

Origin and hydrogeological setting of saline groundwater discharges to the Athabasca River: Geochemical and isotopic characterization of the hyporheic zone

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ABSTRACT

Identifying impacts of oil sands development on aquatic ecosystems requires understanding of the natural background water quality. In the Athabasca Oil Sands Region of Alberta this is challenging because the Athabasca River is incised directly into bitumen saturated sands of the McMurray Formation, and other saline Cretaceous and Devonian formations. This study compares the geochemical and isotopic composition of porewater sampled from the alluvial sediment beneath the Athabasca River with regional groundwater data to identify the geological origin of these saline groundwaters, and improve characterization of natural background sources of solutes entering the Athabasca River. Terrain conductivity surveys conducted along the Athabasca River were used to identify areas with evidence of saline groundwater discharge. Porewater samples were obtained from the alluvial sediment using drive point piezometers installed between 1 and 3 m below the water-sediment interface and were analyzed for $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{34}\text{S}-\text{SO}_4$, $\delta^{18}\text{O}-\text{SO}_4$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}-\text{DIC}$, $\delta^{13}\text{C}-\text{DOC}$, ^3H , and ^{14}C . The porewater in the alluvial sediment showed variable degrees of mixing with the overlying Athabasca River water, but the geochemical and isotopic composition in zones 1, 3 and 5 are consistent with discharge of saline groundwater from Cretaceous or Devonian units. The low percentages of modern carbon, and $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{34}\text{S}-\text{SO}_4$, $\delta^{18}\text{O}-\text{SO}_4$, and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures in the deepest porewater samples from Zones 1, 3 and 5 indicate glaciogenic water with high total dissolved solids originating from Devonian sourced solutes. These saline groundwater discharge zones occur where higher horizontal hydraulic gradients coincide with areas of higher salinity in the adjacent Cretaceous and Devonian aquifers, and areas with vertical connectivity with underlying Devonian aquifers. The results of this study demonstrate the influence of groundwater-surface water interactions and saline bedrock formation water discharge to water quality along some reaches of the Athabasca River which need to be considered in monitoring and water management strategies.

1. Introduction

The Athabasca Oil Sands Region (AOSR) of Northeastern Alberta represents an important energy reserve for Canada and the world. Identifying potential impacts of oil sands development on aquatic ecosystems requires understanding of the natural background water quality. The Athabasca River and its tributaries are incised directly into bitumen saturated sands of the McMurray Formation, as well as other saline Cretaceous and Devonian formations so there are many natural background sources and pathways for organics and salinity to reach rivers in the region. The input of saline groundwater from these

formations has been attributed as the cause for increases in chloride along this reach of the river (Jasechko et al., 2012; Gue et al., 2017), but better understanding of the composition, sources and spatial distribution of natural saline groundwater inputs are needed to improve our ability to identify anthropogenic impacts to water quality. Saline groundwater has been observed discharging near the Athabasca River as springs (Hitchon et al., 1969; Ozoray et al., 1980; Grasby and Chen, 2005; Gue et al., 2015), in saline fens adjacent to the river (Stewart and Lemay, 2011; Wells and Price, 2015), and more directly as riverbed seepage in alluvial sediment beneath the river (Gibson et al., 2011, 2013). Electromagnetic surveys along the Athabasca River between

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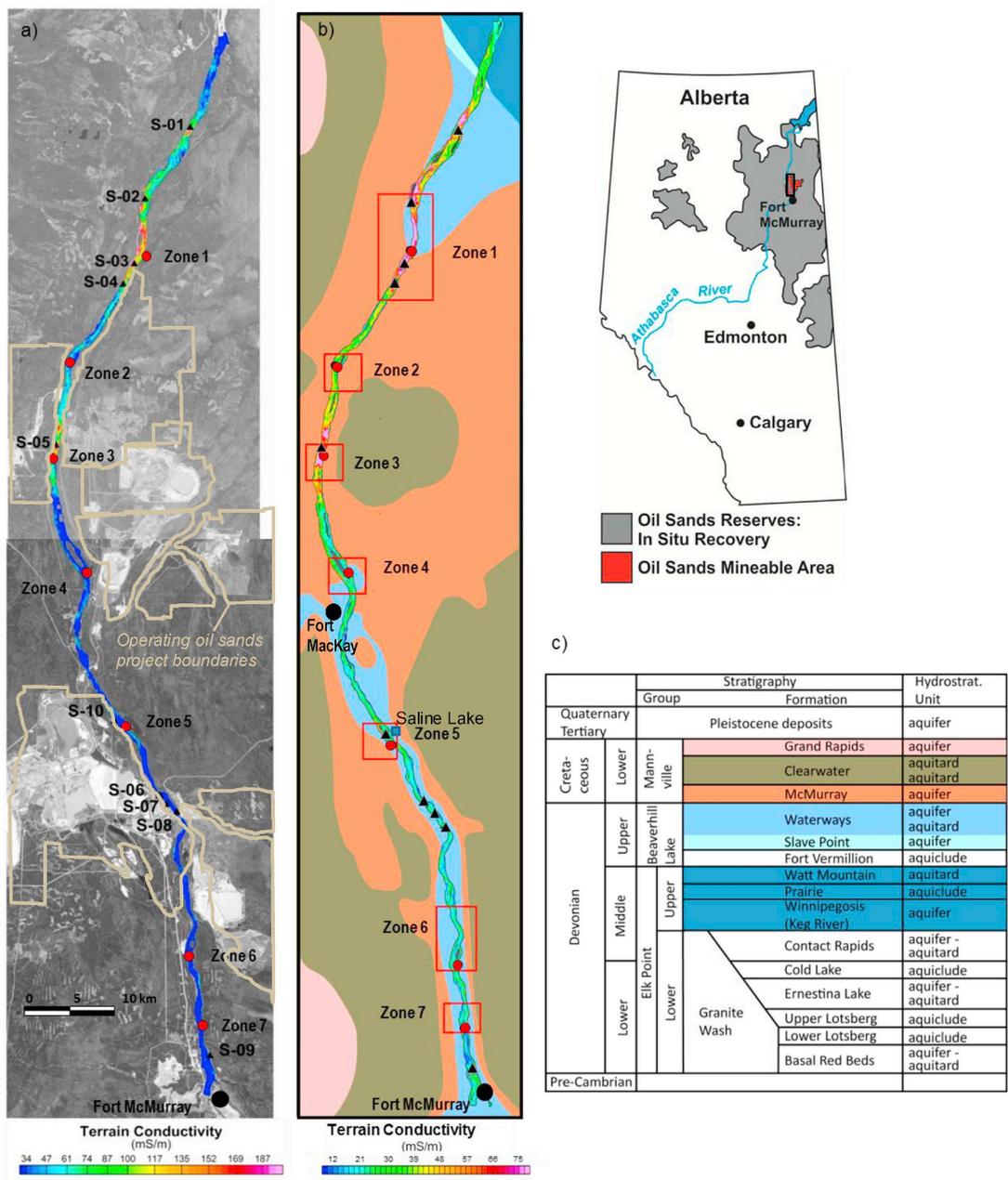


Fig. 1. The results of the low resolution terrain conductivity survey (a) and high resolution survey shown with bedrock geology (b) and the location of the porewater sampling locations (black triangles, 2009 samples, red circles October 2010 samples) and zones discussed in the text. The shading within the Athabasca River show the terrain conductivity with different resolutions (note different scales, low resolution left, higher resolution right). The lease boundaries for oil sands mining operations active as of 2018 are shown in beige. Inset shows the location of the Athabasca River and c) shows the legend with shading corresponding to the geological units shown in (b). Geology is modified from [Prior et al. \(2013\)](#). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fort McMurray and the confluence with the Firebag River were used to identify areas with elevated terrain conductivity to evaluate if these areas show evidence of saline groundwater discharge ([Gibson et al., 2013](#)). Previous work on porewater sampled from alluvial sediments in areas with elevated terrain conductivity, found that these saline porewaters had major ion compositions and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures similar to Cretaceous and Devonian saline groundwater suggesting that groundwater discharge from these units as a likely source of saline groundwater discharging to the Athabasca River ([Gibson et al., 2013](#)). Here we present an expanded suite of geochemical and isotopic data for the same porewater samples previously described in [Gibson et al.](#)

(2013) and compare them with regional groundwater and river water datasets to better understand the distribution, sources and hydrogeological controls on these saline groundwater inputs.

1.1. Geological setting and hydrostratigraphy

The study area includes the 125 km reach of the Athabasca River from Fort McMurray north to the Firebag River ([Fig. 1a](#)) in an area with extensive surface mining developments. Over the study area the river incises Cretaceous (McMurray) and Devonian (Waterways, Slave Point and Keg River) formations ([Fig. 1b](#)). The complete stratigraphic

sequence includes a Precambrian basement with very low hydraulic conductivity, overlain by Devonian and Cretaceous formations, which are in turn overlain by Quaternary surficial deposits (Fig. 1c). Geological and hydrostratigraphic features of the study region were described in detail by Hackbarth and Nastasa (1979), Bachu and Underschultz (1993), Bachu et al. (1991, 1993), Barson et al. (2001), and CEMA (2010a and b) and are summarized below. The study area is located at the eastern edge of the Western Canadian Sedimentary Basin (WCSB). The most important hydrostratigraphic units for regional flow include: Granite Wash Formation (also called the La Loche Formation), Keg River Formation (also called the Methy Formation), water bearing sand at the base of the McMurray Formation (Basal Aquifer) and Quaternary deposits (Hackbarth and Nastasa, 1979). Groundwater flow is generally to the northeast towards the edge of the basin. Groundwater flow in the Devonian Elk Point Group (Fig. 1c) has been described as a regional flow system driven by recharge in the Rocky Mountain overthrust belt and discharge in northeastern Alberta and Saskatchewan (Bachu et al., 1993). Grasby et al. (2000) found evidence that this regional flow system was never fully flushed with meteoric water, and it has been suggested that injection of glacial meltwater caused temporary disruptions to the regional flow (Grasby and Chen, 2005). The overlying units also generally have groundwater flow towards the northeast, but are more influenced by topographic and physiographic features. The four main hydrostratigraphic units are generally not well-connected except where faults, karst or fractures introduced by collapse features associated with dissolution of the Prairie Evaporite Formation have created local areas of hydraulic connectivity (Sproule, 1974; Cotterill and Hamilton, 1995; Broughton, 2013, 2015; Cowie et al., 2015). Local sub-glacial blowhole punctures have also been identified (Broughton, pers. Comm.). Hydraulic head measurements (Hackbarth and Nastasa, 1979; Bachu and Underschultz, 1993) and salinity distribution (Cowie et al., 2015) indicate that there is some communication across these regional aquitards.

Information about groundwater quality in the AOSR are available from a variety of sources, including data compiled to establish pre-development baseline conditions (CEMA, 2010a; WorleyParsons, 2009; Lemay et al., 2005), monitoring data collected as part of provincial programs (CEMA, 2010b, WorleyParsons, 2011; Integrated Sustainability, 2013; Matrix Solutions Inc. 2013, 2014) as well as individual groundwater studies (Cowie et al., 2015; Gue et al., 2015; Lemay, 2002). The reach of the Athabasca River between Fort McMurray and the confluence with the Firebag River falls with the Northern Athabasca Oil Sands (NAOS) region, and groundwater data from this region is the most relevant for the study area. In the NAOS efforts to establish baseline groundwater quality included compilation of over 132,300 geochemical analyses from nearly 1500 groundwater wells (CEMA, 2010a). Annual monitoring of the NAOS GOWN wells has occasionally included isotopic analyses (CEMA, 2010a; Integrated Sustainability Consultants Ltd, 2013) that have provided geochemical and isotopic data for aquifers in the study area. However, many of the aquifers continue in the Southern Athabasca Oil Sands (SAOS) region, and the separation of the monitoring programs is not related to a geological boundary so data from this region may be applicable for some areas of the NAOS.

1.1.1. Devonian Formations

The Granite Wash (La Loche Formation) consists mainly of feldspathic and gritty sandstone, but includes some sandy dolomite, mudstone, shale and thin, minor beds of anhydrite and gypsum (Norris, 1973). This Lower Devonian unit overlies the Precambrian basement and although there is limited geochemical (CEMA, 2010a; b) or hydrodynamic data available it is thought to be isolated from topographical influences, and part of the regional flow regime with groundwater flow direction to the northeast (Bachu et al., 1993). The overlying Devonian succession in the area is comprised of a series of carbonate aquifers separated by intervening evaporite deposits and

shaly to marly aquitards. Middle Devonian units include the Keg River (Methy) or Winnipegosis Formation, comprised mainly of reefal dolomites, underlain by fine clastic beds of the McLean River Formation and overlain by the Prairie Evaporite and Slave Point Formations. Groundwater in these units is characterized by extremely high salinity, particularly in the vicinity of evaporitic beds, where the Prairie Evaporites are still preserved. The Prairie Evaporite Formation is composed of halite and anhydrite, as well as carbonates and shale. This unit is generally only present west of the Athabasca River and is considered an aquiclude. The lower part of the Prairie Evaporite Formation, consisting largely of anhydrite, is also known as the Muskeg Formation. The Slave Point Formation is a thin unit (< 15 m thick) that consists of limestone, silty limestone and siltstone and is present as a very narrow outcrop area, just north of the seep sampling survey locations in the study area (Fig. 1). Upper Devonian units include the Waterways, Cooking Lake, Ireton and Grosmont Formations. The Waterways Formation is the main Devonian unit present as outcrop along the Athabasca River in the study area (Fig. 1). The different members of the Waterways Formation form an alternating series of calcareous shales and carbonates (Bachu et al., 1991). A wide range of total dissolved solids (TDS) has been reported for the Waterways Formation and is largely dependent on the proximity to the Sewetakun Fault (Hackbarth and Nastasa, 1979). In the NAOS Devonian groundwater salinity decreases rapidly from around 100,000 mg L⁻¹ close to the Sewetakun Fault to values of less than 1000 mg L⁻¹ at a distance of 10 km from the fault (CEMA, 2010a).

