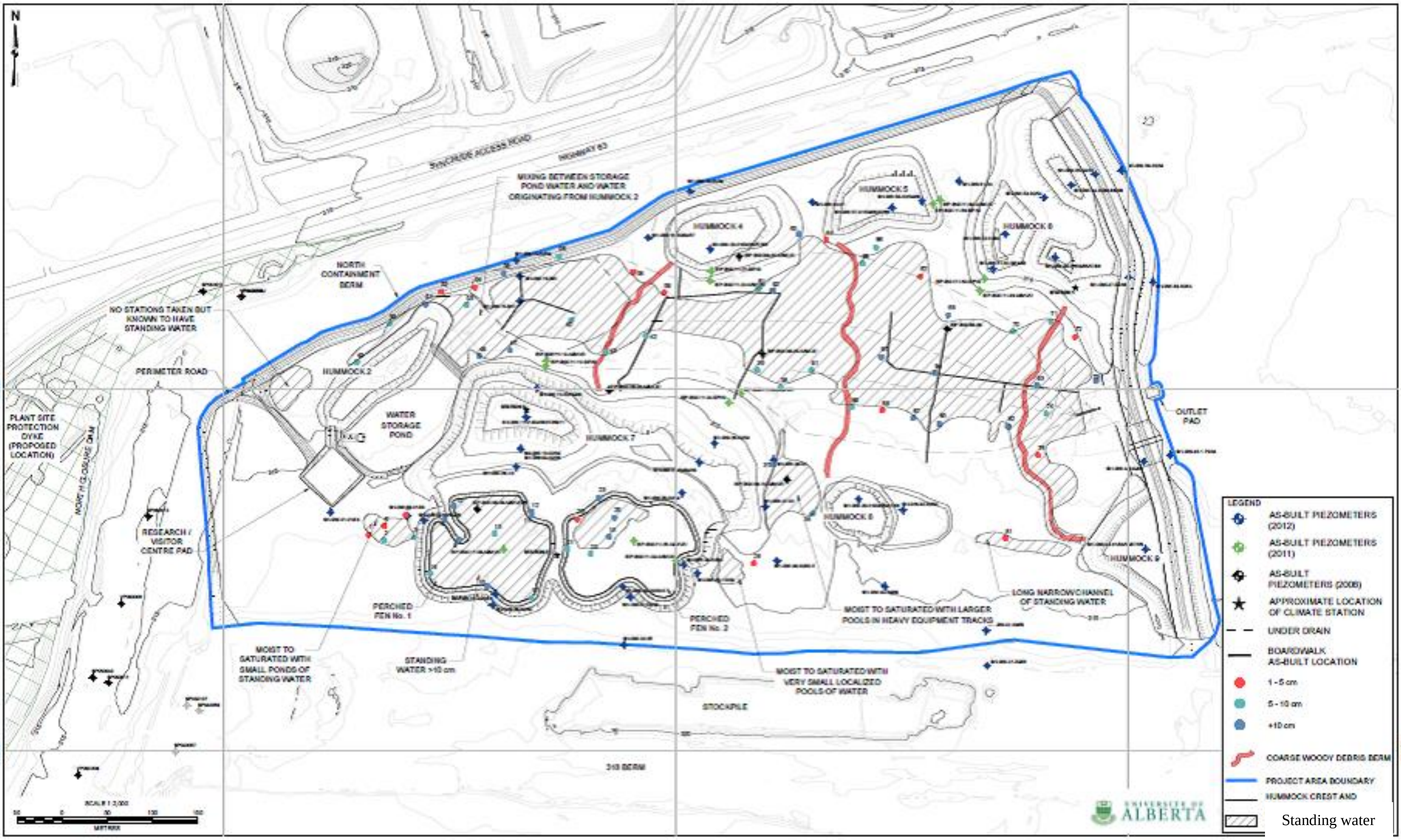

Figure 4.4. 2013 wetness map of the SFW. Data collected on September 23, 2013 (BCG, 2014).

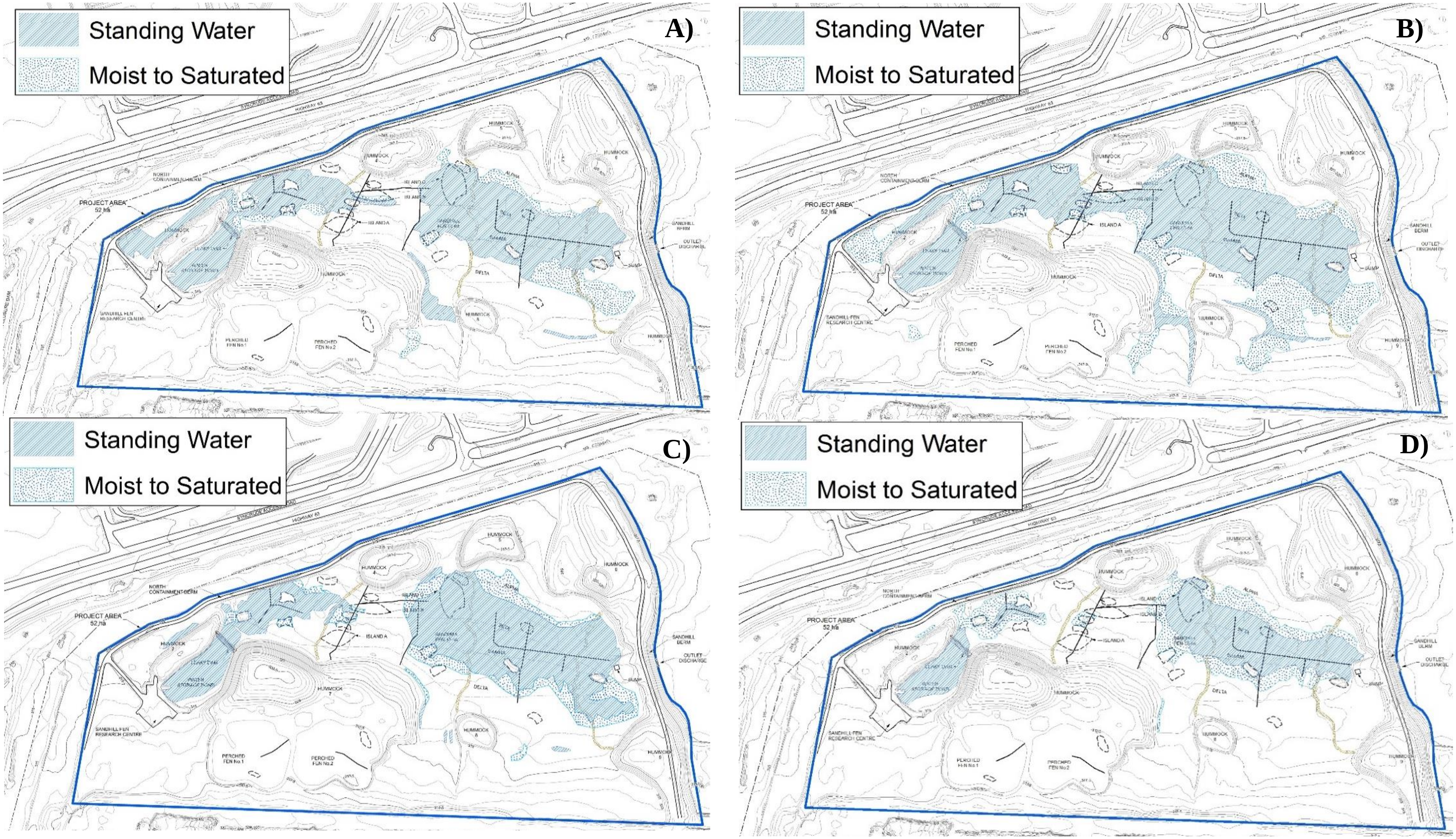

Figure 4.5. Wetness maps of the SFW in a) May, b) June, c) July and d) August, 2014. Maps provided by Dr. Carl Mendoza, University of Alberta.

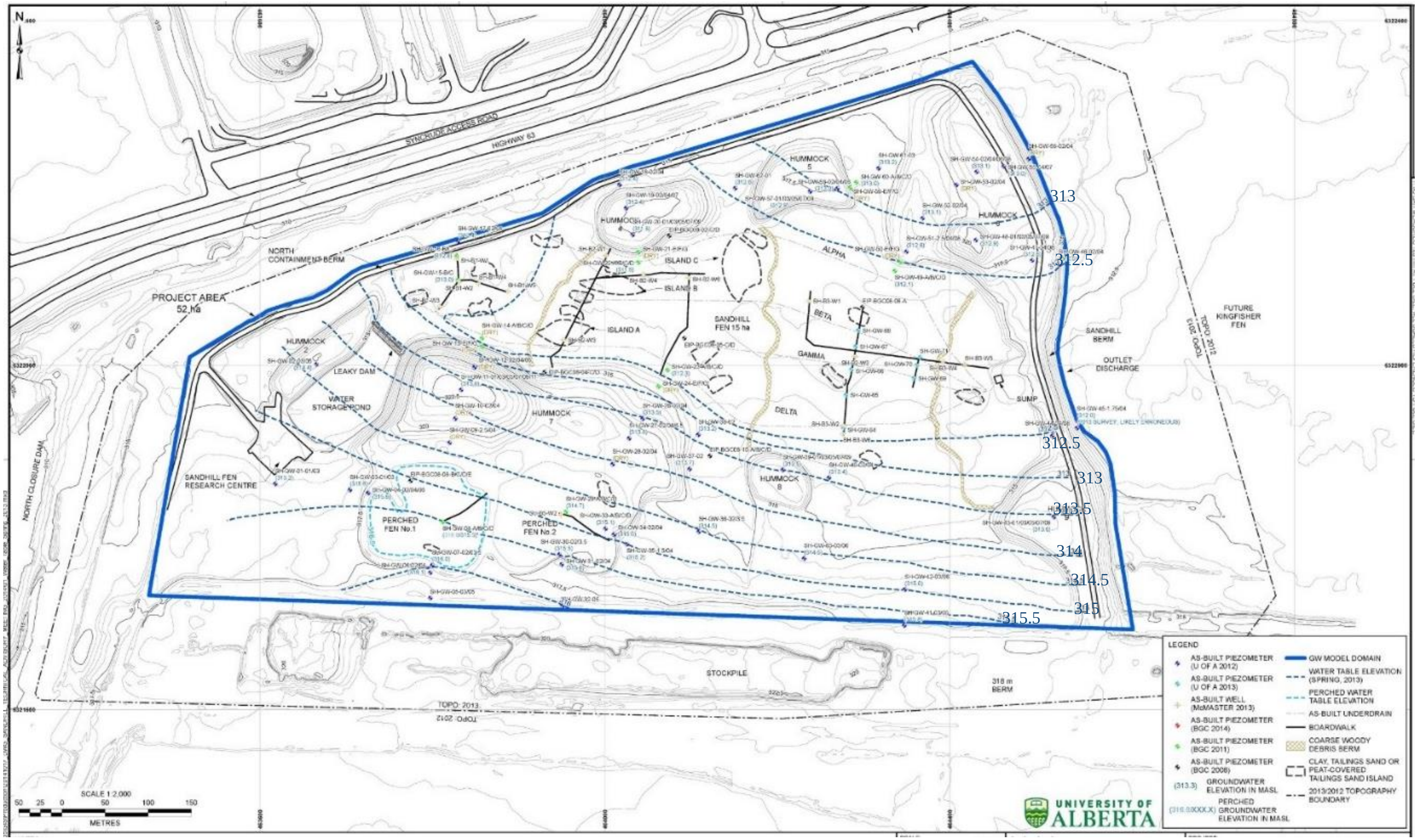

Figure 4.6. 2013 groundwater elevation in the SFW (BGC, 2015)

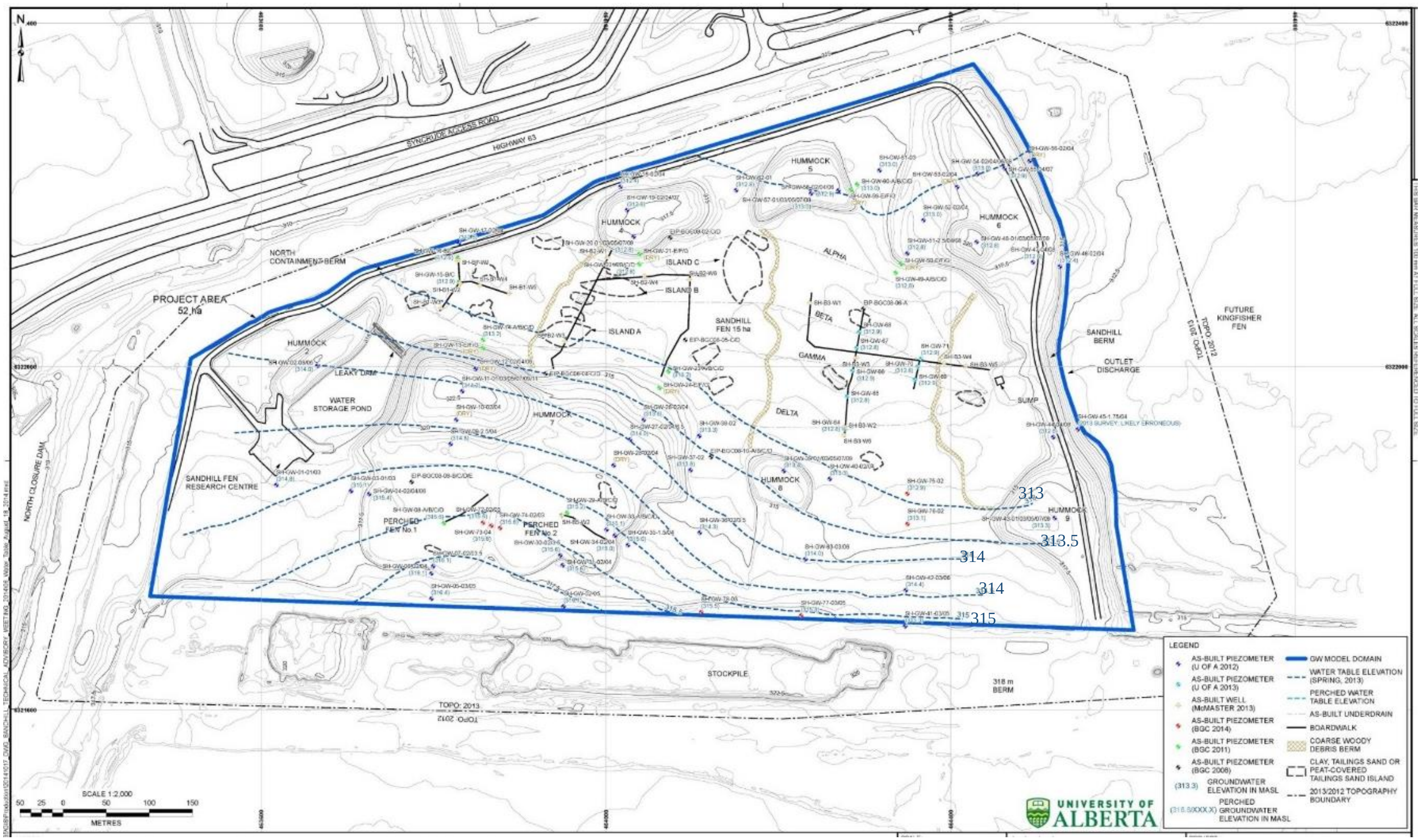

Figure 4.7. 2014 groundwater elevation in the SFW (BCG, 2015).