The Upper Devonian Waterways Formation is expected to act as a hydraulic barrier between the deeper, Middle Devonian aquifers (Keg River and La Loche Formations) and the overlying Cretaceous and surficial aquifers. Hydraulic conductivities in the Waterways Formation range between 9×10^{-12} to 1×10^{-8} m s⁻¹ (Bachu et al., 1991; CEMA, 2010a) and it is thought to limit the horizontal or vertical groundwater flow except where secondary permeability is present. Secondary permeability introduced through faults (Cotterill and Hamilton, 1995), karst and collapse features (Sproule, 1974; Broughton, 2013) may have caused increased permeability in the Upper Devonian and created conduits for Devonian groundwater to mix with overlying Cretaceous formations. The range in TDS reported for the Waterways Formation is 1000 mg L⁻¹ to 100,000 mg L⁻¹ (Sproule, 1974) and 780 mg L⁻¹ to 29,000 mg L⁻¹ (CEMA, 2010a). TDS in the Waterways Formation decreases rapidly from the very high values found near the Sewetakun Fault, to values of less than 1000 mg L⁻¹ at 10 km from the fault (CEMA, 2010b). In the northeastern portion of the study area, where the Waterways Formation is absent, the Devonian outcrops along the river include very limited exposures of the Slave Point Formation, and then reaches adjacent to the Middle Devonian Keg River Formation (Fig. 1). The Slave Point Formation is a thin rock unit composed of limestone, siltstone and minor dolomitic limestone, and is brecciated in places (Norris, 1973). The Keg River Formation is a potentially important water bearing unit that consists of reef and non-reef limestones or dolomites (Cotterill and Hamilton, 1995). The TDS of groundwaters for this formation in the NAOS are in the range of 4700–7780 mg L⁻¹ (CEMA, 2010a) and halite, and anhydrite and gypsum have been observed as infilling in pore-space (Greiner, 1956).

1.1.2. Cretaceous formations

The Cretaceous units in the study area include sandy aquifers and shaly aquitards of the Mannville Group and Colorado Group equivalents (Barson et al., 2001) and are separated from the underlying Devonian units by a major erosional unconformity. The Mannville Group includes the basal McMurray aquifer and the McMurray-Wabiskaw aquifer/aquitard system, containing the main oil sands deposits within poorly lithified, bitumen-saturated sandstone. These units are overlain by the Clearwater aquitard, and the Grand Rapids aquifer, the latter of which is almost completely eroded away along the study reach.

The McMurray Basal Aquifer is present between the top of Devonian formations and the base of the McMurray Formation oil sands. The

thickness of this unit depends on the topography of the Devonian erosional surface and show wide variations through the area. Regionally the water quality associated with the McMurray Basal Aquifer is typically Na–HCO₃–Cl type water with highly variable salinity. Groundwater in this aquifer is typically in the non-saline range (< 4000 mg L⁻¹ TDS) but across the NAOS TDS has been found to range from 182 mg L⁻¹ to 278,000 mg L⁻¹ (CEMA, 2010a) and with higher salinity values associated with the Prairie Evaporite dissolution scarp (Cowie et al., 2015).

The Clearwater Formation is the major aquitard isolating the McMurray Formation oil sands from the overlying Grand Rapids Formation and Quaternary sediments. The Grand Rapids Formation is porous and water-bearing and flow within this unit is controlled by topography and local-scale hydraulic conductivity distributions. Groundwater is expected to flow from the upland areas in the southeast and northwest to the lower areas in the central portion of the study area, likely discharging at subcrops and/or outcrops particularly along river valley and steep slopes.

1.2. Conceptual models for brine evolution in the AOSR

The presence of saline groundwater springs along the Athabasca River have been noted since some of the earliest records for the region (Bell, 1884; Carrigy, 1959; Norris, 1973; Hitchon et al., 1969; Ozoray et al., 1980) and have since been the focus of studies aimed at better understanding their evolution (Grasby and Chen, 2005; Gue et al., 2015; Wells and Price, 2015). The major ion composition of the saline springs are consistent with the dissolution of Elk Point Evaporites (Hitchon et al., 1969), but the very negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of these springs is not consistent with deep basin brines. Observations that saline groundwater springs located along the Athabasca River have geochemical compositions consistent with the dissolution of evaporites, but $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures similar to the ranges expected for glacial recharge led to the development of the conceptual model for groundwater evolution proposed by Grasby and Chen (2005). This conceptual model suggests that modern-day flow systems in the region may not be indicative of historical movement of water, especially during the Pleistocene when high permeability carbonate units may have acted as preferential subglacial drains. Grasby and Chen (2005) supported the idea of a Devonian evaporite source for the dissolved solutes, but suggested that temporary reversal of the regional groundwater flow regime by Pleistocene glacial meltwater allowed these waters to reach and dissolve the Prairie Evaporite Formation, accounting for not only the high dissolved solute and major ion composition, but also the depleted glaciogenic $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of the spring water.

Groundwater modelling by Lemieux et al. (2008) describes the potential role of subglacial meltwater on regional groundwater systems in Canada, concluding that they substantially impact surface/subsurface water exchanges, including significant injection of meltwater during ice sheet growth, and groundwater exfiltration during ice sheet regression.

1.3. Groundwater surface water interactions with the Athabasca River

Upstream of Fort McMurray hydraulic head measurements in units adjacent to the Athabasca River show that the river may act as a discharge point, primarily for shallow aquifers (Quaternary and Cretaceous Clearwater or Grand Rapids), but also for the McMurray Formation and Upper Devonian units (Hackbarth and Nastasa, 1979; Bachu and Underschultz, 1993). There are still relatively few measurements available for Devonian units, but groundwater monitoring in the McMurray Formation in the vicinity of development along the Athabasca River have provided a clearer picture of potentiometric surfaces in the area, particularly for the McMurray Basal aquifer. Flow in the McMurray Basal aquifer is towards the Athabasca River, with the potentiometric surface having a gradient of 0.002 increasing to 0.003 near the Athabasca River (CEMA, 2010a,b; Integrated Sustainability

Consultants Ltd, 2013). Numerical groundwater modelling indicates that groundwater from the basal McMurray aquifer discharges to the Athabasca River contributing to baseflow, but that discharge rates are expected to be insignificant when compared to the flow rate in the Athabasca River (CEMA, 2010a,b; Integrated Sustainability Consultants Ltd, 2013).

Estimates of the overall contribution of saline groundwater have been made using chloride (Jasechko et al., 2012) and chloride stable isotope mass balance models (Gue et al., 2017). Jasechko et al. (2012) used monthly river discharge and chloride data for the Athabasca River to calculate inputs of saline groundwater along specific reaches of the river for monitoring stations both upstream (Hinton) and downstream (Old Fort) of Fort McMurray, and found that the reach of the river between Fort McMurray and Old Fort, where the river channel is incised directly over Cretaceous and Devonian units and where majority of oil sands mining activity occurs, is where the greatest saline groundwater inputs occur. This chloride mass balance modelling showed that even discharge of small volumes of high salinity groundwater (0.1–3% of Athabasca River discharge, or 500–3400 L/s) can account for the overall increases in Cl observed over the reach of the Athabasca River between Fort McMurray and Old Fort (Jasechko et al., 2012). Gue et al. (2017) used data from saline springs sampled along the Athabasca and Clearwater Rivers with a chloride mass and stable isotope balance approach to estimate the fluxes of saline groundwater using endmembers representative of saline and meteoric sources of chloride and upstream and downstream concentrations. The saline groundwater discharge rates for the Athabasca River, estimate that saline groundwater inputs comprise < 2% of river discharge or 134 ± 64 L/s, which were lower than those calculated by Jasechko et al. (2012). However, Gue et al. (2015) reached a similar conclusion that these small discharges are significant sources of major ions (accounting for 0.04–39% of major ion concentrations) and chloride (contributing 12–18% of monthly Cl flux), particularly under low-flow winter conditions. Gue et al. (2017) used these fluxes to calculate the total loadings of metals and PAHs associated with saline groundwater fluxes and found both to be negligible (< 1% and < 0.03% respectively).

The Jasechko et al. (2012) and Gue et al. (2017) studies showed the overall importance of saline groundwater discharge to the chemistry of the Athabasca River in the reach adjacent to oil sands activities, but these studies did not provide information about where these discharges occur, or possible hydrogeological controls. To better constrain the spatial distribution of these saline groundwater inputs Gibson et al. (2013) used electromagnetic surveys to identify areas of elevated river bed conductivity to select porewater sampling locations for sampling for geochemical and isotopic analyses. The major ion composition and $\delta^{18}\text{O}$ signatures of porewater in some of the saline groundwater zones (Zones 1, 3 and 5) were used as evidence that these saline groundwaters originated from Cretaceous and Devonian formations.

Here we expand on the original interpretation, using previously unpublished isotopic and trace element data for the same water samples discussed in Gibson et al. (2013), and incorporating data from regional groundwater datasets available for the area to improve understanding of the sources and hydrogeological controls on these saline groundwater inputs.

2. Methods

The samples used in the current study were collected during the same sampling campaigns originally described in Gibson et al. (2013), and briefly summarized below. The electromagnetic surveys were used to identify areas of elevated river bed conductivity and to select porewater sampling locations. The distributions of geochemical and isotopic parameters within the porewater profiles obtained from the alluvial sediment beneath the Athabasca River in the zones of elevated terrain conductivity were used to identify porewater samples without evidence

of significant mixing with river water that could be considered potential end-members. These porewater samples were compared with regional groundwater datasets to evaluate potential hydrogeological sources.

2.1. Electromagnetic surveys

The electromagnetic survey method followed the general approach described by Butler et al. (2004) was previously described in Gibson et al. (2013) and consisted of waterborne electromagnetic (EM) terrain conductivity surveys along the Athabasca River through the primary area of oil-sands-mining development from Fort McMurray downstream to the confluence of the Firebag River (Fig. 1a and b). Data was collected using a Geonics EM31 terrain conductivity meter coupled to a Trimble GeoXH differential global positioning system, mounted in a 4.5-m inflatable jet boat. The EM31 was operated in vertical-dipole mode and measured the combined terrain conductivity of the soil matrix and pore fluids. Maximum depth of investigation by the EM31 was approximately 6 m below the water surface, with the peak response originating from a depth of 1.5 m below the water surface. A Garmin GPS-bathymetry unit was used to collect bathymetry data and positional information was collected using a Garmin GPS unit, both of which were recorded to a data logger. The terrain conductivity readings were corrected for variations in water depth using electrical conductivity and bathymetry data measured during the survey. The corrected EM31 conductivity data should be representative of the terrain conductivity of the river bottom sediments and associated pore fluids. Throughout the field campaign, quality control was monitored continuously.

The terrain conductivity mapping from two major field campaigns were used to identify the zones for porewater sampling. A preliminary survey was conducted in June of 2009 and covered the entire 125-km reach of the river (Fig. 1a) (originally described in Gibson et al., 2013). In September 2010, a high-resolution survey provided more detailed assessments of seven zones (Fig. 1b). Approximately 339,000 EM31 terrain conductivity measurements were collected along the 125-km reach of the Athabasca River during these two surveys.

2.2. Porewater and river water sampling

The porewater sampling campaigns targeted areas with high terrain conductivity identified along the 125-km reach of the Athabasca River (Fig. 1a and b). As described in Gibson et al. (2013), elevated terrain conductivity values ($> 80 \text{ mS m}^{-1}$) were measured in broad, continuous zones around Zone 1 and Zone 3 and in smaller, discrete areas within Zones 4, 5, 6 and 7. Porewater from an area with background terrain conductivity values (Zone 2) was also sampled so that the composition of porewater in an area with no evidence for discharging saline groundwater could be obtained for comparison. Porewater sampling was carried out during two campaigns in August 2009 and in October 2010.

Porewater from the sediments underlying the river were sampled using drive-point piezometers (DPPs) that were installed into the alluvial sediments. Sampling occurred at targeted locations where either background (Zone 2) or elevated riverbed terrain conductivities were measured during the EM31 survey. Each piezometer consisted of a 1.9 cm (3/4-inch) diameter stainless-steel drive-point tip screened over a 15-cm interval and attached to steel pipe lined with 1.6-cm diameter polyethylene tubing. All DPPs were installed manually using a slide hammer. During the preliminary survey (2009), these devices were driven 0.5–1 m below the riverbed surface, and only one depth was sampled from each sampling location (Fig. 1, black triangles). In the follow-up survey, three nests of DPPs were installed in close proximity to depths between 0.75 and 3 m in each of the sampling locations (Fig. 1, red circles). During DPP installations visual inspection of the alluvial sediment found some variability in sediment type (Zone 1 consisted of unconsolidated sandy alluvial sediment; Zone 2 was mainly sand with some clay content; Zone 3 consisted of fine to medium

grained sand; Zone 4 consisted of coarse and fine grained sands; Zone 5 had angular pebbles and cobbles, sand and clay; Zone 6 consisted of sandy alluvial sediments; and Zone 7 included fine sands with gravel) and at all locations but Zone 5 the DPP were installed to 3 m without meeting any significant barriers. In Zone 5 the slide hammer reached an impenetrable layer, suspected to be the limestone material present in outcrops in this location, so the deepest DPP in this zone could only be installed to about 1.4 m below the water sediment interface. The sampling location for Zone 5 is about 500 m from Saline Lake (57.08°N, Longitude. -111.53°W), a saline lake situated southeast of Fort MacKay. In Zone 6 the river banks both consist of exposed McMurray Formation cliffs. In this zone an area with elevated terrain conductivity on the east side of the river was originally targeted for DPP installation; however, the high clay content and low yields from test DPPs installed in this location weren't suitable for porewater collection. The Zone 6 DPPs were instead installed in an area with lower terrain conductivity values, and sandier substrate. Unfortunately, water levels could not be measured in the DPPs because of logistical constraints so vertical hydraulic gradients could not be determined for each sampling location.

DPPs were developed and purged for 15 min using a peristaltic pump. Measurements of pH, oxidation-reduction potential (Eh), dissolved oxygen (DO), specific conductance (EC) and temperature were made in a sealed flow-through cell until values stabilized. Eh calibration was checked in Zobells solution (Nordstrom, 1977) and Light's solution (Light, 1972). Calibration of pH was made with standard buffer solutions of pH 4, 7, and 10. Measurements of alkalinity were made in the field on filtered samples by titrating with 0.16 N H_2SO_4 to the bromocresol green–methyl red endpoint of pH 4.5.

In both porewater sampling campaigns samples were analyzed for major anions and cations, dissolved metals, DOC, naphthenic acids, and stable isotopes including $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), $\delta^{34}\text{S}$ – SO_4 , $\delta^{18}\text{O}$ – SO_4 , $\delta^{13}\text{C}$ of dissolved organic carbon (DOC), $\delta^{11}\text{B}$, $\delta^{37}\text{Cl}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Radiogenic isotopes ^3H and ^{14}C were analyzed in selected samples to determine the age of seep waters. All of the above samples were field filtered using 0.45 μm cellulose nitrate filters except those for naphthenic acids, enriched tritium (^3H) and ^{14}C . Samples were refrigerated immediately after sampling and shipped to the various laboratories for analyses.

Surface water samples from the Athabasca River were collected a few meters upstream of all porewater sampling locations using surface water grab sampling protocols (RAMP, 2008). Sample bottles were submerged to a depth of approximately 30 cm, uncapped and filled, and recapped at depth. Each bottle was triple-rinsed using this procedure prior to the final sample collection. Field parameters were measured at each surface water station using a YSI multi-probe. Surface water samples were also collected at the southern and northern most reaches of the survey and adjacent to the porewater sampling locations. Geochemical and Isotopic Analyses.

2.3. Analytical methods

Water samples were analyzed using ion chromatography (IC) for anions, inductively coupled plasma-mass spectrometry (ICP-MS) for trace elements, and inductively coupled plasma-optical emission spectrometry (ICP-OES) for major cations. Charge balance errors (CBE) were determined and only samples with $< 10\%$ CBE were included. DOC was determined using combustion and infrared detection. Naphthenic acids were measured by low level Fourier Transform Infrared spectroscopy (FTIR) using the method of Holowenko et al. (2002). The oxygen and hydrogen composition of water, and the carbon isotope composition of dissolved inorganic carbon (DIC) were measured at InnoTech Alberta (2009 samples) and at the University of Calgary (2010 samples). The oxygen isotopic composition of water samples was determined using the H_2O – CO_2 equilibration method of Nelson (2000) on a Delta V Advantage and GasBench II peripheral with an uncertainty of about $\pm 0.2\%$. Hydrogen (deuterium) isotopic compositions in water

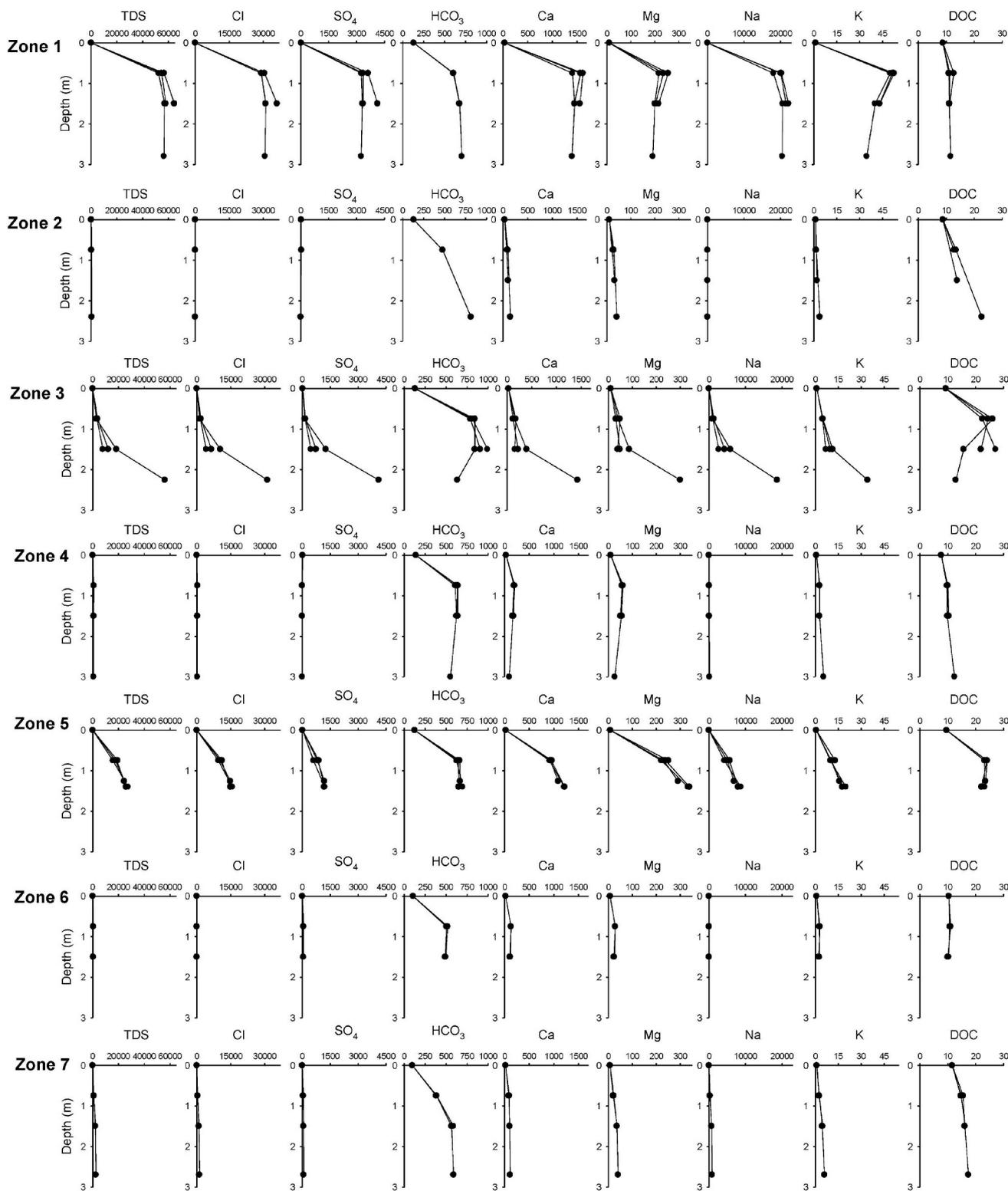


Fig. 2. Depth profiles of total dissolved solids (TDS), major ions, and dissolved organic carbon (DOC) in porewater sampled from alluvial sediment beneath the Athabasca River. Multiple profiles are available for some locations with multiple piezometer nests. Data from samples of river water were used for the 0 m depth values. All values are in mg L^{-1} .

were measured on a Delta V Advantage mass spectrometer with an HDevice peripheral by reduction of water to H_2 gas using chromium metal as an active reducing agent. Vienna Standard Mean Ocean Water (V-SMOW) and Standard Light Antarctic Precipitation (SLAP2) were used for internal calibration and oxygen and deuterium isotope ratios are expressed in delta notation ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) relative to V-SMOW and

the lab reported uncertainty was about $\pm 1.0\%$. Values of $\delta^{13}\text{C}$ -DIC were determined using the method of Assayag et al. (2006) using a Delta V Advantage mass spectrometer and Gas Bench II peripheral, and were reported relative to Vienna Pee Dee Belemnite (V-PDB) standard with an uncertainty of about $\pm 0.1\%$. Values of $\delta^{13}\text{C}$ -DOC were determined using continuous flow isotope ratio mass spectrometry after

preparation to remove the inorganic carbon using phosphoric acid and saturated potassium persulfate. The $\delta^{13}\text{C}$ -DOC results were reported relative to Vienna Pee Dee Belemnite with an uncertainty of $\pm 0.3\%$.

The sulfur, boron and strontium (2010 samples) isotopic compositions were measured at the University of Calgary. The method described in Giesemann et al. (1994) was used to determine sulfur-isotope ratios of dissolved sulfate, by dissolving BaCl_2 in water samples to precipitate BaSO_4 . The BaSO_4 was dried then converted into SO_2 in an elemental analyzer coupled to a mass spectrometer in continuous flow mode. Measurements of $\delta^{34}\text{S}$ are reported relative to the Vienna Canyon Diablo Troilite (V-CDT) standard and results are reported with an uncertainty of about $\pm 0.5\%$. The BaSO_4 precipitate was further analyzed for oxygen-isotope analysis by pyrolysis in a high temperature conversion/elemental analyzer interfaced to an isotope-ratio mass spectrometer with results reported with an uncertainty of about $\pm 0.5\%$. Boron isotope abundance measurements were made on water samples that were purified by microsublimation (Grobe et al., 2000) and analyzed on a thermal ionization mass spectrometer (Williams et al., 2001). Values of $\delta^{11}\text{B}$ are reported relative to $\delta^{11}\text{B}_{\text{SRM951}}$ standard and the lab reported an uncertainty of $\pm 2\%$. Strontium was extracted from the waters using ion exchange resin columns, eluted with deionized water, evaporated and then analyzed using positive ion thermal ionization mass spectrometry with a Thermo Electron Triton (PTIMS) instrument using the method described by Burton et al. (2002) using reference material SRM987. Measurement uncertainty in the $^{87}\text{Sr}/^{86}\text{Sr}$ ranged was ± 0.0001 . Tritium, chlorine and ^{14}C were measured at the University of Waterloo. Chlorine isotope analysis was measured by continuous flow isotope ratio mass spectrometry using the method described by Shouakar-Stash et al. (2005). The method involved the precipitation of dissolved chloride to silver chloride (AgCl), followed by the conversion of silver chloride to methyl chloride (CH_3Cl). Methyl chloride is then isolated on a GC column and the isotope ratio is measured using an IRMS. Results are reported relative to Standard Mean Ocean Chloride (SMOC) with an uncertainty of $\pm 0.2\%$. Tritium was measured at the University of Waterloo using electrolytic enrichment and liquid scintillation counting (Morgenstern and Taylor, 2009) with a detection limit of 0.08 TU and a measurement uncertainty from 0.02 to 0.08 TU. The ^{14}C content was determined using accelerator mass spectrometry (AMS) and are expressed in percent modern carbon (pMC) using the definition by Stuiver and Polach (1997). The measurement uncertainty for ^{14}C ranged from 0.2 to 0.5 pMC.

2.4. Speciation modelling

Saturation indices were determined using the equilibrium/mass-transfer model PHREEQC 2.18 (Parkhurst and Appelo, 1999) using the WATEQ4F (Ball and Nordstrom, 1991) database.

3. Results

3.1. Porewater profiles

The 2010 porewater sampling campaign was successful in installing piezometers and obtaining samples from greater depths within the alluvial sediment than the 2009 campaign, and are used here to generate depth profiles of major ions (Fig. 2) and isotopes (Fig. 3) (see Supplemental Material Tables S1a and S1b for the full porewater dataset). The vertical distribution of metals (Fig. S1) and saturation indices for selected mineral phases (Fig. S2) are described in the supplemental material. The porewater profiles show different degrees of mixing between river water and discharging saline groundwater depending on the sampling zone and depth beneath the water-sediment interface. The EM survey did not identify any elevated terrain conductivity areas in Zone 2, so the distribution of geochemical and isotopic parameters with depth in this zone can be used to characterize areas with background terrain conductivity. The river water chemistry

adjacent to each porewater sampling location was plotted at 0 m depth on the depth profiles (Figs. 3–5), and multiple profiles are shown for zones where data from multiple piezometer nests are available.