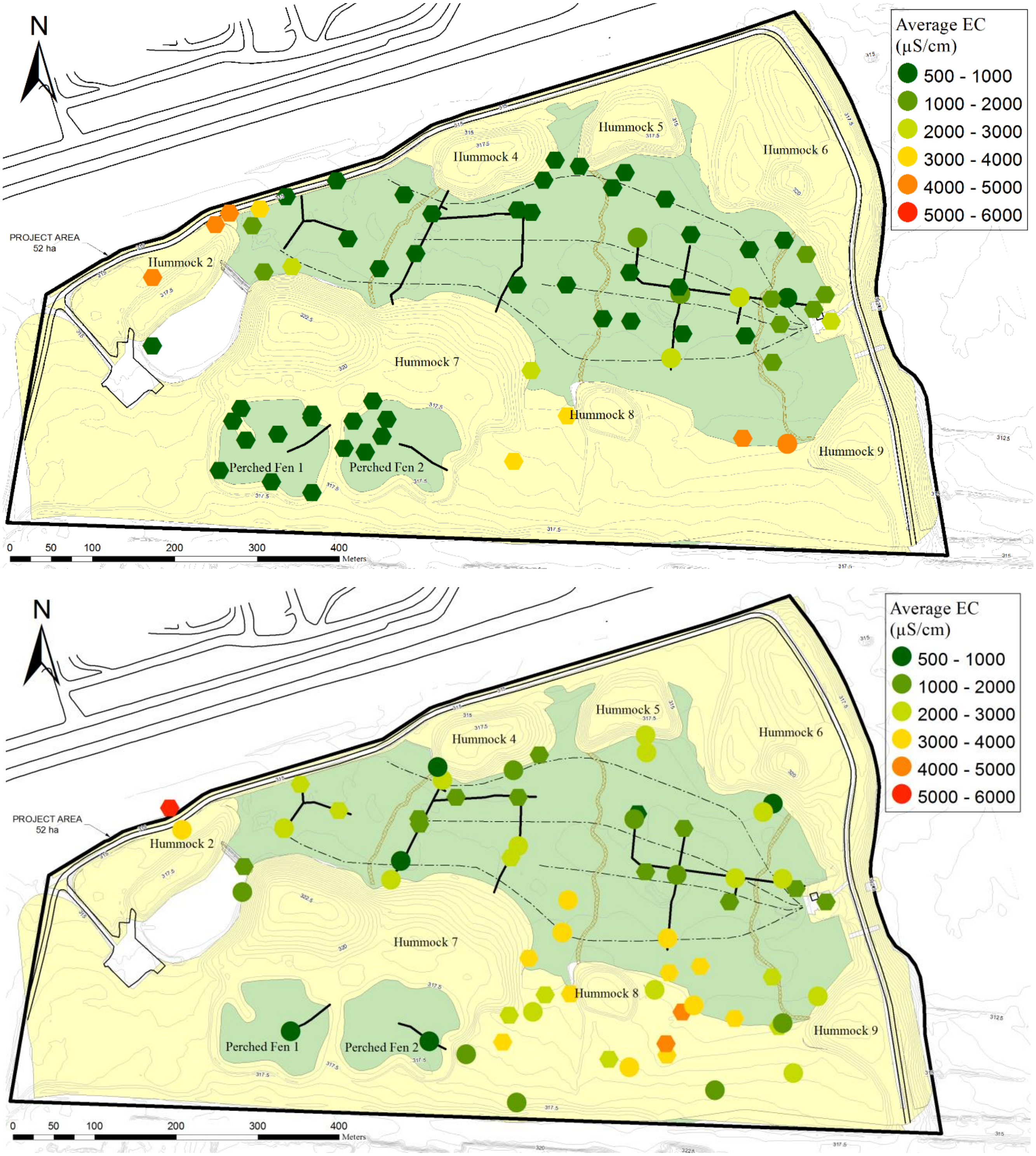

Figure 4.8. Average electrical conductivity of surface and near surface waters in SFW from May – October in 2013 (top) and 2014 (bottom). Hexagon and circle data points represent surface and well samples, respectively.

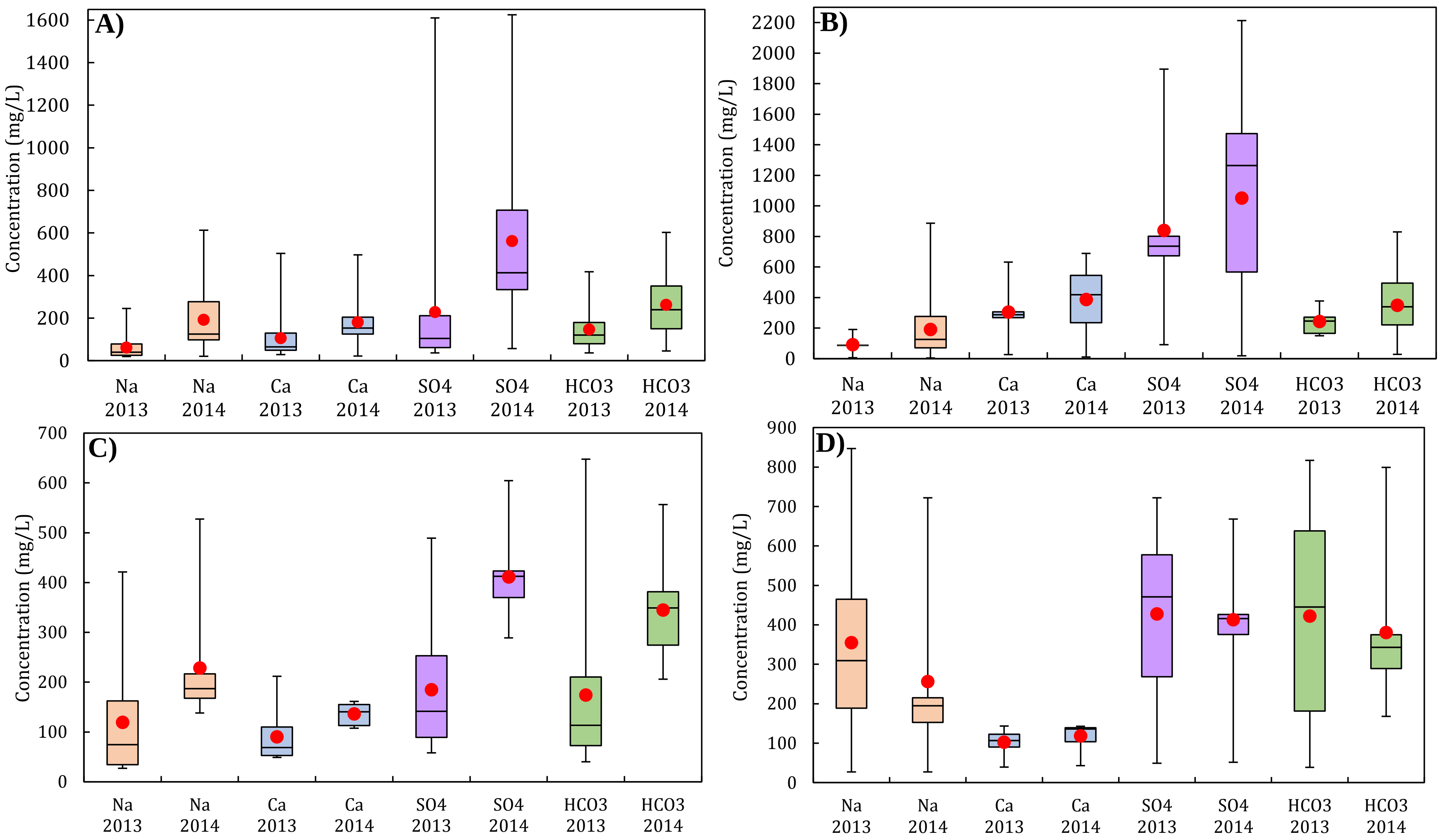

Figure 4.9. Box plots of major ion concentrations in 2013 and 2014 in the a) lowlands, b) transition/uplands, c) OP and d) SUMP. Red points indicate the mean.

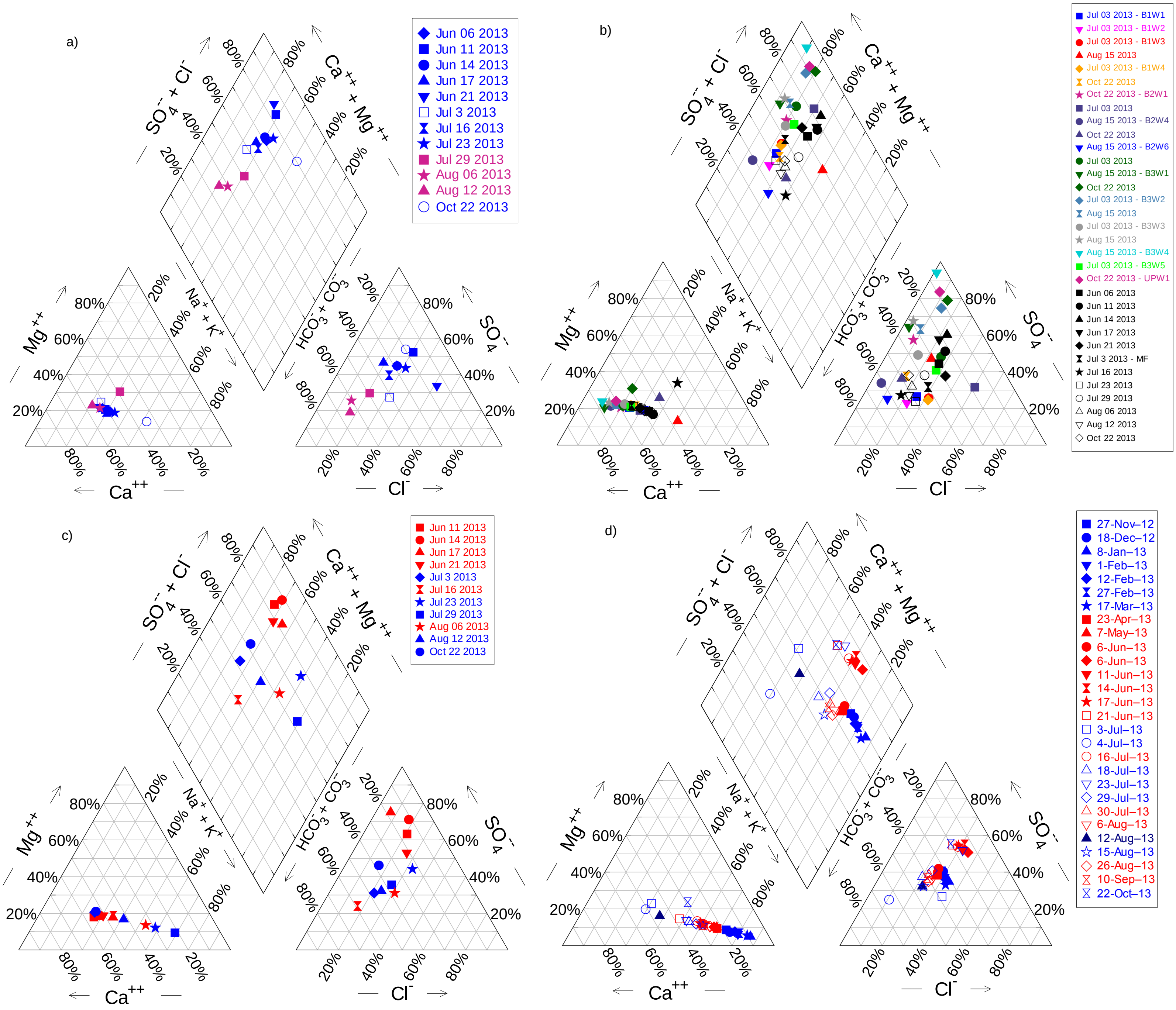

Figure 4.10. Piper diagrams of water samples collected at a) Water storage pond, b) Wells and MF, c) OP and d) SUMP in 2013. Red, blue and pink (WSP only) data points represent when the outflow pump was on and off and when the inflow pump was on, respectively.