The distribution of field parameters differed between the various sampling zones, with diurnal variations in river water temperature over the eight-day sampling period likely accounting for some of the differences in river water temperatures and the resulting temperature depth profiles. Temperature profiles within alluvial sediments can be used to evaluate groundwater discharge to surface waters (Conant, 2004). In areas with a substantial hyporheic zone, with low groundwater discharge fluxes one would expect river temperatures to persist to greater depths beneath the water-sediment interface. In contrast, areas with high groundwater discharge fluxes tend to have temperatures more typical of groundwater at depths closer to the water-sediment interface (Conant, 2004). Average groundwater temperatures in the region were between 4 and 8 °C (CEMA, 2010a,b), and the elevated temperatures ($> 8\text{ °C}$) at depth in the alluvial river sediments may be due to diurnal temperature fluctuations due to heat conduction from late summer river water. Nonetheless, during the October sampling, lower temperatures associated with river water ($< 6\text{ °C}$) were present at $> 0.75\text{ m}$ in Zones 2, 6 and 7 indicating increased proportions of river water present in the alluvial sediment at depth in these zones. In Zones 1, 3, 4 and 5 groundwater temperatures are present in the alluvial sediment at shallower depths, closer to the water-sediment interface, consistent with greater fluxes of groundwater discharge at these locations.

Specific conductivity profiles showed the presence of high conductivity water ($> 40,000\ \mu\text{S cm}^{-1}$) at fairly shallow depths in Zones 1, 3, and 5 (Gibson et al., 2013). At Zone 1 even at 0.75 m below the water-sediment interface, porewater EC values are around $80,000\ \mu\text{S cm}^{-1}$, whereas at Zone 3 similar specific conductance values are not reached until $> 2\text{ m}$ depth. The presence of higher salinity water closer to the water-sediment interface at Zones 1 and 3 are consistent with these being areas of saline groundwater discharge through the alluvial sediment. The ECs measured in porewater in the alluvial sediment at Zone 5 do not reach the same levels as in Zones 1 or 3, but the deepest piezometer at this location was only installed at 1.4 m below the water-sediment interface, compared to $> 2\text{ m}$ depths at Zones 1 and 3. Porewater in Zone 5 had an EC of $40,000\ \mu\text{S cm}^{-1}$ at 0.75 m below the river-sediment interface. The EC of porewater with depth at Zones 2, 4, 6 and 7 increased slightly with depth, but remained low. The EC of porewater in Zone 2, the background location without elevated terrain conductivity, ranged from $600\ \mu\text{S cm}^{-1}$ at 0.75 m depth to $1130\ \mu\text{S cm}^{-1}$ at 2.4 m depth. This is higher than river water ($260\ \mu\text{S cm}^{-1}$ to $373\ \mu\text{S cm}^{-1}$). In Zones 1, 2 and 7 there was minimal dissolved oxygen (DO) in porewater below 0.75 m depths. Differences in the DO profiles for different piezometers located within the same zone show the spatial variability in the mixing depth between oxygenated river water and groundwater.

Vertical profiles in TDS and major ions (Fig. 2) show the same general trends as the EC profiles. At Zone 1 the high TDS porewater was present at shallow depths, near the water-sediment interface. The depth profiles at Zone 3 were more subdued, but similar concentrations of TDS and most major ions that were found at 0.75 m depth at Zone 1 were present at about 2 m depth at Zone 3. Exceptions include Mg, K, SO_4 and DOC, which had slightly higher maximum concentrations in Zone 3, than in Zone 1. The major ion concentrations in the porewater samples from Zone 5 were not as high as those from Zones 1 and 3, but this may be due to the shallower depths reached by the DPPs in this location. Zone 2 had almost no depth gradients in TDS or major ion concentrations, except for HCO_3 and DOC. The increase in HCO_3 and DOC at this location could indicate a background source of these solutes, possibly due to the dissolution of carbonates or degradation of organic matter within the alluvial sediment. This type of background profile was also typical for the data from Zones 4, 6 and 7.

The depth profiles for metals and metalloid concentrations are

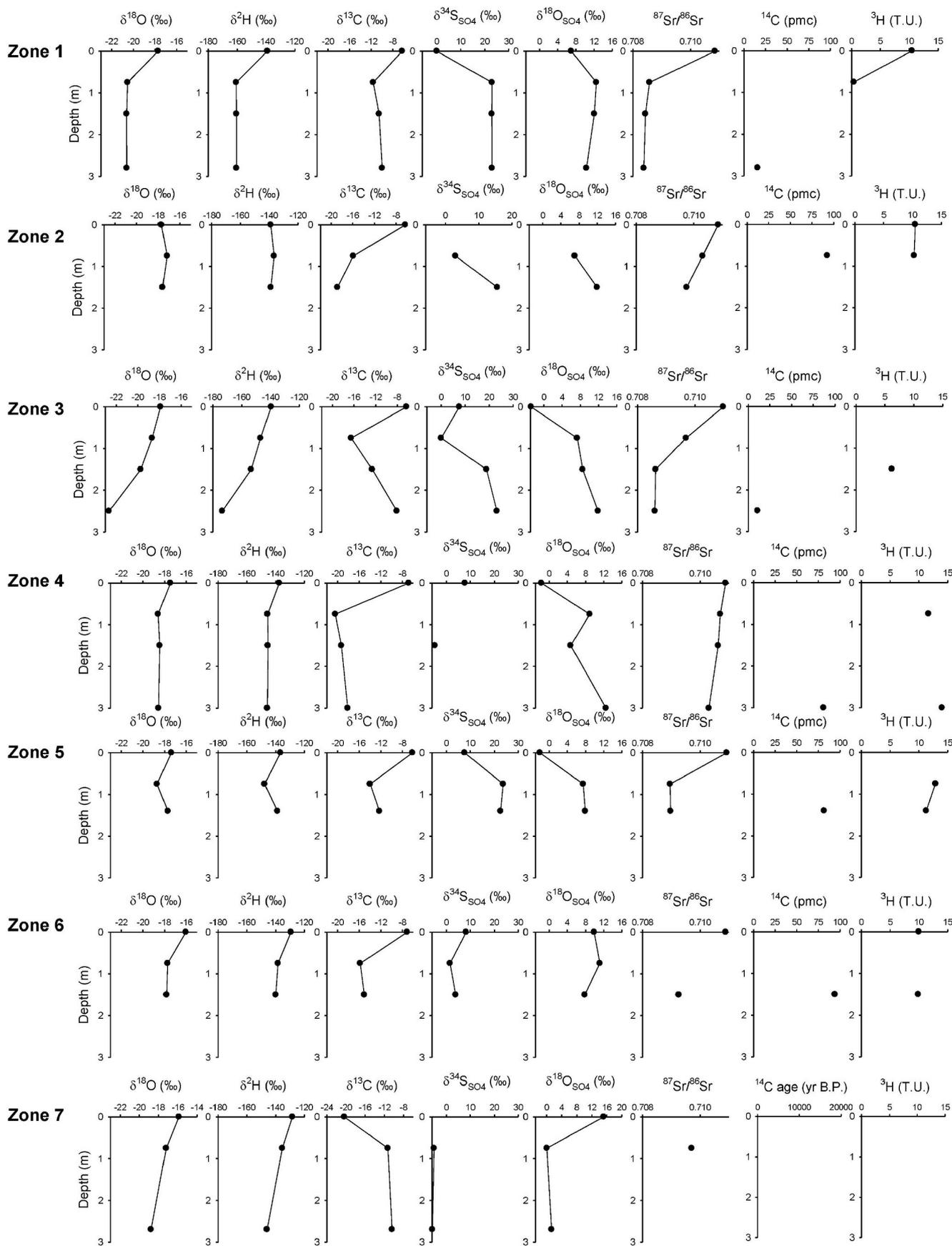


Fig. 3. Depth profiles for selected isotopic parameters measured in porewater sampled from alluvial sediment beneath the Athabasca River. Multiple profiles are available for some locations with multiple piezometer nests. Samples of river water were used for the 0 m depth values.

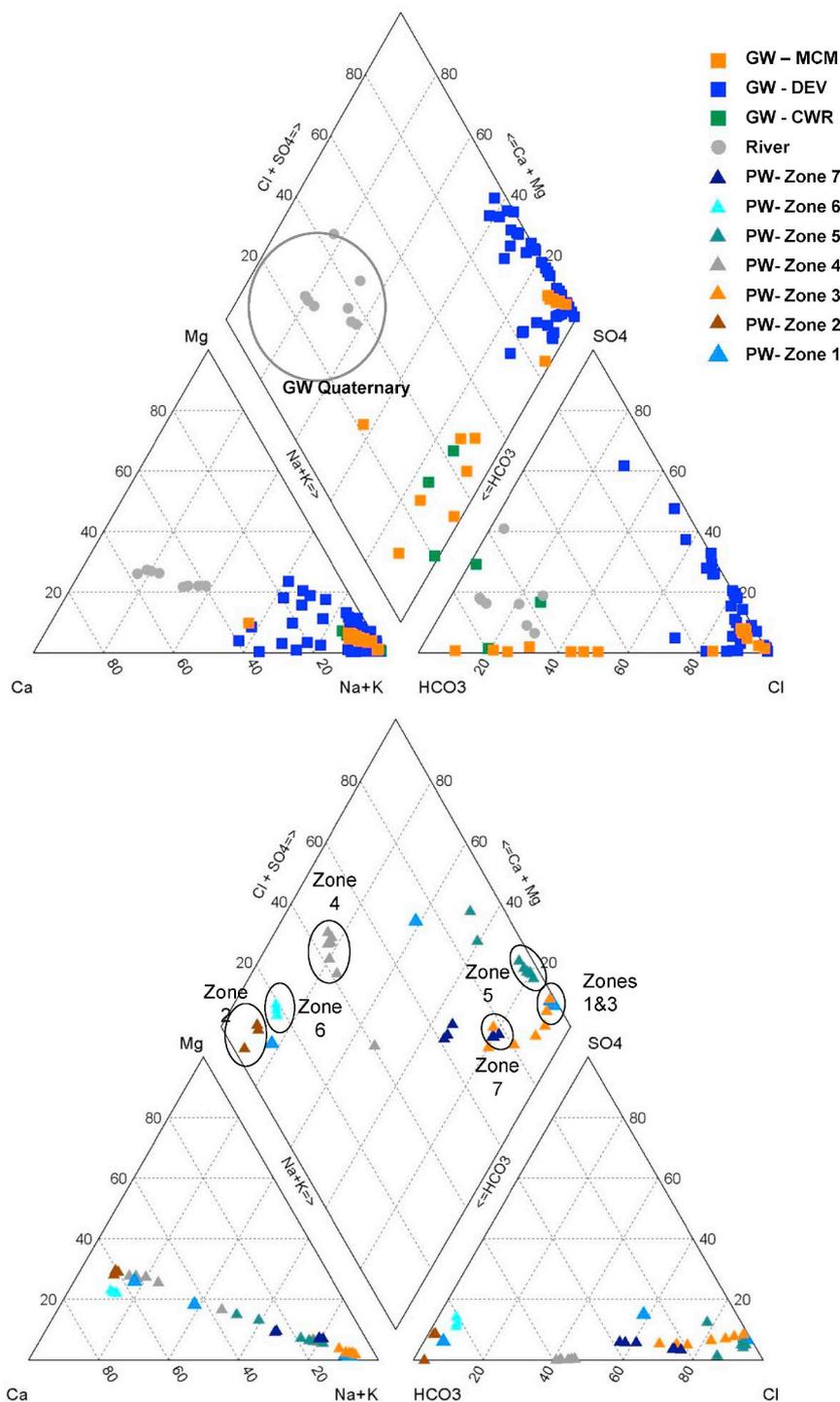


Fig. 4. Piper plot showing major ion geochemistry of groundwaters (GW) from regional aquifers (top) (CEMA, 2010a,b; Gibson et al., 2011) and the porewater (PW) sampled from the alluvial sediments (bottom). The range for Quaternary groundwater are shown for comparison. Abbreviations for groundwater (GW) samples are: MCM, McMurray Formation; DEV, Devonian formations, CWR, Clearwater Formation.

described in more detail in the supplemental material (Fig. S1), but in general the highest porewater metal and metalloid concentrations were associated with sampling locations with the highest total dissolved solids, at the deepest sampling locations in Zones 1, 3 and 5. However, the detection limits for some trace elements in some samples were high, because of matrix effects in some of the high TDS samples from Zones 1, 3 and 5. The vertical distribution of B, Li and Sr resembled those for EC and major ions at Zones 1 and 3 with similar maximum concentrations between the two zones.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of river water ranged between -16 and -18‰ and -130 to -140‰ respectively (Fig. 3). The porewater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values became more negative with depth, particularly in the profiles from Zones 1 ($\delta^{18}\text{O} = -20.6\text{‰}$) and 3 ($\delta^{18}\text{O} = -22.7\text{‰}$). There were very limited variations in the vertical profiles of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the porewater profiles from Zones 2, 4, 6 and 7 where EC and major ion profiles were the most subdued. In these zones porewater tended to have more positive values, similar to the range of $\delta^{18}\text{O}$ values found in river water, present at greater depths.

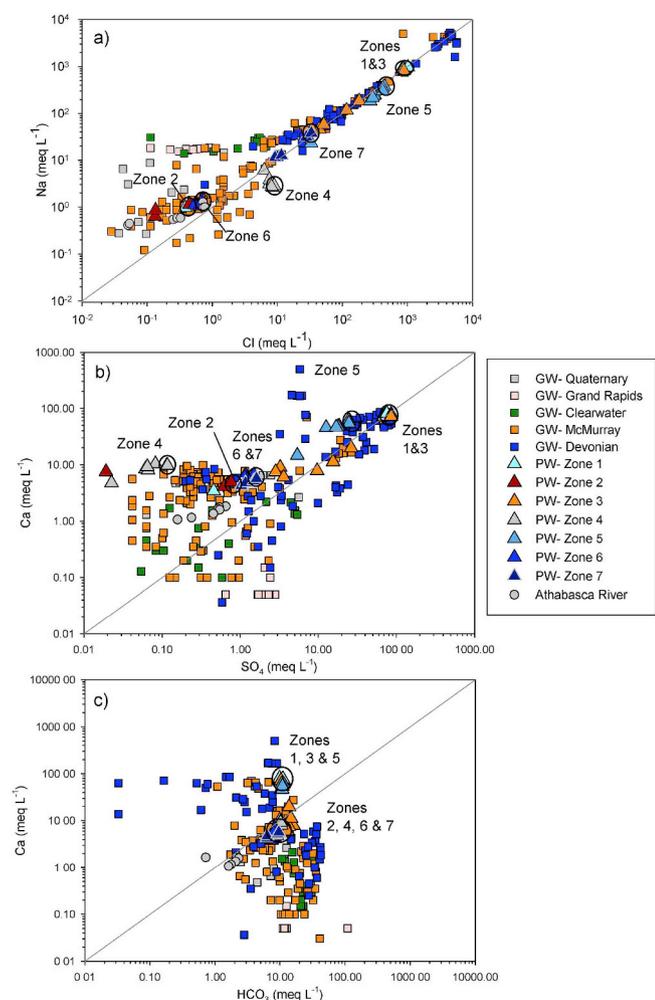


Fig. 5. Comparison of a) Na:Cl b) Ca:SO₄ and c) Ca:HCO₃ between the porewater (PW) samples in the various zones and regional groundwater (GW) datasets and the Athabasca River with 1:1 lines for comparison.

The $\delta^{13}\text{C}$ -DIC of river water was close to -8‰ at all sampling locations except for Zone 7, where it was -20‰ (Fig. 3). This sampling location is just downstream of where the Clearwater River and Clark Creek join the Athabasca River, so the values measured at this location may be due to mixing with these tributaries. The porewater sampled from about 0.75 m below the water-sediment at Zones 1–6 had $\delta^{13}\text{C}$ signatures between -12‰ and -20‰ . Decreases in $\delta^{13}\text{C}$ of porewater tended to occur as the HCO₃ concentrations increased. Zone 2 porewaters are near equilibrium with some carbonate minerals (Fig. S2 calcite, barite) at this depth, but most of the other porewater samples are supersaturated with respect to carbonates. The $\delta^{13}\text{C}$ of DIC in Zones 2 and 4, at depths where HCO₃ is elevated, is around -20‰ consistent with, bacterially mediated reduction of sulfate or organic matter (Figs. 2 and 3).

In Zones 1, 3 and 5 the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ signatures of porewater sulfate increased with depth reaching $\delta^{34}\text{S}$ values $> 20\text{‰}$ and $\delta^{18}\text{O} > 8\text{‰}$ that are typical of sulfate originating from the dissolution of evaporite minerals (Fig. 3). The saturation indices for gypsum and anhydrite are close to zero in these locations (0.75 m at Zone 1; 2.3 m at Zone 3; 0.75 at Zone 5; Fig. S2), indicating equilibrium with these mineral phases. Porewater from Zones 2, 4, 6 and 7 had $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values that either decreased or remained fairly constant with depth, within the range typically found for sulfate originating from oxidation of sulfide minerals. Sulfate reduction may be occurring at depth in some locations with reducing conditions; however, the decreases in sulfate concentration and $\delta^{34}\text{S}$ values would be difficult to distinguish on top of the

elevated concentrations of sulfate present at these locations.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of river water were fairly high (radiogenic) and within the range typically found in shallow Quaternary aquifers (Lemay, 2002) due to weathering of silicates (Fig. 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of porewater from Zones 1, 3 and 5 decrease with depth, reaching values of < 0.709 for the deepest sampling locations where the high TDS porewater were sampled. Consistent with the conceptual model of the saline groundwater discharge evolving from dissolution of the Prairie Evaporite Formation by glaciogenic water (Grasby and Chen, 2005), the highest TDS porewater samples from Zone 1, 3 and 5 have $^{87}\text{Sr}/^{86}\text{Sr}$ values that are within the range reported for the Prairie Evaporite Formation (0.70781–0.70789; Horita et al., 1996) and high concentrations of Sr that Connolly et al. (1990 a,b) suggested were the result of flushing of meteoric water through Cretaceous formations. The porewater in Zones 2, 4, 6, and 7 had $^{87}\text{Sr}/^{86}\text{Sr} > 0.709$ and very low Cl and Sr concentrations, consistent with weathering of silicate minerals (Connolly et al. (1990 a,b) and similar to Quaternary groundwater samples for the area (Lemay, 2002).

The ^{14}C of DIC and ^3H can be used to evaluate the age of solutes and groundwater present in the porewater profiles (Fig. 3). The Athabasca River had ^3H concentrations of about 10 TU, which is consistent with the expected range for modern surface waters in Alberta (Gibson et al., 2015b). In the 2009 survey ^3H was detected in all of the porewater samples, indicating mixing with river water in the alluvial sediments even to 1 m depth beneath the water-sediment interface. In the 2010 sampling campaign DPP were installed to deeper depths to try to access an unmixed groundwater endmember. Porewater from Zone 1 had ^3H concentrations below detection (< 0.8 TU) at 0.75 m depth below the water-sediment interface indicating no river water at that depth. Only one ^3H measurement is available for Zone 3, from 1.5 m below the water-sediment interface. ^3H was detected at this depth, but this coincides with fairly low solute concentrations consistent with some mixing of river water with saline groundwater at this depth. The lowest percentages of modern carbon were measured in Zones 1 and 3 at locations with high TDS. The ^3H and ^{14}C data available for Zone 5 indicate mixing with river water at 1.4 m depth, where porewater with fairly high solute concentrations were measured (e.g. Cl = 15,700 mg L⁻¹). Greater mixing with river water in the alluvial sediments at Zone 5 would explain the lower solute concentrations than those measured in Zones 1 and 3. Porewater from Zones 2, 4 and 6 have ^3H present at the deepest sampling locations (1 m, 3 m and 1.5 m respectively) and these samples also have fairly high percentages of modern carbon.

The isotopic composition of boron was not measured on all samples, and with such sparse data it is difficult to use this parameter to identify potential endmembers or trends. None of the river samples from the 2010 survey were analyzed for $\delta^{11}\text{B}$; however, the Athabasca River samples from the 2009 sampling survey had $\delta^{11}\text{B}$ values that ranged between 16 and 20‰. The deepest samples from Zone 1 and Zone 3 piezometers had the highest B concentrations (2–3 mg L⁻¹) and $\delta^{11}\text{B}$ values between 22 and 29‰ (no data available for Zone 5). Boron concentrations in porewater from Zones 2, 4 and 5 were less than the detection limit (0.05 mg L⁻¹). Porewater from Zone 7 had B concentrations that ranged between 0.147 mg L⁻¹ and 0.628 mg L⁻¹ and a $\delta^{11}\text{B}$ signature of 31‰.

4. Discussion

4.1. Geochemical processes occurring in the alluvial sediment

The vertical distribution of the field, geochemical and isotopic parameters with depth within the alluvial sediment in the various zones indicate different rates of groundwater discharge that have resulted in differing degrees of mixing with river water. Differences in groundwater discharge through the alluvial sediment are likely driven by differences in the vertical and horizontal hydraulic gradients along specific reaches of the river, combined with variations in the hydraulic

properties of the alluvial sediments themselves. The distribution of ^3H and ^{14}C as well as other geochemical parameters clearly indicate different degrees of mixing between river water and a discharging groundwater end-member. In the cases of Zones 1, 3 and 5 there is evidence of mixing between river water and a saline groundwater end-member; whereas at Zones 2, 4, and 6 the depth profiles show a much deeper penetration of river water and no evidence of a saline groundwater endmember. The porewater profiles from Zone 7 show no evidence of discharge of a high salinity groundwater, but the absence of ^3H could indicate more limited penetration of river water and discharge of low salinity groundwater.

Variations in porewater geochemical composition with depth could also be due to differences in geochemical processes occurring within the alluvial sediment in some zones or due to mixing with an endmember other than river water or saline groundwater. Information about the composition of the alluvial sediments is only available from observations made during the installation of the DPPs, but there was some variability between the different zones. The sediments observed during installation of the DPP were described as unconsolidated sand (Zones 1, 3, 4, and 6) with some clay (Zone 2) or gravel (Zone 7). Zone 5 differed in that the riverbed consisted of cobbles and pebbles with a sandy matrix. The deepest piezometer could only be installed at 1.4 m below the water-sediment interface, possibly indicating a thinner alluvial cover and closer proximity of the underlying bedrock at this location. Variations in hydraulic conductivity, mineralogy and potential for precipitation dissolution, ion exchange and redox reactions within the alluvial sediment may account for some of the small-scale variations between the different porewater profiles (Figs. 2 and 3) and differences in the major ion ratios at Zones 1, 3 and 5 (Figs. 4 and 5), but not the large distinction between the high salinity endmembers of Zones 1, 3 and 5, and the other zones.

4.2. Comparisons with potential Cretaceous and Devonian endmembers

The data from the 2010 porewater sampling campaign can be compared with regional groundwater and surface water datasets available for the region to identify potential source formations. Groundwater geochemical and isotopic data are available for selected Groundwater Observation Well Network (GOWN) wells located in the North Athabasca Oil Sands area (CEMA, 2010a; Integrated Sustainability Consultants Ltd, 2013), and other sampling campaigns conducted in the area such as Gibson et al. (2011), and Lemay (2002). Surface water geochemical and isotopic data were compiled from the Long-Term River Network (Hebben, 2009) and other sampling campaigns conducted along this reach of the Athabasca River (Gibson et al., 2011; Gue et al., 2015) (Tables 1–3, Figs. 4–8). The GOWN data from the NAOS includes geochemical and isotopic data from Quaternary aquifers, Cretaceous (Grand Rapids, Clearwater, Basal McMurray aquifer), Upper Devonian (Waterways and Slave Point), Middle Devonian (Prairie Evaporite and Keg River) and Lower Devonian (Granite Wash) formations. The Devonian Formations that outcrop along the Athabasca River include the Waterways, Slave Point and Keg River Formations, but the geochemical and isotopic data available from Devonian groundwater samples and springs outcropping along the Athabasca River were not typically identified by formation, so data from all Devonian units have been combined.

4.2.1. Major ion geochemistry

The major ion geochemistry of the porewater sampled from different discharge zones are consistent with varying degrees of mixing between Athabasca River water and McMurray or Devonian groundwater (Fig. 4; Table 1). The Athabasca River water has a dilute, mixed cation- HCO_3 type composition (RAMP, 2014). Quaternary groundwater typically has a Ca–Mg–Na– HCO_3 composition and plot in a similar area on a Piper plots as the river samples (Lemay, 2002; Ozoray, 1974; Ozoray et al., 1980; CEMA, 2010a). Devonian groundwater data for the

NAOS includes samples from the Prairie Evaporite/Beaverhill Lake/Keg River (Methy) (PBM) and the Granite Wash Formations. There were slight differences between the Devonian waters, with PBM groundwaters having a Na–Cl to Na–Cl– SO_4 /Na–Ca–Mg–Cl type compositions, and the Granite Wash Formation having lower proportions of Mg than the PBM samples and a Na–Cl, Na–Ca–Cl, or Na–Cl– SO_4 composition. Groundwater data for the McMurray Formation varied from Na–Ca– HCO_3 composition to Na–Cl composition; however, samples with the highest salinity and total dissolved solutes tended to have Na–Cl composition. The major ion geochemistry of water from this formation tends to have lower proportions of sulfate and magnesium. Groundwater from the Clearwater Formation had a Na– HCO_3 composition.

The major-ion composition of the saline porewaters from Zones 1, 3 and 7 plot along mixing lines between the river water and McMurray and Devonian groundwaters (Fig. 4), with the shallower samples having major ion compositions similar to river water, trending towards a Na–Cl composition with depth. All of the porewater samples from Zone 2 and Zone 6 retain a major ion composition similar to river water, and do not show any evidence of mixing with saline or non-saline groundwater, consistent with these being zones without significant saline groundwater discharge. The highest TDS samples from porewater from Zones 1, 3 and 5 (i.e. deepest porewater samples, with least evidence of mixing with river water) have Na–Cl compositions, similar to McMurray Formation or Devonian waters. There was a shallow Zone 1 porewater sample from the 2009 sampling campaign with a major ion composition similar to river water (Zone 1), but the data from the 2010 porewater sampling campaign showed a systematic shift towards Na–Cl type waters, with greater sampling depth. Porewater from Zone 7 plots along a mixing line towards Na–Cl type waters, but the concentrations of porewater at this zone, do not approach the high concentrations present at Zones 1, 3 or 5 (Fig. 3). The porewater sampled from Zone 4 had a somewhat anomalous major ion composition compared to the other porewater sampling zones with no evidence of saline groundwater discharge, primarily because of the very low sulfate concentrations. For most of the samples in this zone sulfate concentrations were not high enough to permit sulfur isotope analyses, but where measurements could be made the negative $\delta^{34}\text{S}$ values (Fig. 5) are consistent with sulfate reduction. None of the porewater samples showed evidence of mixing with Na– HCO_3 type waters typical of the Clearwater Formation or low salinity portions of the McMurray Formation.