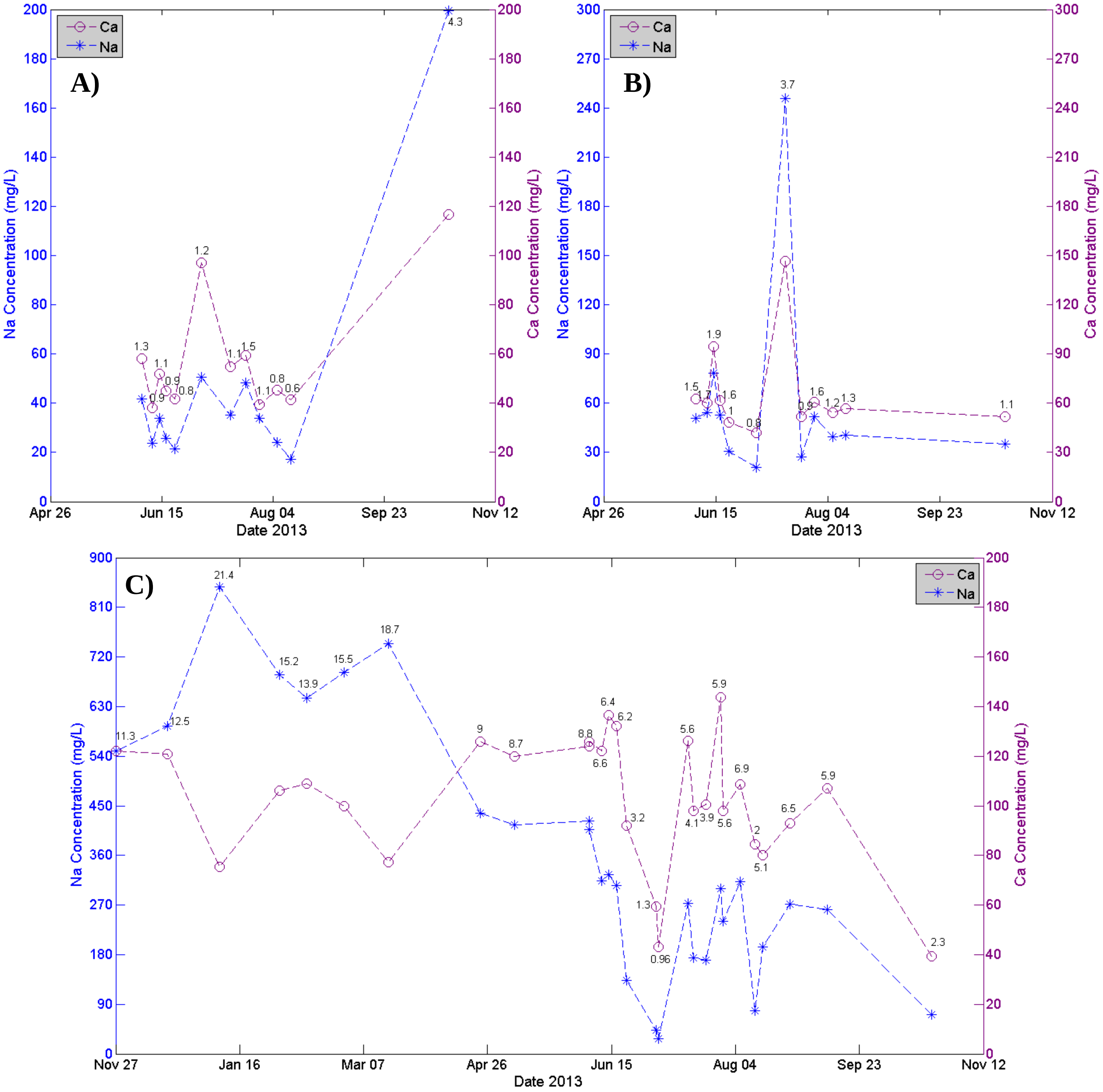

Figure 4.11. Absolute sodium and calcium concentrations of the a) WSP, b) MF and c) SUMP in 2013. Numbers represent the calculated SAR value for each sample.

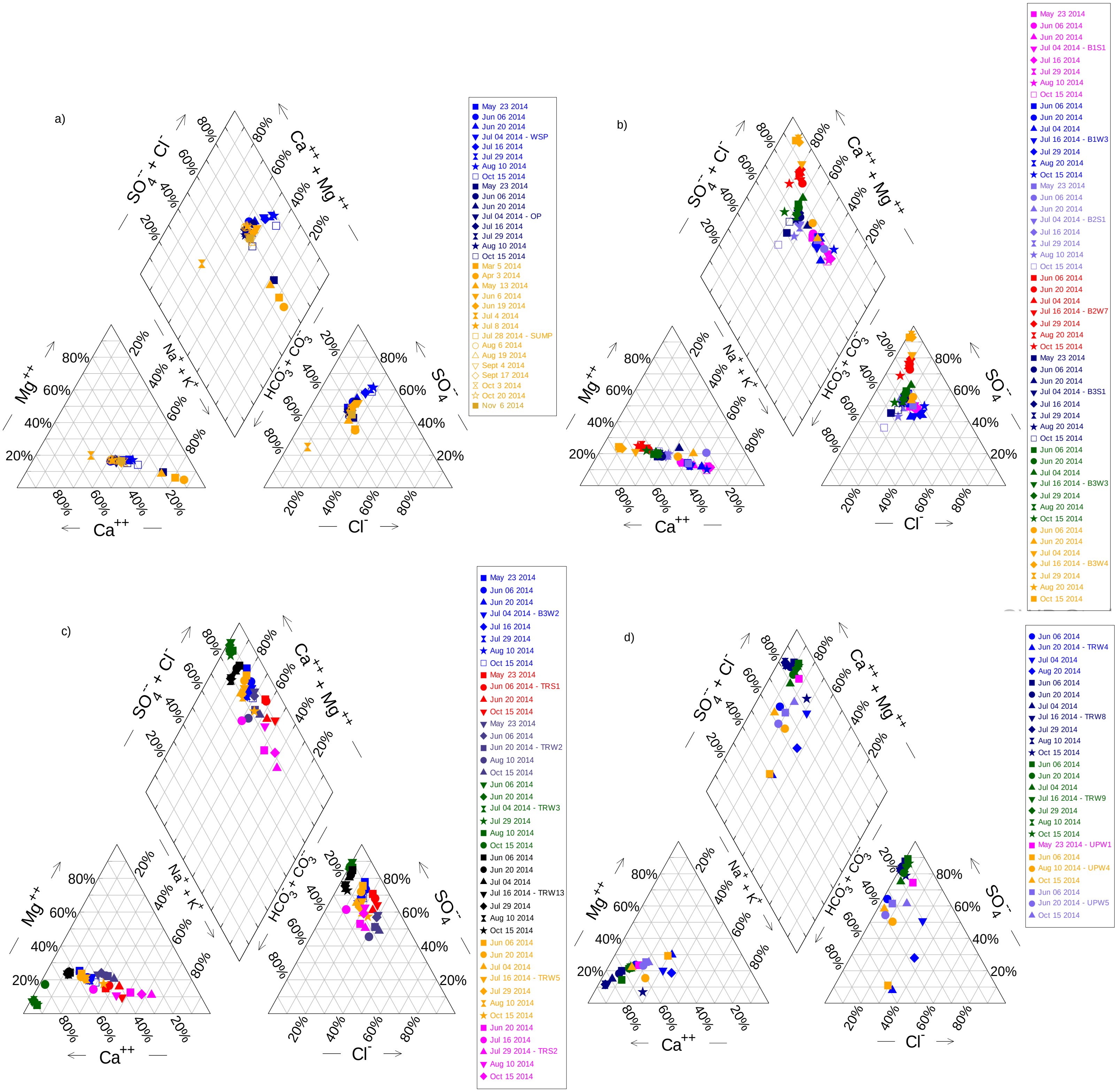

Figure 4.12. Piper diagrams of surface and well samples by location within SFW in 2014: a) input and output water, b) lowland, c) transition and d) uplands.

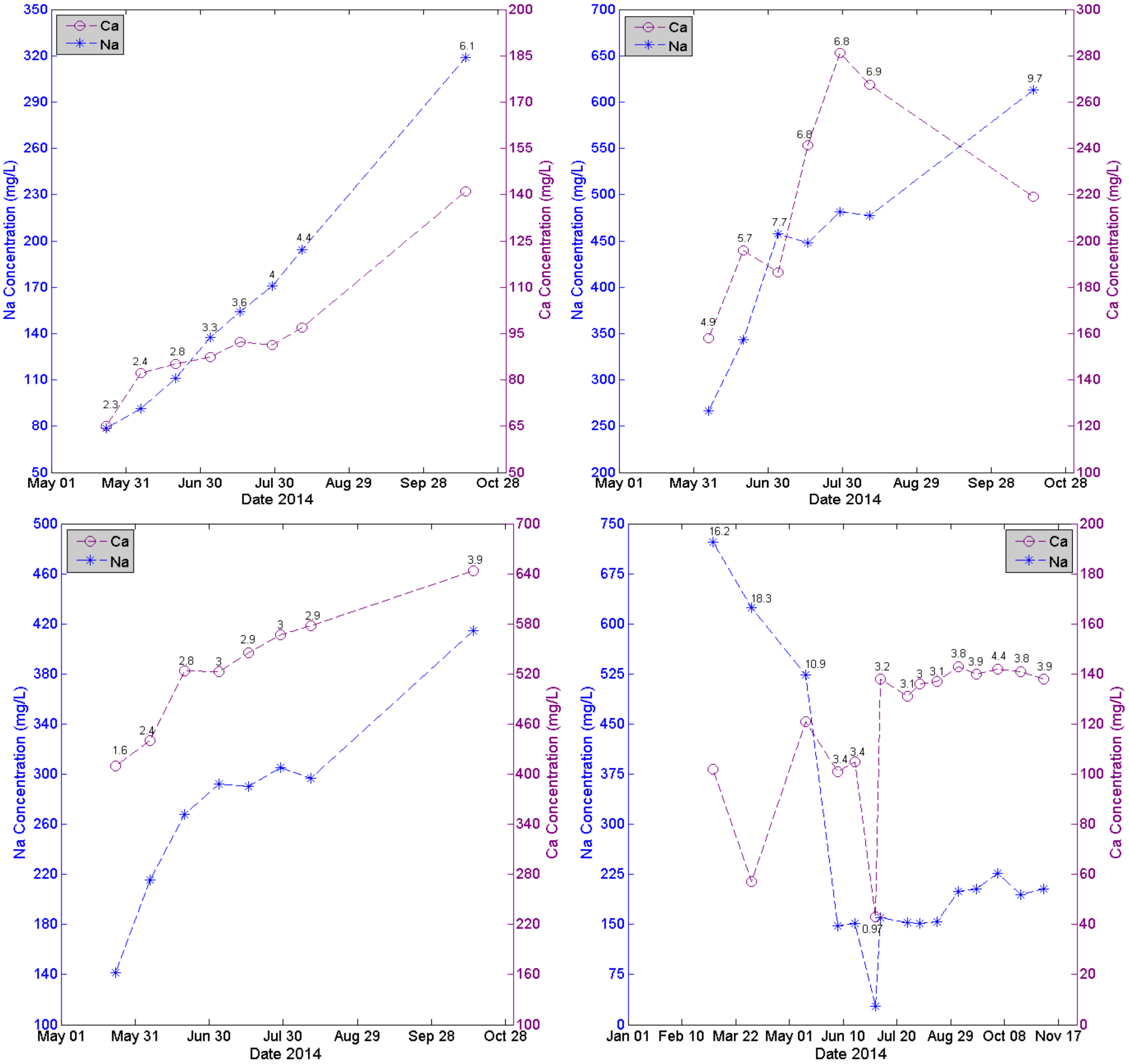

Figure 4.13. Absolute sodium and calcium concentrations of the a) WSP, b) B1-W3, c) B3-W2, and d) SUMP in 2013. Numbers represent the calculated SAR value for each sample.

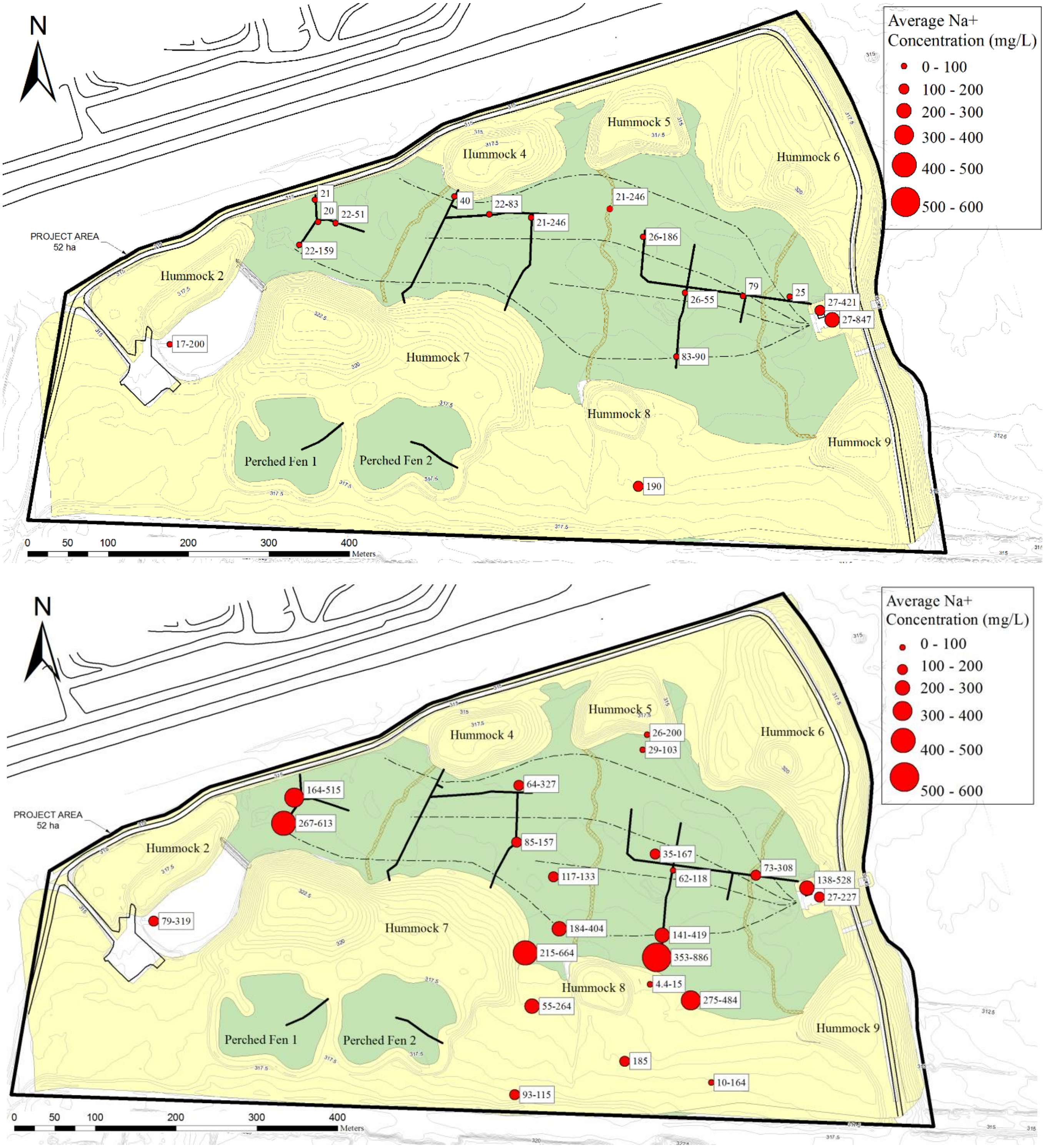

Figure 4.14. Average sodium concentrations (mg/L) in a) 2013 (top) and 2014 (bottom). Number indicates the range of values recorded at each sampling location.

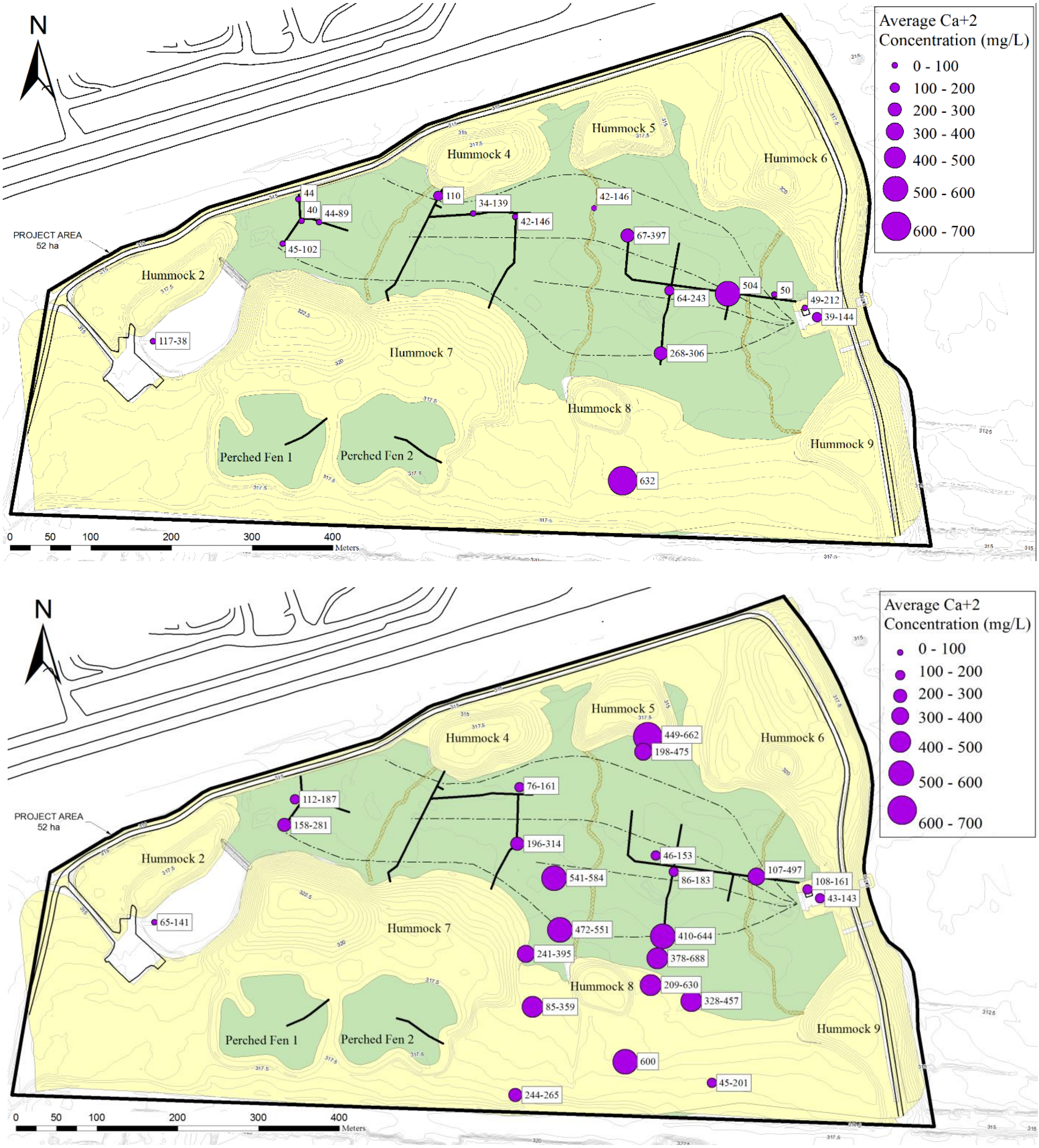

Figure 4.15. Average calcium concentrations (mg/L) in 2013 (top) and 2014 (bottom). Number indicates the range of values recorded at each sampling location.

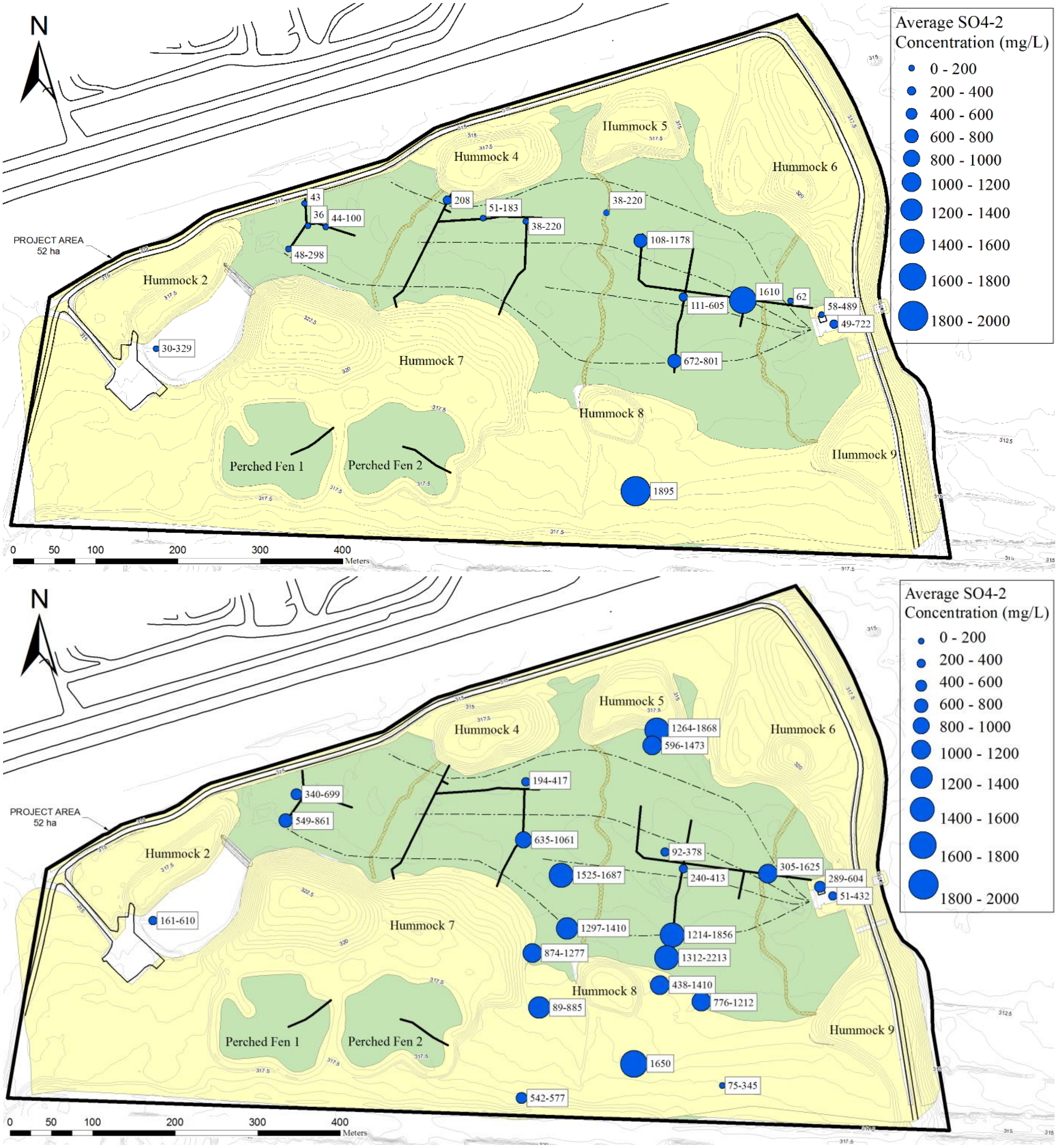

Figure 4.16. Average sulphate concentrations (mg/L) in 2013 (top) and 2014 (bottom). Number indicates the range of values recorded at each sampling location.

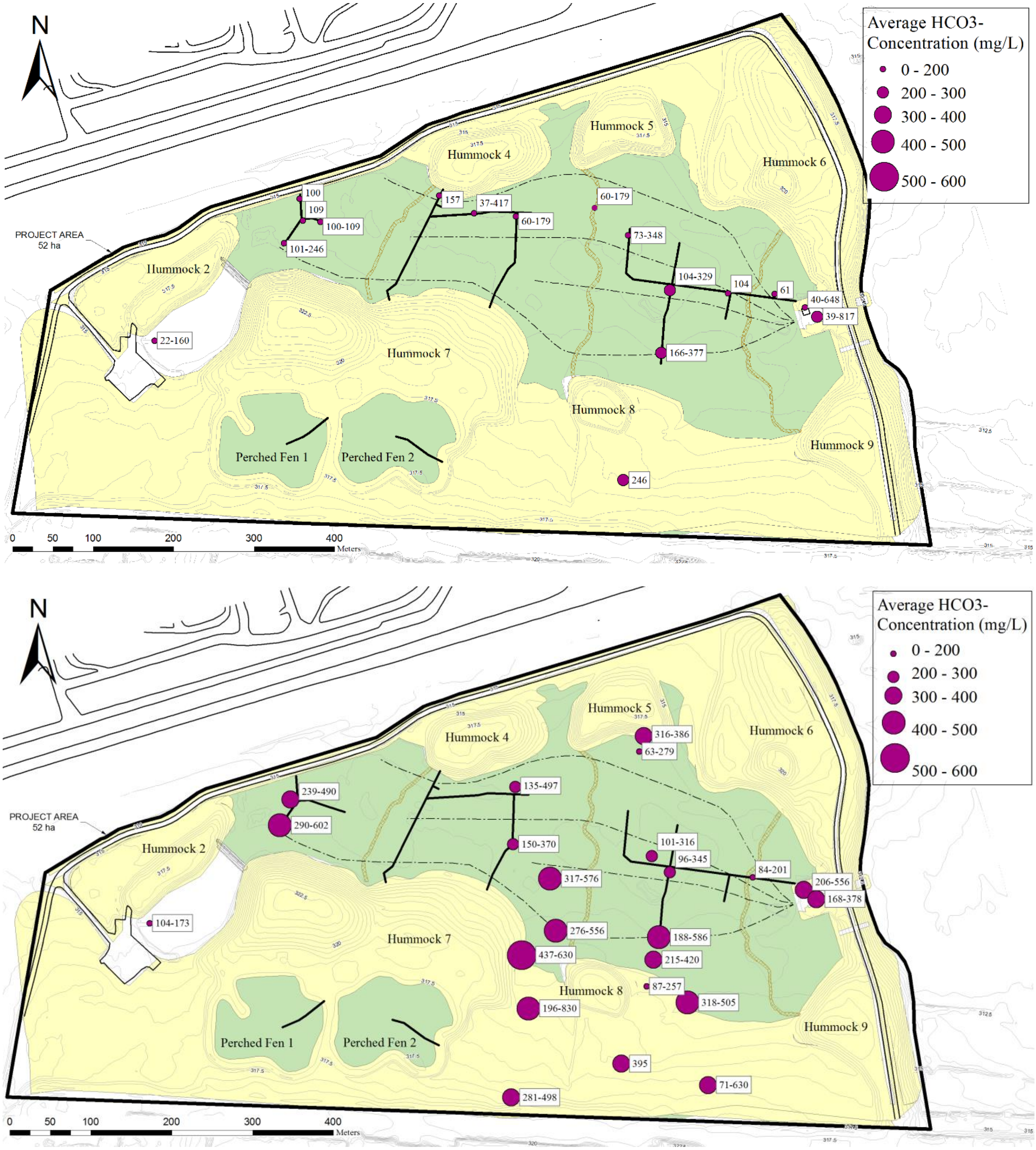

Figure 4.17. Average bicarbonate concentrations (mg/L) in 2013 (top) and 2014 (bottom). Number indicates the range of values recorded at each sampling location.

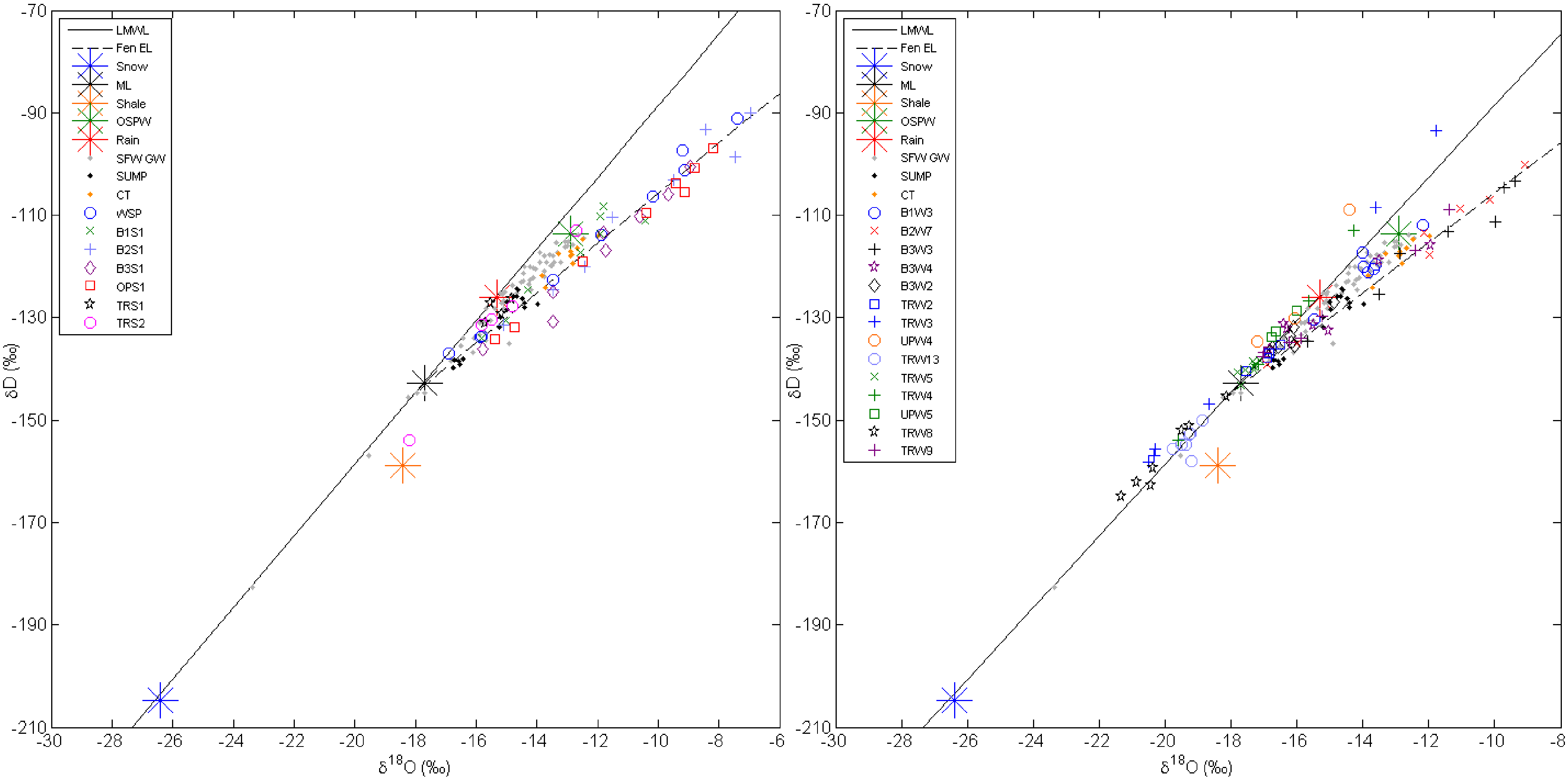

Figure 4.18. Isotope results for SFW sites in 2014 plotted with source waters from Baer, 2014 for comparison.