The deepest porewater samples from Zones 1 and 3 and 5 showed the least evidence of mixing with river water and represent our closest approximation to potential groundwater sources discharging to the river. The deepest porewaters from Zones 1, 3 and 5 have TDS and major ion concentrations within the ranges measured in the McMurray and Devonian groundwaters in the region (Tables S1a and 1). Cl concentrations were near 36,000, 31,000 and 16,000 in the most saline porewaters from Zones 1, 3 and 5, which is above the highest Cl concentrations measured in groundwaters from Quaternary units or the Clearwater Formation, but well below the maximum concentrations measured in the McMurray Formation or Upper Devonian formations (Table 1).

The dissolution of halite will produce equal molal concentrations of sodium and chloride, so the Na:Cl ratios in porewater and the potential groundwater sources (Fig. 5a) can be used to evaluate the contribution of halite dissolution to the geochemical evolution. Devonian brines from deeper portions of the WCSB, farther away from the Prairie Evaporite dissolution edge tend to have Na:Cl ratios < 0.8 indicating evaporation of seawater altered by water rock interactions (Simpson, 1999; Grasby and Chen, 2005). The saline springs observed on the banks of the Athabasca River have Na:Cl ratios, closer to 1 (Grasby and Chen, 2005; Gue et al., 2015), consistent with the salinity in these springs having originating from the dissolution of halite, and distinct from the deeper basin waters farther away from the Prairie Evaporite dissolution

Table 1

Statistics for dissolved major ion concentrations measured from the Athabasca River (AR) and groundwater from Quaternary, Clearwater, McMurray and Devonian Formations from CEMA (2010a,b), Gibson et al. (2011) and Lemay (2002). Historical AR data was measured downstream of the mining operations at Old Fort, from 1957 to 2007 (Hebben, 2009). Number of samples analyzed is represented by n. Where available surface water quality guidelines (WQG) for the protection of freshwater aquatic life are included for comparison (AESRD, 2014).

Formation	EC	HCO ₃	TDS	SO ₄	Cl	Na	Ca	Mg	K
	mS cm ⁻¹	mg L ⁻¹							
<i>WQG</i>					120**				
<i>Athabasca R-Historical</i>									
Average	0.33	142	183	26	20	21	35	9.6	1.3
Maximum	0.72	226	342	62	65	55	60	27	8.2
Minimum	0.17	79	102	9	1.2	4.6	19	4	0.1
N	252	221	137	272	272	272	272	271	267
<i>Athabasca R-this study</i>									
Average	0.32	111	156	20	13	17	32	9.3	1.2
Maximum	0.66	141	193	31	27	29	46	13	2.0
Minimum	0.20	44	135	7.6	1.8	9.5	21	6.4	0.6
N	15	7	6	11	11	13	13	13	13
<i>Quaternary Fm.</i>									
Average	1.9	481	531	71	8.9	99	52	34	5.1
Maximum	6.1	770	1100	270	53	330	130	68	16
Minimum	0.71	150	130	0.11	0.26	6.2	7.9	2.8	0.80
N	6	8	8	7	10	10	10	10	10
<i>Clearwater Fm.</i>									
Average	3.2	1203	2042	72	445	748	17	8	21
Maximum	7.0	1897	4005	260	2000	1556	44	31	118
Minimum	0.08	659	980	< 1.0	4	320	2	< 1.0	< 1.0
N	20	18	19	20	20	20	20	20	20
<i>McMurray Fm.</i>									
Average	2.8	701	20,763	279	10,179	7590	156	51	30
Maximum	21	2508	278,340	3897	171,800	114,062	1397	420	274
Minimum	0.19	66	196	< 1.0	0.20	2.8	0.61	< 1.0	< 1.0
N	118	124	134	130	137	138	138	138	138
<i>Devonian Fm.</i>									
Average	0.3	726	76,686	1051	41,686	23,994	964	431	210
Maximum	210	2600	405,587	4147	204,000	120,313	9979	6305	1875
Minimum	0.29	< 5.0	654	< 1.0	27	69	< 1.0	< 1.0	4.0
N	70	66	82	82	82	82	82	82	82

edge. Most of the low TDS Cretaceous and Quaternary groundwaters have much higher proportions of Na than can be accounted for by halite dissolution alone. At low salinities, the Grand Rapids and Clearwater Formations tended to have higher Na:Cl values than those measured in the McMurray Formation. The high TDS porewater samples had Na:Cl very close to 1 (Zones 1 and 3), or slightly < 1 (Zone 5). The low TDS porewater samples tended to have Na:Cl ratios > 1 (Zone 2 = 3 to 6; Zone 6 = 2, Zone 7 = 1.1 to 1.2) with the exception of lower ratios found in Zone 4 (Na:Cl = 0.3 to 0.97). The high TDS and concentrations of Na and Cl in the high TDS porewaters are consistent with Devonian and some McMurray Formation groundwaters.

Similarly, the molal ratios of Ca to SO₄ can be used to evaluate the contribution of gypsum and anhydrite dissolution to groundwater evolution (Fig. 5b). The highest TDS waters from Zones 1 and 3 plot along the 1:1 line for Ca and SO₄ and are similar to the maximum concentrations reported for the McMurray, or Devonian Formations. These porewater samples are near equilibrium with respect to anhydrite and gypsum (Fig. S2). The porewater from Zones 2, 4, 6 and 7 all plot above the 1:1 line for Ca:SO₄.

The Athabasca River samples have Ca:HCO₃ values near 1 consistent with carbonate dissolution being a control on these ions (Fig. 5c). The highest TDS porewater samples from Zones 1, 3 and 5 have higher ratios, more similar to some of the Devonian groundwater samples likely due to inputs of Ca from gypsum dissolution.

The range in metal and metalloid concentrations measured in the deepest porewater samples are within the ranges found in Cretaceous and Devonian formation waters (Table 2). Further discussion is

provided in the Supplementary Material.

4.2.2. Dissolved organics

The concentrations of Dissolved Organic Carbon (DOC) measured in the porewater were generally higher than the concentrations present in the Athabasca River (DOC median 8–10 mgL⁻¹ at Old Fort; Hebben, 2009) (Fig. S3). The Athabasca River water samples typically had naphthenic acid concentrations below the detection limit (FTIR, < 0.10 mg L⁻¹). The highest DOC concentrations were measured at Zones 2, 3, and 5 (Fig. S3) and were not necessarily associated with the highest salinities. The high salinity porewaters sampled at depth from Zones 1, 3 and 5 differed in their DOC concentrations, with Zones 3 and 5 having average DOC concentrations around 21–23 mg L⁻¹ and Zone 1 having an average DOC concentration of 11 mg L⁻¹. There was very little variation in DOC concentrations with depth. The porewater at Zone 5 had slightly lower Cl concentrations, but higher DOC than the porewater at Zones 1 and 3. In contrast, the naphthenic acid concentrations in porewater from Zones 1 and 3 were slightly higher than those measured in Zone 5.

Concentrations of BTEX and F1 and F2 were below detection limits in all surface water and porewater samples collected. The absence of detectable concentrations of these compounds in porewater suggests that groundwater is unlikely to represent a significant natural source of these petroleum hydrocarbons. Naphthenic acids were detected in surface waters (0.1–0.7 mg L⁻¹) and porewater (0.1–2.4 mg L⁻¹), but were present at lower concentrations than have been measured in groundwater wells completed in the Basal McMurray Aquifers

Table 2

Statistical summary for selected dissolved metal (oid) concentrations measured from the Athabasca River and groundwater from Quaternary, Clearwater, McMurray and Devonian Formations from CEMA (2010a,b), Gibson et al. (2011) and Lemay (2002). Historical AR data was measured downstream of the mining operations at Old Fort, from 1994 to 2007 (Hebben, 2009). Number of samples analyzed is represented by n. Where available surface water quality guidelines (WQG) for the protection of freshwater aquatic life are included for comparison (AESRD, 2014).

Formation	As	B	Ba	Fe	Li	Mn	Mo	Se	Sr	V	U
	$\mu\text{g L}^{-1}$										
WQG for PAL	5 (total)	1500 (total)		300			73 (total)	1 (total)			15 (total)
Athabasca R-Historical											
Average	0.47	25	55	167	6.0	17	0.72	0.24	215	0.46	0.29
Maximum	1.1	60	268	1160	11	176	2.6	1.2	437	0.69	0.20
Minimum	0.10	5.0	33	5.0	2.0	0.50	0.10	0.05	105	0.23	0.50
N	34	34	34	156	34	138	32	20	34	20	34
Athabasca R-this study											
Average	0.90	9.2	52	226	3.7	19	0.80	0.12	196	0.26	0.24
Maximum	2.5	44	83	431	9.6	58	4.9	0.38	287	1.0	0.43
Minimum	< 0.4	< 50	19	82	< 1	1.1	< 0.5	< 0.4	106	< 0.1	< 0.1
N	10	13	10	11	11	11	11	9	11	11	11
Quaternary Fm.											
Average	0.89	567	62	1373	90	127	13	1.3	500	0.24	1.0
Maximum	4.0	1200	160	3900	230	400	57	4.3	2100	0.42	5.2
Minimum	0.25	33	17	76	19	4.3	0.34	0.13	89	0.07	0.005
N	8	8	10	6	8	8	9	7	10	2	6
Clearwater Fm.											
Average	8	2020	50	518	116	51	5.4	2.5	463	8.2	0.40
Maximum	20	3700	120	1100	160	194	10	6.2	1130	15	0.62
Minimum	1.6	720	10	190	20	0	0.73	0.3	40	1	0.10
N	4	5	7	5	5	8	5	3	7	2	3
McMurray Fm.											
Average	1.5	1390	113	4105	383	628	2.8	4.9	3825	1.1	0.28
Maximum	4.9	5900	280	18,000	1600	8770	5.6	23	35,000	1.4	0.80
Minimum	0.27	41	11	69	27	2	0.21	0.33	37	0.63	< dl
N	8	11	23	20	15	32	9	7	26	3	5
Devonian Fm.											
Average	2.9	2650	580	13,270	1050	80	50	< 60	4200	< 1	< 0.1
Maximum	4.5	4000	1300	27,000	1500	2	130	< 60	9800	< 1	< 0.1
Minimum	< 10	1200	< 200	< 5	300	15	< 6	< 60	790	< 1	< 0.1
N	9	4	9	4	4	9	8	8	8	4	4

(4–77 mg L⁻¹; CEMA, 2010 a,b) and Devonian Waterways Formation (1–64 mg L⁻¹; CEMA, 2010a,b).

4.2.3. Stable water isotopes

The stable isotope signatures of oxygen and hydrogen ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in groundwater can be used to identify mixing trends between locally-recharged, modern groundwater and other isotopically-distinct sources. Recharge from modern precipitation in the study area would be expected to have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures similar to the weighted mean of annual precipitation ($\delta^{18}\text{O} = -17.5\text{‰}$ and $\delta^2\text{H} = -142\text{‰}$, Baer et al., 2016; -17.7 and -135 ; Birks et al., 2002). Therefore, groundwater samples with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures that are depleted in the heavy isotopes relative to modern precipitation (more negative) indicate the presence of water recharged during colder climate periods (e.g. glaciogenic sources). Groundwater samples with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures that are more positive than modern precipitation can indicate recharge under warmer conditions, or connate water with an evaporative signature.

The low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and high salinities measured in Devonian groundwater springs in the study area, near the terminus of the Western Canada Sedimentary Basin (WCSB), have been attributed to dissolution of the Prairie Evaporite Formation by recharging glacial meltwater (Grasby and Chen, 2005). In contrast, high salinity waters found deeper in the WCSB often have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values closer to 0‰, attributed to seawater trapped during sedimentation (i.e. connate

waters) (Connolly et al., 1990a,b; Simpson, 1999). A compilation of regional groundwater isotope data (Table 3) reveals broadly overlapping ranges of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, but with a systematic depletion in average values with depth. Groundwaters generally plot along the LMWL (Fig. 6) with a trend towards more negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with depth (Table 3). Devonian formation waters had the most negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures, with a general trend of more positive $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures in formations located at shallower depths within the stratigraphic profile. There is some overlap between the McMurray Formation and Devonian $\delta^{18}\text{O}$ signatures, consistent with the idea that vertical pathways connect these hydrostratigraphic units (Cowie et al., 2015).

Lakes in the AOSR plot along a local evaporation line (LEL $\delta^2\text{H} = 5.2 \delta^{18}\text{O} - 50.6$; Gibson et al., 2015a) due to the systematic enrichment in ^{18}O that occurs during evaporation. The Athabasca River samples from the 2009 and 2010 sampling period tend to plot just below the LMWL along the LEL (Fig. 6) (Gibson et al., 2016). Where the saline porewater sample $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values plot relative to the GMWL and LEL can be used to identify evaporation or mixing of groundwaters recharged under different climate regimes.