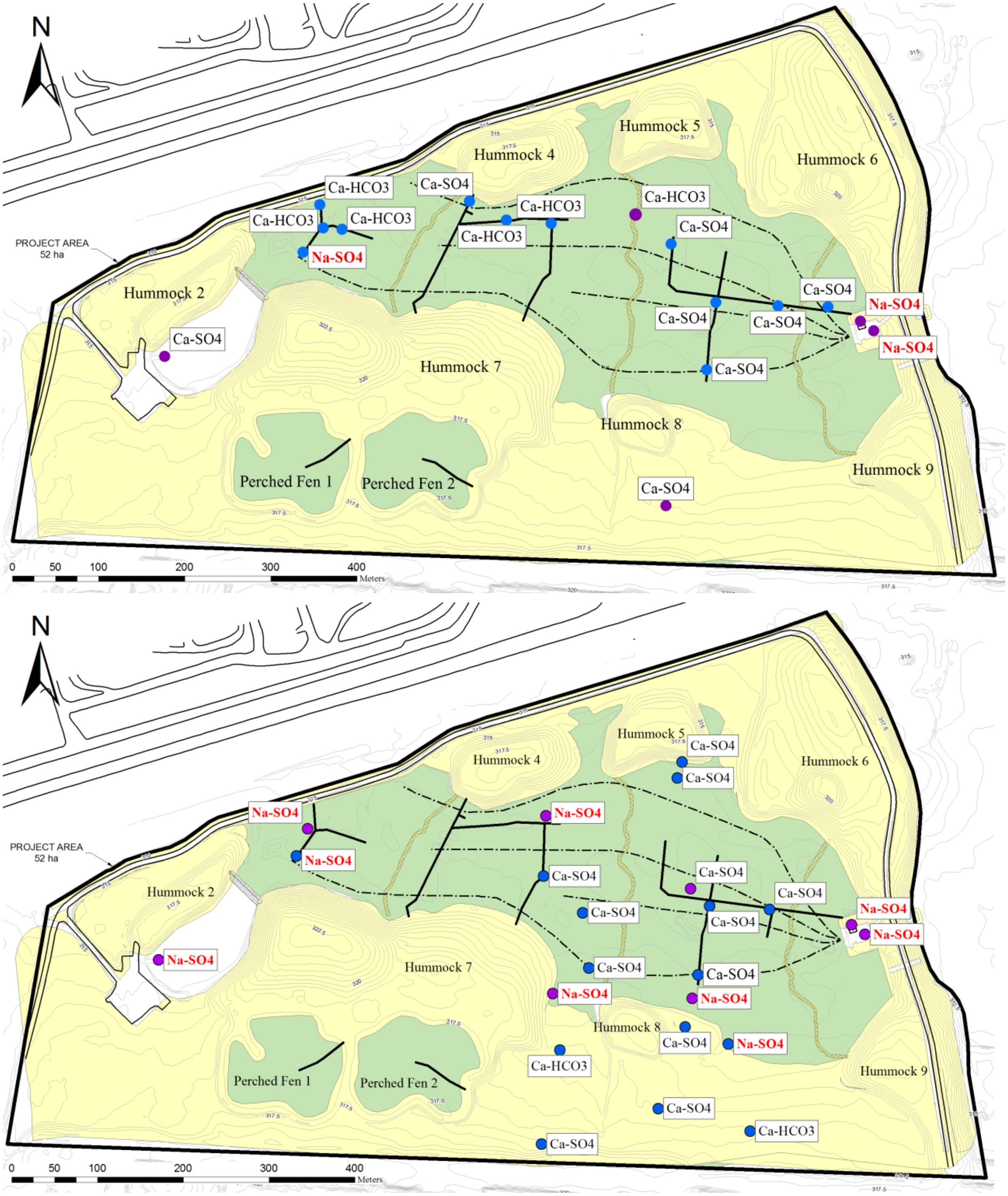

Figure 5.1. Average water type for surface and subsurface water samples in 2013 (top) and 2014 (bottom). Purple and blue points indicate grab and near-surface well samples, respectively.

APPENDIX A – Supplemental Data

Table A1. All major ion data from 2013.

Sample ID	Date 2013	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	SO4 (mg/L)	Alk (mg/L)	HCO3 (mg/L)	SAR	Water Type
OP	11-Jun-13	28.6	2.1	10.7	54.3	32.3	132.9	35.0	42.7	0.93	Ca-SO4
	14-Jun-13	40.2	3.1	14.4	66.3	36.8	201.4	33.0	40.3	1.17	Ca-SO4
	17-Jun-13	74.4	4.4	20.4	87.9	21.0	304.7	75.0	91.5	1.86	Ca-SO4
	21-Jun-13	45.5	3.3	15.4	68.9	55.1	154.0	64.0	78.1	1.29	Ca-SO4
	3-Jul-13	26.9	2.2	11.9	51.5	29.6	58.3	93.0	113.5	0.88	Ca-HCO3
	16-Jul-13	180.8	10.6	52.9	212.0	36.2	68.9	177.0	215.9	2.88	Ca-HCO3
	23-Jul-13	233.6	6.1	26.0	104.1	169.8	308.1	168.0	205.0	5.31	Na-SO4
	29-Jul-13	421.4	9.3	30.1	116.1	277.4	488.9	531.0	647.8	9.01	Na-HCO3
	6-Aug-13	87.4	3.7	12.1	48.8	80.7	109.8	139.0	169.6	2.90	Na-HCO3
	12-Aug-13	144.3	6.0	32.0	131.6	77.7	141.5	199.0	242.8	2.93	Na-HCO3
	22-Oct-13	27.4	1.6	12.0	50.3	16.5	64.3	55.0	67.1	0.90	Ca-SO4
	Average	119.1	4.8	21.6	90.2	75.7	184.8	142.6	174.0	2.7	Na-SO4
	Std Dev	121.9	3.0	12.9	49.5	79.7	133.2	141.5	172.7	2.5	-
	Max Value	421.4	10.6	52.9	212.0	277.4	488.9	531.0	647.8	9.0	-
	Min Value	26.9	1.6	10.7	48.8	16.5	58.3	33.0	40.3	0.9	-
WSP	6-Jun-13	41.6	1.7	13.9	58.0	42.1	96.2	64.0	78.1	1.27	Ca-SO4
	11-Jun-13	23.8	1.2	9.2	38.0	28.5	65.9	22.0	26.8	0.90	Ca-SO4
	14-Jun-13	34.0	1.6	12.3	51.7	39.3	89.5	59.0	72.0	1.10	Ca-SO4
	17-Jun-13	25.7	1.5	11.0	44.9	17.2	56.7	43.0	52.5	0.89	Ca-SO4
	21-Jun-13	21.4	1.6	10.4	41.8	44.8	39.7	18.0	22.0	0.77	Ca-Cl
	3-Jul-13	50.5	4.8	28.5	97.1	25.5	29.7	46.0	56.1	1.16	Ca-HCO3
	16-Jul-13	35.3	1.6	12.4	54.8	34.1	72.3	66.0	80.5	1.12	Ca-HCO3
	23-Jul-13	48.2	1.8	14.2	59.4	50.1	94.5	56.0	68.3	1.46	Ca-SO4
	29-Jul-13	34.0	2.8	18.7	39.3	18.2	34.4	60.0	73.2	1.12	Ca-HCO3
	6-Aug-13	24.2	1.3	11.0	45.2	22.1	52.9	131.0	159.8	0.84	Ca-HCO3
	12-Aug-13	17.2	1.2	10.3	41.5	22.6	34.2	121.0	147.6	0.62	Ca-HCO3
	22-Oct-13	199.6	5.2	28.4	116.6	117.7	328.6	125.0	152.5	4.30	Na-SO4
	Average	46.3	2.2	15.0	57.4	38.5	82.9	67.6	82.5	1.3	Ca-SO4
	Std Dev	49.4	1.4	6.7	24.6	27.2	81.0	38.2	46.6	1.0	-
	Max Value	199.6	5.2	28.5	116.6	117.7	328.6	131.0	159.8	4.3	-
	Min Value	17.2	1.2	9.2	38.0	17.2	29.7	18.0	22.0	0.6	-
Vault	27-Nov-12	549.0	11.4	34.6	122.0	322.0	644.0		635.0	11.30	Na-SO4
	18-Dec-12	595.0	12.0	30.6	121.0	353.0	673.0		657.0	12.51	Na-SO4
	8-Jan-13	847.0	15.0	26.0	75.5	521.0	722.0		817.0	21.44	Na-Cl
	1-Feb-13	687.0	12.9	29.3	106.0	402.0	660.0		730.0	15.23	Na-SO4
	12-Feb-13	646.0	13.0	33.0	109.0	397.0	662.0		726.0	13.92	Na-SO4
	27-Feb-13	692.0	10.0	31.0	100.0	429.0	667.0		738.0	15.50	Na-Cl
	17-Mar-13	744.0	13.0	26.0	77.4	464.0	622.0		803.0	18.68	Na-Cl

	23-Apr-13	437.0	9.9	32.0	126.0	277.0	542.0		614.0	9.00	Na-HCO3
	7-May-13	416.0	9.4	32.2	120.0	279.0	537.0		648.0	8.71	Na-HCO3
	6-Jun-13	423.0	10.0	32.1	124.0	255.0	563.0		554.0	8.76	Na-SO4
	6-Jun-13	406.6	9.2	33.2	125.9	276.9	541.9	157.0	191.5	8.30	Na-SO4
	11-Jun-13	313.8	7.8	31.6	122.0	209.2	468.8	149.0	181.8	6.55	Na-SO4
	14-Jun-13	325.8	8.2	35.0	136.5	217.4	516.1	131.0	159.8	6.44	Na-SO4
	17-Jun-13	305.7	7.7	33.6	132.3	190.8	487.2	156.0	190.3	6.15	Na-SO4
	21-Jun-13	132.9	4.8	21.7	92.1	94.0	268.4	99.0	120.8	3.24	Na-SO4
	3-Jul-13	42.7	3.9	17.9	59.4	47.6	49.3	74.0	90.3	1.25	Ca-HCO3
	4-Jul-13	27.1	2.5	10.2	43.0	16.4	51.4		168.0	0.96	Ca-HCO3
	16-Jul-13	273.6	7.6	34.2	126.1	174.8	440.0	148.0	180.6	5.58	Na-SO4
	18-Jul-13	174.0	5.9	22.9	98.1	107.0	268.0		384.0	4.11	Na-HCO3
	23-Jul-13	169.4	5.7	24.4	100.5	120.9	266.1	85.0	103.7	3.93	Na-SO4
	29-Jul-13	300.1	8.5	32.7	143.6	200.2	473.0	435.0	530.7	5.88	Na-HCO3
	30-Jul-13	240.0	7.3	24.1	97.9	141.0	323.0		411.0	5.63	Na-HCO3
	6-Aug-13	312.4	7.9	27.7	108.7	204.4	390.5	435.0	530.7	6.92	Na-HCO3
	12-Aug-13	78.0	3.3	18.0	84.6	72.5	138.2	201.0	245.2	2.01	Ca-HCO3
	15-Aug-13	194.0	5.3	18.7	80.0	121.0	226.0		396.0	5.07	Na-HCO3
	26-Aug-13	271.0	7.2	23.1	92.9	174.0	336.0		498.0	6.52	Na-HCO3
	10-Sep-13	261.0	6.8	25.6	107.0	159.0	343.0		480.0	5.88	Na-HCO3
	22-Oct-13	71.9	2.9	19.4	39.4	28.2	86.5	32.0	39.0	2.34	Na-SO4
	Average	354.9	8.2	27.2	102.5	223.4	427.3	175.2	422.3	7.9	Na-SO4
	Std Dev	224.8	3.3	6.4	26.7	134.8	201.8	129.5	248.4	5.2	-
	Max Value	847.0	15.0	35.0	143.6	521.0	722.0	435.0	817.0	21.4	-
	Min Value	27.1	2.5	10.2	39.4	16.4	49.3	32.0	39.0	1.0	-
MF	6-Jun-13	50.7	1.8	14.7	62.8	58.0	128.2	86.0	104.9	1.50	Ca-SO4
	11-Jun-13	54.5	1.7	13.3	60.3	56.3	146.3	66.0	80.5	1.65	Ca-SO4
	14-Jun-13	78.4	3.1	22.0	94.7	62.5	220.4	64.0	78.1	1.89	Ca-SO4
	17-Jun-13	52.9	2.1	13.9	61.4	33.7	127.3	50.0	61.0	1.59	Ca-SO4
	21-Jun-13	30.8	1.7	11.6	48.3	40.5	61.7	49.0	59.8	1.03	Ca-Cl
	3-Jul-13	20.8	1.4	10.2	41.7	25.2	37.9	50.0	61.0	0.75	Ca-HCO3
	16-Jul-13	245.9	17.0	114.6	146.4	28.9	60.1	126.0	153.7	3.70	Na-HCO3
	23-Jul-13	27.1	2.7	12.5	51.9	36.4	44.2	97.0	118.3	0.88	Ca-HCO3
	29-Jul-13	51.8	1.7	13.9	60.4	53.3	116.5	123.0	150.1	1.56	Ca-HCO3
	6-Aug-13	39.3	2.3	12.9	54.5	40.2	84.6	131.0	159.8	1.24	Ca-HCO3
	12-Aug-13	40.7	1.7	13.2	56.5	44.0	74.9	147.0	179.3	1.27	Ca-HCO3
	22-Oct-13	34.9	1.6	12.6	51.9	21.2	68.4	86.0	104.9	1.13	Ca-HCO3
	Average	60.6	3.2	22.1	65.9	41.7	97.5	89.6	109.3	1.5	Ca-SO4
	Std Dev	60.3	4.4	29.3	28.5	13.5	52.5	35.1	42.8	0.8	-
	Max Value	245.9	17.0	114.6	146.4	62.5	220.4	147.0	179.3	3.7	-
	Min Value	20.8	1.4	10.2	41.7	21.2	37.9	49.0	59.8	0.7	-
B1W1	03-Jul-13	21.1	1.3	9.8	44.1	31.1	43.4	82.0	100.0	0.75	Ca-HCO3
B1W3	3-Jul-13	21.8	1.6	10.8	45.3	43.7	47.9	83.0	101.3	0.76	Ca-HCO3

	15-Aug-13	159.3	3.9	22.4	101.7	103.5	297.5	202.0	246.4	3.73	Na-SO4
	Average	90.6	2.7	16.6	73.5	73.6	172.7	142.5	173.9	2.2	Na-SO4
	Std Dev	97.3	1.6	8.2	39.9	42.3	176.5	84.1	102.7	2.1	-
B1W2	03-Jul-13	19.6	1.4	9.8	40.2	26.3	36.1	89.0	108.6	0.72	Ca-HCO3
B1W4	3-Jul-13	21.7	1.5	10.6	44.3	42.6	44.3	82.0	100.0	0.76	Ca-HCO3
	22-Oct-13	51.1	1.8	22.1	89.4	30.3	100.2	132.0	161.0	1.25	Ca-HCO3
	Average	36.4	1.6	16.3	66.9	36.4	72.3	107.0	130.5	1.0	Ca-HCO3
	Std Dev	20.8	0.2	8.1	31.9	8.7	39.5	35.4	43.1	0.3	-
B2W1	22-Oct-13	40.2	2.5	23.0	109.6	22.9	208.1	129.0	157.4	0.91	Ca-SO4
B2W4	3-Jul-13	22.0	1.3	7.7	34.3	59.7	50.7	30.0	36.6	0.88	Ca-Cl
	15-Aug-13	35.2	2.4	28.3	139.1	20.8	182.8	342.0	417.2	0.71	Ca-HCO3
	22-Oct-13	82.8	4.4	32.9	81.1	19.6	70.1	101.0	123.2	1.96	Ca-HCO3
	Average	46.7	2.7	23.0	84.9	33.4	101.2	157.7	192.4	1.2	Ca-HCO3
	Std Dev	32.0	1.6	13.4	52.5	22.8	71.3	163.5	199.5	0.7	-
	Max Value	82.8	4.4	32.9	139.1	59.7	182.8	342.0	417.2	2.0	-
	Min Value	22.0	1.3	7.7	34.3	19.6	50.7	30.0	36.6	0.7	-
B2W6	15-Aug-13	35.9	1.5	12.3	51.1	23.1	63.5	164.0	200.1	1.17	Ca-HCO3
B3W1	3-Jul-13	25.7	2.3	14.7	66.5	43.6	107.8	60.0	73.2	0.74	Ca-HCO3
	15-Aug-13	48.2	4.1	45.1	244.0	18.8	539.3	285.0	347.7	0.74	Ca-SO4
	22-Oct-13	185.5	4.0	150.9	397.4	153.8	1178.1	111.0	135.4	2.01	Ca-SO4
	Average	86.5	3.5	70.3	236.0	72.1	608.4	152.0	185.4	1.2	Ca-SO4
	Std Dev	86.5	1.0	71.5	165.6	71.8	538.5	118.0	143.9	0.7	-
	Max Value	185.5	4.1	150.9	397.4	153.8	1178.1	285.0	347.7	2.0	-
	Min Value	25.7	2.3	14.7	66.5	18.8	107.8	60.0	73.2	0.7	-
B3W2	3-Jul-13	90.3	2.6	69.1	305.9	104.3	801.3	136.0	165.9	1.21	Ca-SO4
	15-Aug-13	83.1	2.7	60.0	268.3	71.1	672.0	309.0	377.0	1.19	Ca-SO4
	Average	86.7	2.6	64.6	287.1	87.7	736.7	222.5	271.5	1.2	Ca-SO4
	Std Dev	5.1	0.1	6.4	26.6	23.5	91.4	122.3	149.2	0.0	-
B3W3	3-Jul-13	25.6	2.1	15.2	63.9	25.0	111.1	85.0	103.7	0.75	Ca-SO4
	15-Aug-13	54.5	4.4	53.8	243.1	22.6	605.4	270.0	329.4	0.82	Ca-SO4
	Average	40.0	3.3	34.5	153.5	23.8	358.2	177.5	216.6	0.8	Ca-SO4
	Std Dev	20.4	1.6	27.3	126.7	1.7	349.6	130.8	159.6	0.1	-
B3W4	15-Aug-13	79.0	5.8	108.8	503.6	16.0	1609.9	85.0	103.7	0.83	Ca-SO4
B3W5	3-Jul-13	24.5	1.8	11.4	49.7	31.0	62.0	50.0	61.0	0.82	Ca-SO4
UPW1	22-Oct-13	189.9	4.2	153.5	632.3	132.0	1894.7	202.0	246.4	1.76	Ca-SO4

Table A2. All major ion data from the SFW 2014.

Sample ID	Date 2014	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	SO4 (mg/L)	Alk (mg/L)	HCO3 (mg/L)	SAR	Water Type
B1S1	23-May-14	164.3	3.5	25.9	111.8	119.3	339.7	196.0	239.1	3.6	Na-SO4
	06-Jun-14	183.3	4.2	30.2	129.2	117.0	419.4	206.0	251.3	3.8	Na-SO4
	20-Jun-14	328.5	4.8	39.6	166.8	201.8	652.2	310.0	378.2	5.9	Na-SO4
	04-Jul-14	393.9	6.3	40.2	155.3	251.0	672.8	336.0	409.9	7.3	Na-SO4
	16-Jul-14	452.9	7.0	41.8	144.3	300.1	698.6	357.0	435.5	8.5	Na-SO4
	29-Jul-14	390.2	6.1	38.5	133.5	275.5	612.2	314.0	383.1	7.7	Na-SO4
	10-Aug-14	393.9	7.9	37.6	130.3	266.6	581.4	335.0	408.7	7.8	Na-SO4
	15-Oct-14	515.1	5.4	41.3	186.7	282.2	690.7	402.0	490.4	8.9	Na-SO4
	Average	352.8	5.6	36.9	144.7	226.7	583.4	307.0	374.5	6.7	Na-SO4
	Std Dev	123.1	1.4	5.4	22.4	68.2	124.8	66.8	81.5	1.9	-
	Max	515.1	7.9	41.8	186.7	300.1	698.6	402.0	490.4	8.9	-
	Min	164.3	3.5	25.9	111.8	117.0	339.7	196.0	239.1	3.6	-
B1W3	6-Jun-14	267.0	4.9	39.8	157.9	128.3	548.6	238.0	290.4	4.9	Na-SO4
	20-Jun-14	343.0	4.0	46.2	195.9	208.0	684.8	378.0	461.2	5.7	Na-SO4
	4-Jul-14	457.7	4.7	48.3	186.6	304.7	656.8	478.0	583.2	7.7	Na-SO4
	16-Jul-14	447.7	3.0	55.8	241.2	357.6	742.4	494.0	602.7	6.8	Na-SO4
	29-Jul-14	481.8	6.5	61.9	281.1	437.0	836.6	476.0	580.7	6.8	Na-SO4
	10-Aug-14	477.5	2.1	59.2	267.6	436.0	808.1	413.0	503.9	6.9	Na-SO4
	15-Oct-14	612.7	0.9	51.0	219.3	396.5	861.4	347.0	423.3	9.7	Na-SO4
	Average	441.1	3.7	51.7	221.4	324.0	734.1	403.4	492.2	6.9	Na-SO4
	Std Dev	110.1	1.9	7.8	44.7	118.2	111.9	91.6	111.7	1.5	-
	Max	612.7	6.5	61.9	281.1	437.0	861.4	494.0	602.7	9.7	-
	Min	267.0	0.9	39.8	157.9	128.3	548.6	238.0	290.4	4.9	-
B2S1	23-May-14	213.5	5.4	30.4	124.7	152.3	417.2	220.0	268.4	4.4	Na-SO4
	6-Jun-14	326.9	6.4	61.3	104.5	74.1	311.4	138.0	168.4	6.3	Na-SO4
	20-Jun-14	64.0	1.8	18.6	75.8	41.9	194.3	111.0	135.4	1.7	Ca-SO4
	4-Jul-14	135.9	4.7	35.9	142.7	94.8	377.9	222.0	270.8	2.6	Na-SO4
	16-Jul-14	146.8	3.0	40.7	154.7	109.1	406.3	249.0	303.8	2.7	Na-SO4
	29-Jul-14	156.3	3.2	41.0	154.3	116.1	386.2	253.0	308.7	2.9	Na-SO4
	10-Aug-14	140.8	1.7	38.8	136.3	106.3	310.8	275.0	335.5	2.7	Na-HCO3
	15-Oct-14	126.9	1.1	45.2	161.2	95.9	295.9	407.0	496.5	2.3	Ca-HCO3
	Average	163.9	3.4	39.0	131.8	98.8	337.5	234.4	285.9	3.2	Na-SO4
	Std Dev	77.5	1.9	12.2	29.2	32.0	74.4	90.1	110.0	1.5	-
	Max	326.9	6.4	61.3	161.2	152.3	417.2	407.0	496.5	6.3	-
	Min	64.0	1.1	18.6	75.8	41.9	194.3	111.0	135.4	1.7	-
B2W7	6-Jun-14	84.7	2.2	50.9	196.1	61.5	635.2	123.0	150.1	1.4	Ca-SO4

	20-Jun-14	114.4	2.3	52.8	200.0	78.0	662.0	148.0	180.6	1.9	Ca-SO4
	4-Jul-14	117.8	2.7	71.1	259.9	75.4	862.4	155.0	189.1	1.7	Ca-SO4
	16-Jul-14	157.0	2.6	83.6	298.8	105.8	993.3	216.0	263.5	2.1	Ca-SO4
	29-Jul-14	135.6	3.0	84.7	314.2	87.1	1061.1	167.0	203.7	1.8	Ca-SO4
	10-Aug-14	133.6	3.3	86.9	301.9	86.0	981.7	210.0	256.2	1.7	Ca-SO4
	15-Oct-14	116.5	2.1	81.7	302.4	78.4	879.7	303.0	369.7	1.5	Ca-SO4
	Average	122.8	2.6	73.1	267.6	81.8	867.9	188.9	230.4	1.7	
	Std Dev	22.5	0.4	15.4	50.5	13.5	164.7	60.3	73.6	0.2	-
	Max	157.0	3.3	86.9	314.2	105.8	1061.1	303.0	369.7	2.1	-
	Min	84.7	2.1	50.9	196.1	61.5	635.2	123.0	150.1	1.4	-
B3S1	23-May-14	34.7	2.2	10.5	46.4	22.3	91.8	83.0	101.3	1.2	Ca-SO4
	6-Jun-14	92.8	2.6	25.6	108.1	70.6	289.9	152.0	185.4	2.1	Ca-SO4
	20-Jun-14	166.6	5.9	49.7	121.3	70.5	321.2	153.0	186.7	3.2	Na-SO4
	4-Jul-14	106.1	2.6	33.9	137.4	83.3	361.1	182.0	222.0	2.1	Ca-SO4
	16-Jul-14	114.1	2.8	36.2	138.9	90.6	378.2	188.0	229.4	2.2	Ca-SO4
	29-Jul-14	117.9	1.9	37.0	144.1	90.5	360.8	208.0	253.8	2.3	Ca-SO4
	10-Aug-14	121.4	0.9	37.8	146.1	91.8	357.2	220.0	268.4	2.3	Ca-SO4
	15-Oct-14	111.3	1.7	38.9	153.3	95.9	339.7	259.0	316.0	2.1	Ca-SO4
	Average	108.1	2.6	33.7	124.4	76.9	312.5	180.6	220.4	2.2	Ca-SO4
	Std Dev	36.6	1.5	11.5	34.7	24.1	93.4	52.9	64.6	0.5	-
	Max	166.6	5.9	49.7	153.3	95.9	378.2	259.0	316.0	3.2	-
	Min	34.7	0.9	10.5	46.4	22.3	91.8	83.0	101.3	1.2	-
B3W2	23-May-14	141.3	3.6	109.1	410.2	148.8	1214.0	154.0	187.9	1.6	Ca-SO4
	6-Jun-14	215.5	3.5	103.0	440.4	211.6	1360.1	213.0	259.9	2.4	Ca-SO4
	20-Jun-14	268.1	3.3	115.3	523.9	239.7	1548.6	340.0	414.8	2.8	Ca-SO4
	4-Jul-14	292.3	6.9	131.7	522.9	251.1	1606.1	291.0	355.0	3.0	Ca-SO4
	16-Jul-14	290.5	5.7	120.5	545.2	272.4	1588.9	393.0	479.5	2.9	Ca-SO4
	29-Jul-14	305.3	6.2	125.6	566.5	281.8	1617.2	434.0	529.5	3.0	Ca-SO4
	10-Aug-14	296.6	4.7	126.0	577.5	278.2	1608.5	480.0	585.6	2.9	Ca-SO4
	15-Oct-14	414.8	3.6	138.3	643.7	333.4	1855.7	424.0	517.3	3.9	Ca-SO4
	Average	278.1	4.7	121.2	528.8	252.1	1549.9	341.1	416.2	2.8	Ca-SO4
	Std Dev	78.2	1.4	11.7	74.8	54.8	190.9	114.3	139.4	0.6	-
	Max	414.8	6.9	138.3	643.7	333.4	1855.7	480.0	585.6	3.9	-
	Min	141.3	3.3	103.0	410.2	148.8	1214.0	154.0	187.9	1.6	-
B3W3	6-Jun-14	86.6	2.6	30.2	126.9	69.8	339.6	145.0	176.9	1.8	Ca-SO4
	20-Jun-14	100.9	2.7	34.1	137.6	77.6	362.8	164.0	200.1	2.0	Ca-SO4
	4-Jul-14	62.1	1.4	22.5	86.0	48.8	239.8	79.0	96.4	1.5	Ca-SO4
	16-Jul-14	114.7	3.9	38.5	152.5	90.7	401.7	196.0	239.1	2.1	Ca-SO4
	29-Jul-14	118.4	0.8	38.2	150.5	91.7	381.4	209.0	255.0	2.2	Ca-SO4
	10-Aug-14	117.1	0.3	37.6	147.0	89.9	367.7	212.0	258.6	2.2	Ca-SO4
	15-Oct-14	99.2	1.2	45.7	182.5	81.1	413.0	283.0	345.3	1.7	Ca-SO4