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ values measured in the seeps from Zones 1 and 3, are more negative than the modern groundwater samples (Fig. 6, Table S1b, Table 3), consistent with mixing with glaciogenic groundwater. The mixing between river water and discharging groundwater is evident in the porewater profiles for $\delta^{18}\text{O}$ (Fig. 4) and in their distribution in the

Table 3

Statistics for available regional isotopic data for the Athabasca River (Gibson et al., 2011) and from groundwater from Quaternary, Clearwater, McMurray and Devonian Formations from CEMA (2010a), Gibson et al. (2011) and Lemay (2002). Number of samples analyzed is represented by n.

Formation	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	$\delta^{34}\text{S}$ (‰)	E^3H T.U.	^{14}C (pMC)	$\delta^{13}\text{C-DIC}$ (‰)	$\delta^{13}\text{C-DOC}$ (‰)	$\delta^{11}\text{B}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$ (‰)	$\delta^{37}\text{Cl}$ (‰)
<i>Athabasca River.</i>										
Average	-17.4	-137.35	6.8	10.7	87.2	-8.16	-26.98	17.64	0.7108	-0.17
Maximum	-15.9	-124.77	10.1	13.1	89.5	-5.56	-26.28	19.75	0.7112	0.50
Minimum	-19.4	-150.53	-2.8	7.9	85.9	-20.36	-27.64	15.54	0.7102	-3.2
N	18	18	13	9	6	15	9	2	14	12
<i>Quaternary Fm.</i>										
Average	-19.8	-152.55	29.5	3.5	64.9	-12.36	-28.01	-	0.7108	0.33
Maximum	-18.3	-141.41	29.5	5.3	74.8	-11.93	-27.98	-	0.7112	1.26
Minimum	-21.1	-161.75	29.5	1.6	55.0	-12.78	-28.04	-	0.7104	-0.57
N	11	11	1	2	2	2	2	-	2	9
<i>Clearwater Fm.</i>										
Average	-20.5	-158.86	-	-	-	4.05	-	-	-	-1.36
Maximum	-19.9	-154.13	-	-	-	4.05	-	-	-	-1.36
Minimum	-21.0	-161.69	-	-	-	4.05	-	-	-	-1.36
N	3	3	-	-	-	1	-	-	-	1
<i>McMurray Fm.</i>										
Average	-21.1	-164.93	25.5	1.0	13.8	-9.43	-26.67	29.8	0.7088	0.11
Maximum	-17.4	-140.32	36.3	7.4	83.5	10.41	-21.30	36.2	0.7100	0.81
Minimum	-23.1	-177.19	9.8	< 0.8	0.5	-21.70	-40.40	22.4	0.7080	-0.75
N	20	20	10	17	16	15	16	6	15	5
<i>Devonian Fm.</i>										
Average	-22.4	-171.48	30.1	0.5	6.7	9.22	-27.53	38	0.7085	0.37
Maximum	-21.9	-168.66	41.5	1.6	16.9	12.54	-27.00	44	0.7092	0.62
Minimum	-23.1	-176.39	18.7	< 0.8	0.7	4.24	-27.90	34	0.7082	0.15
N	5	5	2	5	3	3	3	3	3	3

delta-delta plot (Fig. 6). In the porewater profiles from all of the zones except for the porewater profile from Zone 2, have decreasing $\delta^{18}\text{O}$ values with depth (Fig. 3). The most negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were measured at the deepest porewater sample at Zone 3 (-22.7‰ and -174‰) and Zone 1 (-22.6‰ -161‰). These samples have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values similar to groundwater from the McMurray and Devonian formations (Fig. 6).

4.2.4. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate

The high SO_4 concentrations and positive $\delta^{34}\text{S}$ - SO_4 values in porewater from Zones 1, 3 and 5 are consistent with sulfate originating from the dissolution of evaporites (Fig. 7, Table S1b) (Mayer, 2005). Sulfur isotope data for anhydrite from the Prairie Evaporite Formation are between 18.2 and 22.6‰ (Sasaki and Krouse, 1969; Hitchon and Krouse, 1972; Horita et al., 1996). Similar values have been measured in McMurray Formation groundwaters and in some Devonian units (Table 3). The depth profiles for $\delta^{34}\text{S}$ values of sulfate in porewater from Zones 1, 3 and 5 have positive values at depth, where the concentration of sulfate is greatest. At shallower depths, the sulfate concentrations and $\delta^{34}\text{S}$ values are much lower, indicating that some of sulfate at these depths originating from sulfide oxidation (Fig. 7). At intermediate depths the sulfate concentrations are higher than the Athabasca River water, but with lower $\delta^{34}\text{S}$ values, indicating that these decreases cannot be due simply to mixing with river water. The sulfate concentrations and $\delta^{34}\text{S}$ values for porewater from the zones with no indication of saline groundwater discharge (Zones 2, 4, 6 and 7) were much lower than those measured in the high TDS porewater areas. Combining the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for sulfate can further constrain sources of sulfate (Fig. 7, bottom panel). The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate in Athabasca River water are consistent with sulfate originating from sulfide oxidation, or atmospheric deposition. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of the high TDS porewater sampled at depth in Zones 1, 3 and 5 are within the range expected for sulfate originating from the dissolution of evaporites. While very few of the porewater profiles had sulfate isotope data for multiple depths, the data for Zone 3 show the shift from high $\delta^{34}\text{S}$ and

$\delta^{18}\text{O}$ values in the deepest, highest-TDS porewater samples towards more negative $\delta^{34}\text{S}$ values in the shallower samples with lower TDS and lower sulfate concentrations (Fig. 3). The Zone 1 porewater samples all retained the evaporitic sulfate signatures even in the 0.75 m depth sample (Fig. 3), consistent with the presence of saline waters close to the water-sediment interface. Even though some of the shallow, low TDS porewater samples from Zones 2, 3, 4 and 6 plot within the range of atmospheric deposition, their $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ sulfate compositions could also be explained by mixing between Prairie Evaporite and river water, as noted also by Mayer (2005). The deepest samples from Zone 2, despite having low sulfate concentrations, also had $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ labelling consistent with an evaporite source.

4.2.5. $^{87}\text{Sr}/^{86}\text{Sr}$

Strontium isotopes provide additional evidence that the high salinity porewater present in the alluvial sediment has a Devonian origin. Strontium is known to pass from bedrock to soil into biologically-available solutions without measurable fractionation (i.e., retaining the same ratio of ^{87}Sr to ^{86}Sr) (Kawasaki et al., 2002). Strontium isotopic signatures can therefore be a sensitive fingerprint of the source of dissolved solids in groundwater, particularly in calcium-rich groundwater systems. Multiple sources of dissolved solids are evident in the porewater samples including older Devonian sedimentary rocks, intermediate-aged Cretaceous sedimentary rocks and Quaternary sediments.

The $^{87}\text{Sr}/^{86}\text{Sr}$ of porewater sampled from the 2009 and 2010 sampling campaigns indicate mixing of Quaternary with Devonian and Cretaceous sources of Sr at the various sample zones. The high Sr concentrations and range of $^{87}\text{Sr}/^{86}\text{Sr}$ values measured in the deepest porewater samples from Zones 1, 3 and 5 are consistent with Devonian sourced Sr ($^{87}\text{Sr}/^{86}\text{Sr} < 0.709$). Whereas the Athabasca River water and the shallower porewater samples are consistent with Quaternary sources of Sr. The ranges in $^{87}\text{Sr}/^{86}\text{Sr}$ values for porewater and groundwater are distinct from formation waters from downdip portions of the WCSB, which have higher Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ values (Connolly et al., 1990b; Gue et al., 2015). A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Cl

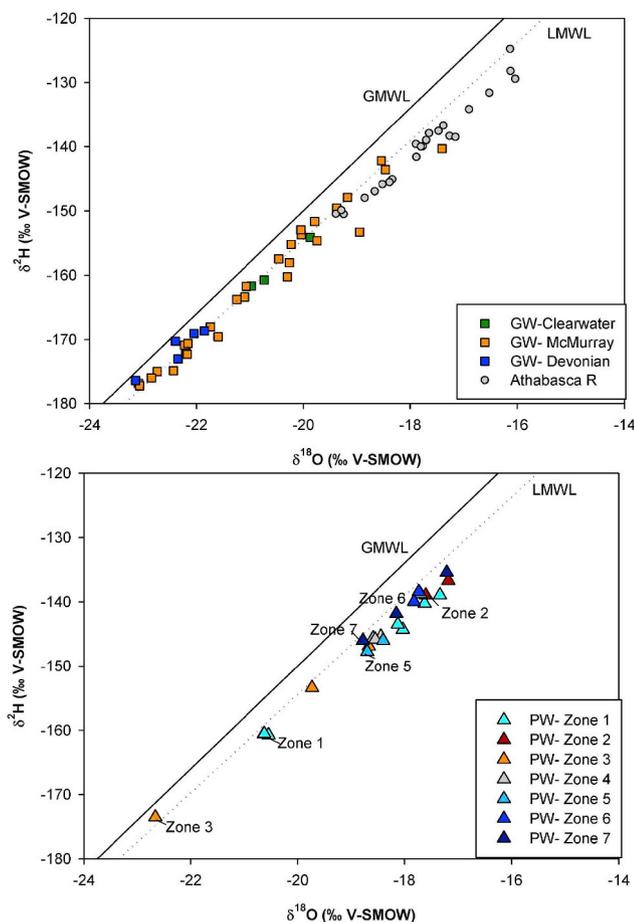


Fig. 6. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ plots for regional groundwater (GW) datasets and the Athabasca River (top panel) and for porewater (PW) sampled in the alluvial sediment during the seep sampling surveys (bottom panel). The Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL) for Edmonton are included for comparison. The deepest porewater sample from each zone is labelled for comparison.

(Fig. 8) shows general ranges of these sources with the porewater and river water data from the 2009 and 2010 surveys with the regional groundwater data. The plot reveals a shallow groundwater mixing zone dominated by strontium from Quaternary and Cretaceous sources, and a deeper mixing zone dominated by strontium derived from Cretaceous and Devonian sources. It is also significant to note that McMurray Formation groundwaters have strontium isotope signatures that are consistent with Devonian bedrock sources. A significant proportion of groundwater samples from the Clearwater and Lower Grand Rapids Formations also appear to contain significant proportions of groundwater derived from Devonian sources. Similar mixing patterns have been noted by Grobe et al. (2000) in the Munsterland Cretaceous Basin in Germany. In that case study, origin of saline groundwater in an evaporite-free carbonate basin was used to identify an allochthonous halite source outside of the basin. In the Southern Athabasca Oil Sands area, these results suggest that Cretaceous groundwater contains salinity derived from deeper Devonian evaporite deposits.

4.3. Hydrogeological controls on saline groundwater discharge

The quality and quantity of groundwater discharge to the Athabasca River along the survey reach will depend on the hydraulic gradients in formations adjacent to the river, the water quality in those aquifers, and the composition and permeability of alluvial sediments present at the river bed. The variations in geochemical and isotopic composition in the porewater sampled in the seven Zones targeted in this survey

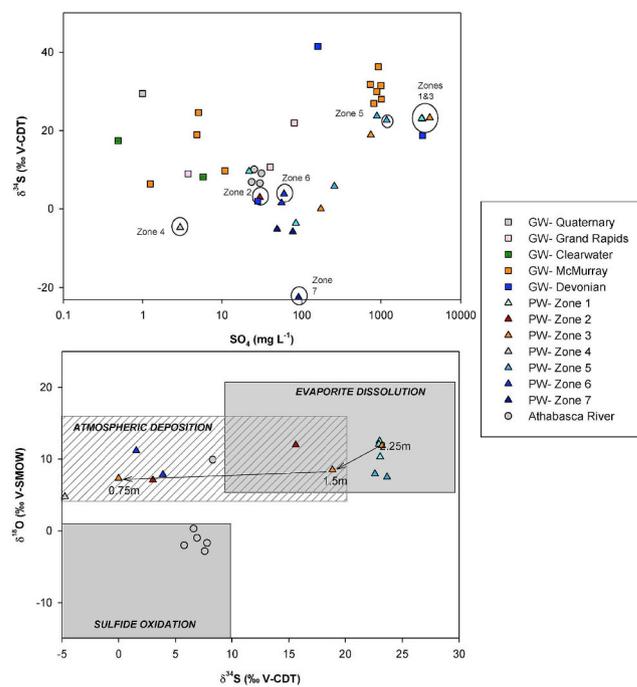


Fig. 7. $\delta^{34}\text{S}$ and sulfate concentration results for the alluvial porewater from the 2010 sampling campaign, with available regional groundwater data (CEMA, 2010a; Gibson et al., 2011; Integrated Sustainability, 2013; and Lemay, 2002) included for comparison (top panel). Fewer samples had both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ measurements for sulfate, but these are shown with typical ranges of sulfate originating from evaporite dissolution, atmospheric deposition, and sulfide oxidation (bottom panel) (Mayer, 2005). Sampling depths are shown beside the symbols for the Zone 3 samples shown in the bottom panel.

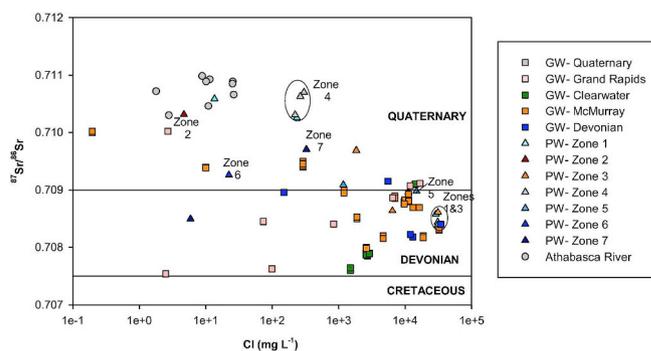


Fig. 8. The $^{87}\text{Sr}/^{86}\text{Sr}$ values for the alluvial porewater from the 2010 sampling campaign, with data available regional groundwater data (CEMA, 2010a,b; Gibson et al., 2011; Lemay, 2002) included for comparison. Typical ranges for Quaternary, Devonian and Cretaceous formations are shown for comparison.

indicate differences in the degree of saline groundwater discharge that reflect differences in hydrogeochemical setting along this reach of the Athabasca River (Fig. 9).

Some insight into the potential origin of the saline groundwater present in alluvial sediment can be gained from looking at variations in the formation water characteristics across the region. The distribution of TDS and Cl in the McMurray Formation (Fig. 9c and d) indicate Cl concentrations of less than 1000 mg L⁻¹ near Zones 4, 5, 6 and 7, but concentrations ranging from 10,000 mg L⁻¹ to 100,000 mg L⁻¹ adjacent to Zones 1–3 (Fig. 9d). Note that significant local variability in TDS and chloride concentrations have also been noted (Cowie, 2013; Sproule, 1974), with the highest salinity McMurray Formation groundwaters (up to 270,000 mg L⁻¹) occurring at locations overlying the partial dissolution edge of the Prairie Evaporite Formation near

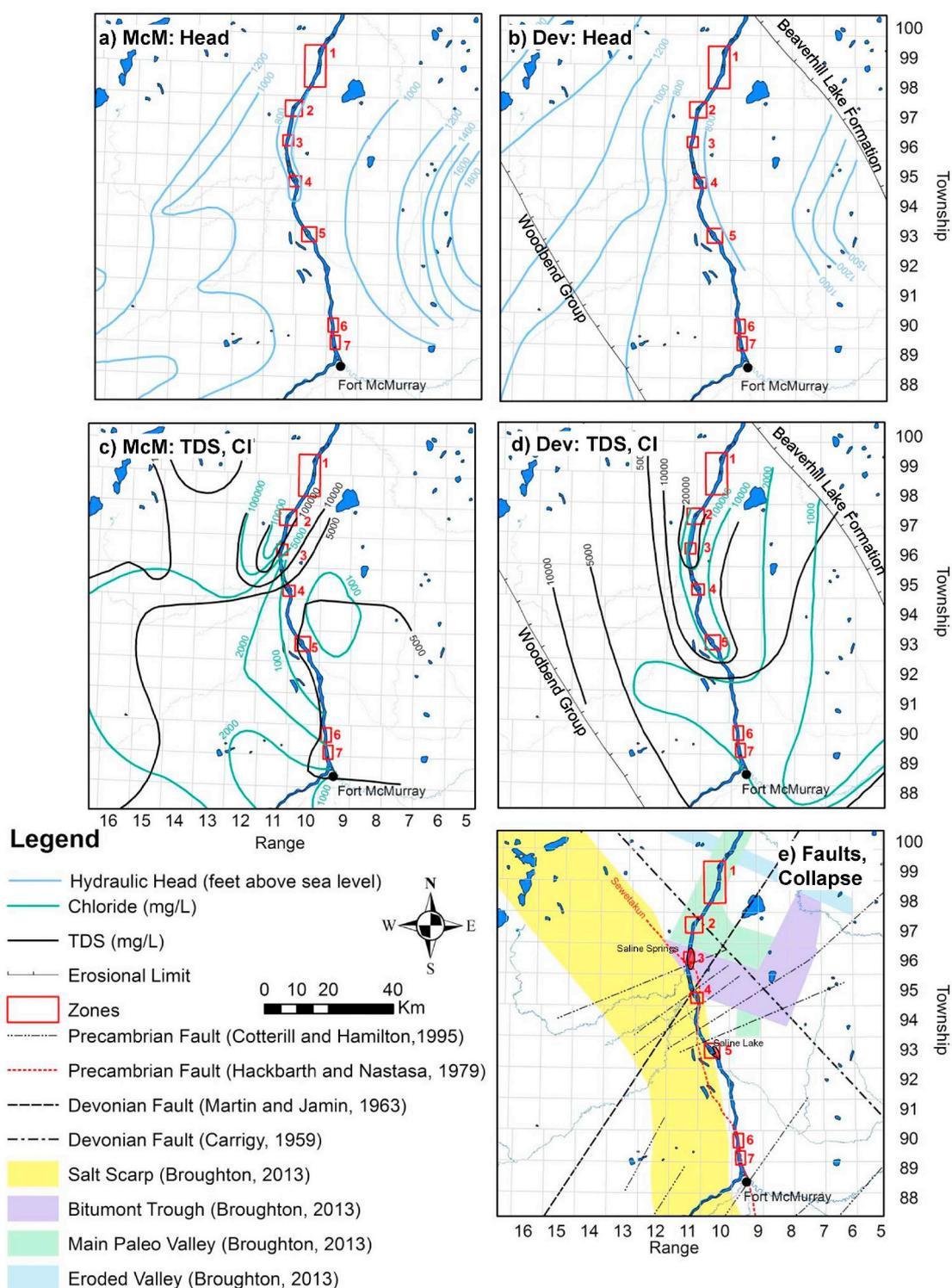


Fig. 9. Porewater sampling zones (red boxes) shown with freshwater hydraulic head and TDS and CL distributions in the McMurray Formation (a and c) and in the Devonian Beaverhill Lake Formation (b and d) (modified from Hackbarth and Nastasa, 1979). The location of Precambrian and Devonian faults, as well as the extent of the Prairie Evaporite dissolution scarp and collapse features are shown with the location of La Saline Lake and locations where saline springs have been observed (Mahood et al., 2012; Gue et al., 2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Zone 3. The dissolution edge is thought to be an area with increased vertical connectivity between Devonian formations and the overlying units possibly because of the evaporite karst dissolution and sub-Cretaceous faulting and/or sinkhole structures (Broughton, 2013; Cowie et al., 2015; Mahood et al., 2012). Mahood et al. (2012) identified a reach of the river with numerous saline springs (located at about Township 11, Range 96) which roughly coincides with Zone 3 of this

survey.

The geochemical and isotopic composition of porewater in the alluvial sediments in Zones 1, 3 and 5 are consistent with the discharge of saline McMurray Formation or Devonian formation groundwaters. The presence of ^3H in Zone 5, along with lower concentrations of most solutes, could indicate greater mixing of saline groundwater with river water at this location where the alluvial sediment consisted of large

cobbles. Limited hydraulic heads in the McMurray Formation and the Upper Devonian (Beaverhill Lake Formation) indicate flow towards the Athabasca River in these units, with slightly steeper horizontal head gradients in the Upper Devonian aquifers in the northern reaches of the river (e.g. Zones 1–4) than in the more southern reaches of the river (Zone 5–7) (Fig. 9b). More importantly the TDS and Cl concentrations in the McMurray Formation and Beaverhill Lake Formation are much higher along the northern reach of the river in the vicinity of Zones 1–5. The absence of saline groundwater in the alluvial sediments at Zones 2 and 4 may be due to the hydraulic properties of the formation or alluvial sediment in the area, or could indicate greater variability in the salinity and head distributions than the regional datasets have captured (Fig. 9 a–d), a feature noted also by Cowie (2013). Zones 2 and 3 are both located along reaches of the river where the McMurray Formation outcrops, but Zone 3 is located much nearer the edge of the dissolution scarp, as well as Devonian collapse features (Fig. 9e). Zone 3 is located much nearer areas of increased vertical connectivity with deeper Devonian saline groundwater.

The most extensive EM terrain anomaly detected in the river surveys occurred in Zone 1 (Fig. 1) starting where the Athabasca River is incised into the Devonian Waterways Formation. This unit is generally considered a barrier to flow, but karst features have been suggested to explain some of the vertical connectivity in areas where the underlying Prairie Evaporite Formation has been eroded (Cowie et al., 2015). Structural deformation and subtle evidence of paleokarst karst have been observed in outcrops of the Waterways Formation along the Athabasca River (Schneider and Grobe, 2014). A McMurray Formation sample from a groundwater well located west of the Athabasca River at Township 99–100 Range 10W4, near the Zone 1 river sampling location, had TDS of 90,000 mg L⁻¹ (Cowie et al., 2015). This area is east of the mapped Prairie Evaporite dissolution edge but overlying large sinkholes in the Devonian surface (Grobe et al., 2000; Broughton, 2013) and consistent with dissolution features providing vertical pathways between the Devonian and shallower formations.

The presence of major structural controls not only influences the pattern of McMurray Formation groundwater compositions (Cowie et al., 2015), but also the location of saline springs located on the river banks (Gue et al., 2015) and in Oxbow Lakes (Ozoray et al., 1980). These saline springs are located along reaches of the river where there are geomorphic features that are consistent with there being underlying structural controls.

Previous studies (Grasby and Chen, 2005; Gue et al., 2015) have shown that saline groundwater springs discharging from outcrops along the banks of the Athabasca are consistent with Devonian formations, and used their geochemical and isotopic composition to develop conceptual models of groundwater evolution in the region. These studies have documented the presence of isolated natural saline groundwater springs on the banks of the river, but the potential magnitude of the contribution of these springs to the water quality of the river is difficult to extrapolate. This study establishes that vertical connectivity to underlying Devonian units is expressed not only as springs on the banks of the rivers, but also as broad zones of saline seepage, and that extended reaches of the river show evidence of Devonian formation waters in the alluvial sediment. Considerable efforts are being made towards developing monitoring programs that can identify potential impacts to aquatic ecosystems from oil sands development, and these require understanding of natural sources of salinity and organics that can enter aquatic ecosystems either through groundwater surface water interactions, or via bank erosion of bitumen-rich sediment or sedimentary rock (e.g. Lower Athabasca Water Quality Monitoring Plan Phase 1; Environment Canada, 2011). While regional monitoring plans have generally taken into consideration the location of oil sands deposits, there is also a need to consider the influence of both saline springs and broader river bed seepage on water quality loads, as a prerequisite to identifying anthropogenic impacts.

5. Summary

Previous studies have documented the geochemistry of groundwater and saline springs along the Athabasca River (Ozoray, 1974; Hackbarth and Nastasa, 1979; Ozoray et al., 1980; Lemay 2002; Grasby and Chen, 2005; CEMA, 2010a,b; Stewart and Lemay 2011; Wells and Price, 2015; Gue et al., 2015); however, few studies have described the characteristics and likely origin of seepage through the river-bed hyporheic zone. The survey results presented here complement the description of selected tracers presented in Gibson et al. (2013) providing additional information on the geochemical and isotopic signatures of porewater in the alluvial sediment beneath the Athabasca River and comparisons with regional data. All of the porewater sampling locations show some degree of mixing with river water, but the distribution of field parameter, geochemical and isotopic parameters indicate a thick hyporheic zone and no evidence of discharging saline groundwater at Zones 2, 4, 6 and 7, and a thin hyporheic zone and evidence of saline groundwater close to the water-sediment interface at Zones 1, 3 and 5. At Zones 1, 3 and 5 the depth profiles of temperature, specific conductance and solutes show the presence of a high salinity groundwater near the water-sediment interface consistent with discharging groundwater becoming more dilute as it ascends and mixes with river water within the hyporheic zone. The Zone 2 DPP were installed in an area where the EM survey did not show elevated terrain conductivity, and the porewater profiles did not include increases in solute concentrations with depth. The porewater profiles from Zones 4, 6 and 7 were similarly subdued.

The geochemical and isotopic composition of the most saline porewater (from the deepest DPP) samples from Zones 1, 3 and 5 are consistent with groundwater from Devonian formations. The Na–Cl composition, and negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are consistent with dissolution of the Prairie Evaporite Formation by infiltrating glacial recharge. The Devonian source for sulfate and strontium is supported by the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ composition of sulfate and the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions, as well as the low modern ^{14}C contents.

Evaporite dissolution resulting from glaciogenic water injection is postulated as the common origin of saline waters in local formation waters, aquifers, springs and in porewater present in the alluvial sediments and hyporheic zone of the river in the North Athabasca Oil Sands Region. The relative contribution of these natural saline groundwater inputs to the overall salt loading of the reach of the Athabasca River adjacent to oil sands activities is not clear. Numerical groundwater simulations conducted to identify potential long-term cumulative effects of oil sands mining predict changes in hydraulic head in the McMurray Formation due to dewatering and disposal in this formation that can result in increases and decreases of groundwater discharge to the Athabasca River (e.g. Deer Creek Energy Limited, 2006), so there is also potential for mining activities to change the input of natural saline groundwater seepage to the Athabasca River and its tributaries over the duration of surface mining operations. Better understanding of the influence of both saline springs and broader river bed seepage on Athabasca River water quality is needed to understand the current natural salinity loading to the river, as well as for designing long-term water management and reclamation strategies.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2018.09.005>.

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