	Average	99.8	1.9	35.3	140.4	78.5	358.0	184.0	224.5	1.9	Ca-SO4
	Std Dev	20.2	1.3	7.3	29.5	15.4	57.6	63.6	77.6	0.3	-
	Max	118.4	3.9	45.7	182.5	91.7	413.0	283.0	345.3	2.2	-
	Min	62.1	0.3	22.5	86.0	48.8	239.8	79.0	96.4	1.5	-
B3W4	6-Jun-14	140.5	4.3	31.1	106.8	89.4	304.8	129.0	157.4	3.1	Na-SO4
	20-Jun-14	307.7	8.6	64.6	150.7	106.0	343.0	165.0	201.3	5.3	Na-SO4
	4-Jul-14	118.1	4.9	69.6	319.0	77.0	1024.7	128.0	156.2	1.6	Ca-SO4
	16-Jul-14	86.0	8.5	98.3	456.1	33.0	1503.7	74.0	90.3	1.0	Ca-SO4
	29-Jul-14	79.3	5.3	104.1	488.9	23.9	1617.0	69.0	84.2	0.9	Ca-SO4
	10-Aug-14	78.4	5.1	103.9	488.8	23.9	1594.9	69.0	84.2	0.8	Ca-SO4
	15-Oct-14	73.3	5.3	109.8	496.9	18.1	1624.5	104.0	126.9	0.8	Ca-SO4
	Average	126.2	6.0	83.1	358.2	53.0	1144.7	105.4	128.6	1.9	Ca-SO4
	Std Dev	83.8	1.8	29.0	168.7	36.6	598.2	37.1	45.3	1.7	-
	Max	307.7	8.6	109.8	496.9	106.0	1624.5	165.0	201.3	5.3	-
	Min	73.3	4.3	31.1	106.8	18.1	304.8	69.0	84.2	0.8	-
OPS1	23-May-14	527.5	12.5	37.6	113.2	271.6	604.3	456.0	556.3	11.0	Na-SO4
	6-Jun-14	144.9	4.5	29.4	113.0	109.3	346.9	169.0	206.2	3.1	Na-SO4
	20-Jun-14	179.3	4.3	32.6	128.2	126.5	377.6	232.0	283.0	3.7	Na-SO4
	4-Jul-14	138.4	3.7	26.2	107.6	98.8	288.9	204.0	248.9	3.1	Na-SO4
	16-Jul-14	175.4	5.3	38.5	152.5	135.5	405.3	272.0	331.8	3.3	Na-SO4
	29-Jul-14	195.1	4.8	41.6	161.3	145.7	422.8	300.0	366.0	3.5	Na-SO4
	10-Aug-14	201.1	4.3	41.9	159.6	150.8	424.7	314.0	383.1	3.7	Na-SO4
	15-Oct-14	263.1	4.0	41.7	153.8	159.0	419.6	312.0	380.6	4.9	Na-SO4
	Average	228.1	5.4	36.2	136.2	149.7	411.2	282.4	344.5	4.5	Na-SO4
	Std Dev	127.0	2.9	6.1	23.0	53.4	91.0	87.8	107.1	2.7	-
	Max	527.5	12.5	41.9	161.3	271.6	604.3	456.0	556.3	11.0	-
	Min	138.4	3.7	26.2	107.6	98.8	288.9	169.0	206.2	3.1	-
TRS1	23-May-14	389.1	10.7	85.0	456.4	334.3	1547.7	199.0	242.8	4.4	Na-SO4
	6-Jun-14	353.0	6.4	83.1	379.2	331.8	1315.0	176.0	214.7	4.3	Na-SO4
	20-Jun-14	457.0	5.4	90.2	377.7	404.1	1312.1	302.0	368.4	5.5	Na-SO4
	15-Oct-14	886.4	11.4	94.5	688.1	672.7	2213.1	344.0	419.7	8.4	Na-SO4
	Average	521.4	8.5	88.2	475.3	435.7	1597.0	255.3	311.4	5.6	Na-SO4
	Std Dev	247.2	3.0	5.1	146.5	161.5	425.3	80.6	98.4	1.9	-
	Max	886.4	11.4	94.5	688.1	672.7	2213.1	344.0	419.7	8.4	-
	Min	353.0	5.4	83.1	377.7	331.8	1312.1	176.0	214.7	4.3	-
TRS2	20-Jun-14	407.5	10.2	53.7	258.0	275.4	873.5	416.0	507.5	6.0	Na-SO4
	16-Jul-14	215.2	10.7	55.7	354.0	122.3	928.3	432.0	527.0	2.8	Ca-SO4
	29-Jul-14	664.3	13.3	62.3	241.0	427.7	1103.4	516.0	629.5	9.9	Na-SO4
	10-Aug-14	439.3	14.0	58.2	394.9	309.1	1277.2	358.0	436.8	5.5	Na-SO4
	15-Oct-14	623.0	9.6	66.4	295.1	318.0	1182.4	402.0	490.4	8.5	Na-SO4

	Average	469.9	11.6	59.2	308.6	290.5	1073.0	424.8	518.3	6.5	Na-SO4
	Std Dev	180.9	2.0	5.1	64.8	110.0	169.8	57.9	70.7	2.8	-
	Max	664.3	14.0	66.4	394.9	427.7	1277.2	516.0	629.5	9.9	-
	Min	215.2	9.6	53.7	241.0	122.3	873.5	358.0	436.8	2.8	-
TRW13	6-Jun-14	125.4	2.2	126.8	541.1	39.7	1687.0	260.0	317.2	1.3	Ca-SO4
	20-Jun-14	118.9	2.4	128.5	545.8	47.4	1638.4	307.0	374.5	1.2	Ca-SO4
	4-Jul-14	120.6	5.5	129.2	553.7	47.2	1602.5	342.0	417.2	1.2	Ca-SO4
	16-Jul-14	116.7	3.8	126.3	567.1	49.4	1580.7	437.0	533.1	1.2	Ca-SO4
	29-Jul-14	119.2	3.7	125.7	572.3	52.8	1551.8	450.0	549.0	1.2	Ca-SO4
	10-Aug-14	123.0	4.1	126.9	573.7	56.3	1525.3	468.0	571.0	1.2	Ca-SO4
	15-Oct-14	132.6	2.8	127.8	583.7	95.5	1557.6	472.0	575.8	1.3	Ca-SO4
	Average	122.4	3.5	127.3	562.5	55.5	1591.9	390.9	476.8	1.2	Ca-SO4
	Std Dev	5.3	1.2	1.2	15.8	18.4	55.8	86.3	105.3	0.05	-
	Max	132.6	5.5	129.2	583.7	95.5	1687.0	472.0	575.8	1.3	-
	Min	116.7	2.2	125.7	541.1	39.7	1525.3	260.0	317.2	1.2	-
TRW2	23-May-14	300.8	3.7	130.0	450.8	453.0	1211.6	261.0	318.4	3.2	Ca-SO4
	6-Jun-14	305.9	3.7	132.0	419.0	432.4	1121.7	278.0	339.2	3.3	Ca-SO4
	20-Jun-14	369.8	3.5	127.6	414.7	527.5	1158.1	408.0	497.8	4.1	Na-SO4
	10-Aug-14	275.3	7.0	99.3	328.0	393.0	776.1	414.0	505.1	3.4	Ca-SO4
	15-Oct-14	484.4	3.7	138.0	457.4	629.2	1191.4	410.0	500.2	5.1	Na-Cl
	Average	347.2	4.3	125.4	414.0	487.0	1091.8	354.2	432.1	3.8	Na-SO4
	Std Dev	84.2	1.5	15.1	51.6	93.3	179.7	77.6	94.7	0.8	-
	Max	484.4	7.0	138.0	457.4	629.2	1211.6	414.0	505.1	5.1	-
	Min	275.3	3.5	99.3	328.0	393.0	776.1	261.0	318.4	3.2	-
TRW3	6-Jun-14	4.4	7.4	28.7	598.1	2.3	1355.4	159.0	194.0	0.05	Ca-SO4
	20-Jun-14	6.9	9.0	33.6	629.6	2.9	1409.9	194.0	236.7	0.07	Ca-SO4
	4-Jul-14	8.3	10.7	31.6	610.7	3.7	1395.7	181.0	220.8	0.09	Ca-SO4
	29-Jul-14	6.8	11.1	7.5	209.2	4.7	438.0	77.0	93.9	0.13	Ca-SO4
	10-Aug-14	9.2	7.6	7.9	228.1	8.9	503.6	71.0	86.6	0.16	Ca-SO4
	15-Oct-14	14.8	12.8	67.3	516.9	5.1	1313.7	211.0	257.4	0.16	Ca-SO4
	Average	8.4	9.8	29.4	465.4	4.6	1069.4	148.8	181.6	0.1	Ca-SO4
	Std Dev	3.5	2.1	21.9	195.1	2.3	465.3	60.4	73.7	0.05	-
	Max	14.8	12.8	67.3	629.6	8.9	1409.9	211.0	257.4	0.2	-
	Min	4.4	7.4	7.5	209.2	2.3	438.0	71.0	86.6	0.05	-
TRW4	6-Jun-14	55.3	2.8	48.5	210.5	12.3	447.2	240.0	292.8	0.9	Ca-SO4
	20-Jun-14	180.1	4.3	91.4	194.4	275.4	88.8	680.0	829.6	2.7	Ca-HCO3
	4-Jul-14	264.1	4.6	90.5	358.6	369.4	884.6	370.0	451.4	3.2	Ca-SO4
	10-Aug-14	77.9	5.2	21.7	85.0	111.2	117.8	161.0	196.4	2.0	Ca-HCO3
	Average	144.4	4.2	63.0	212.1	192.1	384.6	362.8	442.6	2.2	Ca-HCO3

	Std Dev	84.4	0.9	36.2	100.9	2529.9	324.6	205.8	251.1	0.9	-
	Max	264.1	5.2	110.0	358.6	5840.5	884.6	680.0	829.6	3.2	-
	Min	55.3	2.8	21.7	85.0	12.3	88.8	161.0	196.4	0.9	-
TRW5	6-Jun-14	193.4	2.6	125.8	499.7	178.7	1410.4	226.0	275.7	2.0	Ca-SO4
	20-Jun-14	183.5	2.6	106.9	471.9	188.8	1333.4	276.0	336.7	2.0	Ca-SO4
	4-Jul-14	226.1	5.9	120.0	524.6	226.9	1375.7	438.0	534.4	2.3	Ca-SO4
	16-Jul-14	230.5	5.0	117.1	527.0	262.8	1383.2	357.0	435.5	2.4	Ca-SO4
	29-Jul-14	246.7	6.7	121.6	550.5	283.9	1394.3	452.0	551.4	2.5	Ca-SO4
	10-Aug-14	256.0	3.4	118.2	527.0	321.3	1317.0	456.0	556.3	2.6	Ca-SO4
	15-Oct-14	403.6	3.0	109.9	499.3	413.1	1296.7	426.0	519.7	4.3	Ca-SO4
	Average	248.5	4.2	117.1	514.3	267.9	1358.7	375.9	458.5	2.6	Ca-SO4
	Std Dev	73.3	1.7	6.6	25.7	81.8	42.9	92.5	112.9	0.8	-
	Max	403.6	6.7	125.8	550.5	413.1	1410.4	456.0	556.3	4.3	-
	Min	183.5	2.6	106.9	471.9	178.7	1296.7	226.0	275.7	2.0	-
TRW8	6-Jun-14	89.7	4.6	112.4	662.2	11.4	1867.8	259.0	316.0	0.85	Ca-SO4
	20-Jun-14	78.4	6.3	97.4	645.2	9.8	1695.1	314.0	383.1	0.76	Ca-SO4
	4-Jul-14	49.4	7.6	71.4	620.9	7.9	1505.6	316.0	385.5	0.50	Ca-SO4
	16-Jul-14	33.4	10.1	55.2	615.8	7.9	1384.6	302.0	368.4	0.35	Ca-SO4
	29-Jul-14	27.6	8.0	51.0	613.9	8.3	1396.1	287.0	350.1	0.29	Ca-SO4
	10-Aug-14	26.0	7.7	49.8	613.8	9.0	1378.0	285.0	347.7	0.27	Ca-SO4
	15-Oct-14	199.7	15.6	28.4	448.7	64.7	1264.3	264.0	322.1	2.5	Ca-SO4
	Average	72.0	8.6	66.5	602.9	17.0	1498.8	289.6	353.3	0.8	Ca-SO4
	Std Dev	61.6	3.5	29.4	70.5	21.1	211.3	22.6	27.6	0.8	-
	Max	199.7	15.6	112.4	662.2	64.7	1867.8	316.0	385.5	2.5	-
	Min	26.0	4.6	28.4	448.7	7.9	1264.3	259.0	316.0	0.3	-
TRW9	6-Jun-14	28.7	2.1	38.7	198.2	10.1	596.3	52.0	63.4	0.49	Ca-SO4
	20-Jun-14	45.2	2.2	43.9	223.7	19.6	611.8	126.0	153.7	0.72	Ca-SO4
	4-Jul-14	57.8	2.1	50.6	257.5	28.9	663.5	187.0	228.1	0.86	Ca-SO4
	16-Jul-14	74.4	4.0	72.1	363.7	29.0	1043.8	163.0	198.9	0.93	Ca-SO4
	29-Jul-14	88.3	3.4	87.3	436.5	33.6	1299.7	196.0	239.1	1.0	Ca-SO4
	10-Aug-14	97.4	3.3	94.1	465.7	35.7	1353.9	229.0	279.4	1.1	Ca-SO4
	15-Oct-14	102.5	1.9	100.0	474.5	45.9	1472.6	181.0	220.8	1.1	Ca-SO4
	Average	70.6	2.7	69.5	345.7	29.0	1006.0	162.0	197.6	0.9	Ca-SO4
	Std Dev	27.8	0.8	25.3	118.3	11.5	380.1	57.8	70.5	0.2	-
	Max	102.5	4.0	100.0	474.5	45.9	1472.6	229.0	279.4	1.1	-
	Min	28.7	1.9	38.7	198.2	10.1	596.3	52.0	63.4	0.5	-
UPW1	23-May-14	185.3	5.1	141.5	600.3	190.0	1650.8	395.3	2700	1.77	Ca-SO4
UPW4	6-Jun-14	164.2	2.7	86.3	200.5	180.8	90.5	516.0	629.5	2.4	Ca-HCO3
	10-Aug-14	9.5	18.4	6.9	44.8	13.6	75.4	58.0	70.8	0.35	Ca-SO4
	15-Oct-14	36.0	6.0	34.4	166.6	16.9	345.3	234.0	285.5	0.66	Ca-SO4

	Average	69.9	9.0	42.5	137.3	70.4	170.4	269.3	328.6	1.2	Ca-HCO3
	Std Dev	82.7	8.3	40.3	81.9	95.6	151.7	231.0	281.9	1.1	-
	Max	164.2	18.4	86.3	200.5	180.8	345.3	516.0	629.5	2.4	-
	Min	9.5	2.7	6.9	44.8	13.6	75.4	58.0	70.8	0.4	-
UPW5	6-Jun-14	97.1	2.2	68.3	244.4	45.8	576.8	312.0	380.6	1.4	Ca-SO4
	20-Jun-14	93.3	2.5	61.3	250.7	46.7	541.6	408.0	497.8	1.4	Ca-SO4
	15-Oct-14	114.6	7.5	74.9	264.6	100.9	571.1	230.0	280.6	1.6	Ca-SO4
	Average	101.7	4.1	68.2	253.2	64.5	563.2	316.7	386.3	1.5	Ca-SO4
	Std Dev	11.4	3.0	6.8	10.3	31.6	18.9	89.1	108.7	0.1	-
	Max	114.6	7.5	74.9	264.6	100.9	576.8	408.0	497.8	1.6	-
	Min	93.3	2.2	61.3	244.4	45.8	541.6	230.0	280.6	1.4	-
WSP	23-May-14	78.5	2.4	16.1	65.0	48.9	161.4	106.0	129.3	2.3	Na-SO4
	6-Jun-14	91.3	2.3	19.0	82.1	69.5	236.7	123.0	150.1	2.4	Na-SO4
	20-Jun-14	111.0	3.1	22.3	85.2	84.0	280.3	124.0	151.3	2.8	Na-SO4
	4-Jul-14	137.7	5.1	27.4	87.3	110.3	343.3	106.0	129.3	3.3	Na-SO4
	16-Jul-14	154.0	3.0	28.0	92.3	117.3	371.8	113.0	137.9	3.6	Na-SO4
	29-Jul-14	170.8	3.1	30.1	91.3	131.6	406.5	90.0	109.8	4.0	Na-SO4
	10-Aug-14	194.5	3.1	33.3	97.0	147.8	448.4	85.0	103.7	4.3	Na-SO4
	15-Oct-14	319.0	3.0	41.5	141.0	213.1	609.6	142.0	173.2	6.1	Na-SO4
	Average	157.1	3.1	27.2	92.6	115.3	357.2	111.1	135.6	3.6	Na-SO4
	Std Dev	76.4	0.9	8.2	21.8	51.3	138.1	18.7	22.8	1.2	-
	Max	319.0	5.1	41.5	141.0	213.1	609.6	142.0	173.2	6.1	-
	Min	78.5	2.3	16.1	65.0	48.9	161.4	85.0	103.7	2.3	-
SUMP	5-Mar-14	722.0	12.0	29.6	102.0	422.0	668.0		799.0	16.2	Na-HCO3
	3-Apr-14	624.0	12.0	19.0	57.1	336.0	518.0		635.0	18.3	Na-HCO3
	13-May-14	523.0	10.0	33.2	121.0	271.0	613.0		657.0	10.9	Na-SO4
	6-Jun-14	148.0	4.1	26.0	101.0	116.0	340.0		199.0	3.4	Na-SO4
	19-Jun-14	152.0	4.1	27.2	105.0	119.0	363.0		249.0	3.4	Na-SO4
	4-Jul-14	27.1	2.5	10.2	43.0	16.4	51.4		168.0	1.0	Ca-HCO3
	8-Jul-14	160.0	4.1	34.5	138.0	131.0	376.0		282.0	3.2	Na-SO4
	28-Jul-14	153.0	4.2	33.1	131.0	132.0	394.0		296.0	3.1	Na-SO4
	6-Aug-14	152.0	4.2	33.9	136.0	134.0	375.0		302.0	3.0	Na-SO4
	19-Aug-14	154.0	4.4	33.4	137.0	131.0	385.0		296.0	3.1	Na-SO4
	4-Sep-14	200.0	4.0	38.4	143.0	163.0	432.0		372.0	3.8	Na-SO4
	17-Sep-14	203.0	3.8	37.0	140.0	163.0	421.0		378.0	3.9	Na-SO4
	3-Oct-14	227.0	4.2	38.7	142.0	166.0	421.0		364.0	4.4	Na-SO4
	20-Oct-14	195.0	4.0	37.8	141.0	151.0	417.0		343.0	3.8	Na-SO4
	6-Nov-14	203.0	4.0	38.0	138.0	167.0	416.0		364.0	3.9	Na-SO4

	Open Average	623.0	11.3	27.3	93.4	343.0	599.7	-	697.0	15.1	Na-HCO3
	Std Dev	99.504	1.155	7.382	32.81	75.74	75.884	-	89.02	3.82	-
	Max	722.0	12.0	33.2	121.0	422.0	668.0	0.0	799.0	18.3	-
	Min	523.0	10.0	19.0	57.1	271.0	518.0	0.0	635.0	10.9	-
	Closed Average	164.5	4.0	32.4	124.6	132.5	366.0	-	301.1	3.3	Na-SO4
	Std Dev	51.157	0.485	8.126	29.28	40.96	102.91	-	68.68	0.86	-
	Max	227.0	4.4	38.7	143.0	167.0	432.0	0.0	378.0	4.4	-
	Min	27.1	2.5	10.2	43.0	16.4	51.4	0.0	168.0	1.0	-

Table A3. All isotope data 2014 from the SFW.

Sample ID	Date 2014	δD (‰)	δ18O (‰)
B1S1	23-May-14	-130.6	-15.0
	06-Jun-14	-133.9	-15.8
	20-Jun-14	-117.2	-12.6
	04-Jul-14	-113.7	-11.9
	16-Jul-14	-111.0	-10.4
	29-Jul-14	-108.3	-11.8
	10-Aug-14	-110.3	-11.9
	15-Oct-14	-124.7	-14.3
	Average	-118.7	-13.0
	Std Dev	9.8	1.9
B1W3	6-Jun-14	-130.4	-15.5
	20-Jun-14	-119.5	-13.6
	4-Jul-14	-112.0	-12.2
	16-Jul-14	-121.1	-13.9
	29-Jul-14	-120.0	-14.0
	10-Aug-14	-117.3	-14.0
	15-Oct-14	-120.6	-13.7
	Average	-120.1	-13.8
	Std Dev	5.5	1.0
B2S1	23-May-14	-124.6	-13.5
	6-Jun-14	-131.5	-15.1
	20-Jun-14	-120.1	-12.4
	4-Jul-14	-103.2	-9.5
	16-Jul-14	-98.5	-7.5
	29-Jul-14	-90.0	-7.0
	10-Aug-14	-93.3	-8.5
	15-Oct-14	-110.4	-11.5
	Average	-108.9	-10.6

Sample ID	Date 2014	δD (‰)	δ18O (‰)
B3S1	23-May-14	-130.7	-13.5
	6-Jun-14	-136.1	-15.8
	20-Jun-14	-125.1	-13.5
	4-Jul-14	-116.8	-11.7
	16-Jul-14	-110.2	-10.6
	29-Jul-14	-105.9	-9.7
	10-Aug-14	-100.6	-9.0
	15-Oct-14	-113.5	-11.8
	Average	-117.4	-11.9
	Std Dev	12.4	2.2
B3W2	23-May-14	-135.5	-16.1
	6-Jun-14	-136.8	-16.8
	20-Jun-14	-135.8	-16.6
	4-Jul-14	-126.8	-14.9
	16-Jul-14	-133.6	-16.2
	29-Jul-14	-135.9	-16.7
	10-Aug-14	-134.9	-16.2
	15-Oct-14	-131.9	-16.1
	Average	-133.9	-16.2
	Std Dev	3.2	0.6
B3W3	6-Jun-14	-134.6	-15.7
	20-Jun-14	-125.5	-13.5
	4-Jul-14	-113.2	-11.4
	16-Jul-14	-111.2	-10.0
	29-Jul-14	-104.5	-9.7
	10-Aug-14	-103.4	-9.4
	15-Oct-14	-117.4	-12.9
	Average	-115.7	-11.8

	Std Dev	15.2	3.0
B2W7	6-Jun-14	-135.1	-16.0
	20-Jun-14	-107.0	-10.2
	4-Jul-14	-100.0	-9.1
	16-Jul-14	-108.8	-11.0
	29-Jul-14	-113.4	-12.2
	10-Aug-14	-117.8	-12.0
	15-Oct-14	-139.0	-16.9
	Average	-117.3	-12.5
	Std Dev	14.6	2.9

	Std Dev	11.3	2.3
B3W4	6-Jun-14	-132.4	-15.1
	20-Jun-14	-115.8	-11.9
	4-Jul-14	-118.8	-13.5
	16-Jul-14	-131.5	-15.5
	29-Jul-14	-132.0	-16.3
	10-Aug-14	-131.1	-16.4
	15-Oct-14	-136.1	-16.8
	Average	-128.3	-15.1
	Std Dev	7.7	1.8

Sample ID	Date 2014	δD (‰)	δ18O (‰)
OPS1	23-May-14	-134.1	-15.4
	6-Jun-14	-109.6	-10.4
	20-Jun-14	-131.9	-14.7
	4-Jul-14	-119.0	-12.5
	16-Jul-14	-105.4	-9.1
	29-Jul-14	-96.8	-8.2
	10-Aug-14	-100.7	-8.8
	15-Oct-14	-103.9	-9.4
	Average	-112.7	-11.1
	Std Dev	14.2	2.8
TRS1	23-May-14	-129.3	-15.1
	6-Jun-14	-131.1	-15.7
	20-Jun-14	-126.3	-14.9
	15-Oct-14	-127.2	-15.5
	Average	-128.5	-15.3
	Std Dev	2.1	0.4
TRS2	20-Jun-14	-131.4	-15.8

Sample ID	Date 2014	δD (‰)	δ18O (‰)
TRW3	6-Jun-14	-157.0	-20.3
	20-Jun-14	-158.2	-20.5
	4-Jul-14	-155.6	-20.3
	29-Jul-14	-93.6	-11.8
	10-Aug-14	-108.5	-13.6
	15-Oct-14	-146.9	-18.7
	Average	-136.6	-17.5
	Std Dev	28.2	3.8
TRW4	23-May-14	-126.7	-15.6
	6-Jun-14	-153.9	-19.6
	4-Jul-14	-139.2	-17.2
	10-Aug-14	-113.0	-14.3
	Average	-133.2	-16.7
	Std Dev	17.4	2.3
TRW5	6-Jun-14	-140.6	-17.8
	20-Jun-14	-140.2	-17.6
	4-Jul-14	-139.7	-17.3

	16-Jul-14	-113.0	-12.7
	29-Jul-14	-127.7	-14.8
	10-Aug-14	-154.0	-18.2
	15-Oct-14	-130.4	-15.5
	Average	-131.3	-15.4
	Std Dev	14.6905	1.97409
TRW13	6-Jun-14	-154.8	-19.5
	20-Jun-14	-152.9	-19.3
	4-Jul-14	-155.6	-19.8
	16-Jul-14	-158.0	-19.2
	29-Jul-14	-154.9	-19.4
	10-Aug-14	-152.7	-19.2
	15-Oct-14	-150.1	-18.9
	Average	-154.1	-19.3
	Std Dev	2.5	0.3
TRW2	23-May-14	-140.5	-17.5
	6-Jun-14	-137.8	-16.9
	20-Jun-14	-137.0	-16.9
	15-Oct-14	-135.4	-16.5
	Average	-137.7	-16.9
	Std Dev	2.2	0.4

	16-Jul-14	-140.3	-17.3
	29-Jul-14	-138.5	-17.4
	10-Aug-14	-139.1	-17.3
	15-Oct-14	-138.4	-17.1
	Average	-139.5	-17.4
	Std Dev	0.9	0.2
TRW8	6-Jun-14	-151.9	-19.5
	20-Jun-14	-151.2	-19.3
	4-Jul-14	-159.2	-20.4
	16-Jul-14	-162.8	-20.4
	29-Jul-14	-162.1	-20.9
	10-Aug-14	-164.9	-21.3
	15-Oct-14	-145.3	-18.1
	Average	-156.8	-20.0
	Std Dev	7.3	1.1
TRW9	6-Jun-14	-116.8	-12.4
	20-Jun-14	-109.0	-11.4
	4-Jul-14	-129.7	-15.2
	16-Jul-14	-134.9	-16.2
	29-Jul-14	-136.8	-17.0
	10-Aug-14	-134.1	-15.9
	15-Oct-14	-137.7	-17.0
	Average	-128.4	-15.0
	Std Dev	11.1	2.2

Sample ID	Date 2014	δD (‰)	δ18O (‰)
UPW4	6-Jun-14	-130.2	-16.1
	10-Aug-14	-108.9	-14.4
	15-Oct-14	-134.7	-17.2
	Average	-124.6	-15.9

	Std Dev	13.8	1.4
UPW5	6-Jun-14	-133.9	-16.8
	20-Jun-14	-132.7	-16.6
	15-Oct-14	-128.7	-16.0
	Average	-131.7	-16.5
	Std Dev	2.7	0.4
WSP	23-May-14	-133.7	-15.8
	6-Jun-14	-133.7	-15.8
	20-Jun-14	-122.7	-13.5
	4-Jul-14	-113.8	-11.9
	16-Jul-14	-106.4	-10.2
	29-Jul-14	-101.2	-9.1
	10-Aug-14	-91.2	-7.4
	15-Oct-14	-97.4	-9.2
	Average	-112.5	-11.6
	Std Dev	16.2497	3.17866