Quantifying saline groundwater seepage to surface waters in the Athabasca oil sands region

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ABSTRACT

Western Canadian oil sands contain over 170 billion barrels of proven unconventional petroleum reserves currently extracted at 1.8 million barrels per day by either surface mining, or by *in situ* techniques that require subsurface injection of steam and hydrocarbon solvents. Natural high-salinity springs are known to add water and entrained inorganic and organic constituents to the Athabasca River and its tributaries in the region of ongoing bitumen production. However, the magnitude and synoptic distribution of these saline inputs has remained unquantified. Here, a chloride mass balance is used to estimate saline groundwater discharge to the Athabasca River from 1987 to 2010. Results show that the highest saline water discharge rate to the Athabasca River occurs between Ft. McMurray and the Peace-Athabasca Delta, supported by subcrop exposure of lower Cretaceous- and Devonian-aged formations bearing saline waters. Further, the input of saline groundwater is found to be an important control on the chemistry of the lower Athabasca River, despite comprising 10^{-1} to 3% of the Athabasca River's discharge. The flux of natural saline groundwater entering the Athabasca does not appear to have increased or decreased from 1987 to 2010. The origin of seep salinity is interpreted as relict subglacial meltwater that has dissolved Devonian-aged evaporites, supported by saline Na-Cl type waters with low $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios relative to modern precipitation. The magnitude of groundwater discharge and its impact on the Athabasca River's chemistry in the area of ongoing bitumen development warrants the incorporation of natural groundwater seepages into surface water quality monitoring networks.

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1. Introduction

Canada contains 170 billion barrels (roughly 13%) of the world's proven petroleum reserves. Over 95% of Canada's petroleum reserves are natural bitumen deposits located in western Canada. This bitumen is distinguished from conventional crude oil by its high viscosity (>10,000 cP), high density (<10° API), elevated concentrations of S and some metals such as Ni and V due to partial biodegradation (Gosselin et al., 2010), and low energy recovery on energy invested (EROEI) ratios when produced (2:1–6:1; Murphy and Hall, 2010). The largest bitumen deposit is in the Athabasca oil sands region (AOSR). The deposit is currently used to produce ∼1.8 million barrels per day through either (1) surface mining projects adjacent to the Athabasca River, or by (2) *in situ* extraction techniques that inject steam and hydrocarbon-based solvents where bitumen is deeper than approximately 50 m. The two techniques currently account for a similar amount of production in the AOSR. However, over 80% of recoverable bitumen is too deep for surface mining; therefore, *in situ* development is anticipated to overtake surface mining as the leading production mode.

Policy of the Province of Alberta stipulates that no process-affected water may discharge into the natural environment until waters can be reclaimed, referring to waters used during the extraction and refining of petroleum products that have not been reclaimed (detoxified). Process-affected waters from surface mining are currently retained in large exposed ponds, and contain roughly 0.7 km³ of tailings in 130 km² of constructed ponds (Gosselin et al., 2010). However, past instances of tailings pond dyke seepage that was found to be acutely toxic to some aquatic species (Hrudey, 1975), and ongoing fatalities to migratory birds (Timoney and Ronconi, 2010) may provoke disposing process-affected waters into subsurface reservoirs as an alternative to exposed tailings ponds. Successfully containing *in situ* injections and process-affected waters at depth requires that these fluids remain in the subsurface. A thorough evaluation of the feasibility of such approaches must rely on a sound understanding of subsurface–surface hydrologic connections. However, the absence of a continuous regional aquitard and the presence of saline springs emanating from bitumen-bearing strata and formations targeted

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for wastewater disposal (Bachu and Underschultz, 1993; Barson et al., 2001; Gibson et al., 2011) raises doubts over just how long injected fluids will be sequestered at depth.

Despite knowledge of these subsurface connections (e.g. springs and seeps; Ozoray, 1974; Grasby and Chen, 2005; Gibson et al., 2011; Stewart and Lemay, 2011), no study has yet quantitatively assessed the flux from the bitumen-bearing McMurray formation or deeper Devonian-aged carbonates into surface waters. Here, a first approximation of the combined flux of groundwater from lower Cretaceous- and Devonian-aged formations into surface waters along a synoptic profile of the Athabasca River is calculated using Cl$^-$ data from the Long-Term River Network and a new dataset of monthly δ^{18}O and δ^2H values in Athabasca River waters.

2. Study area

The Athabasca oil sands region (AOSR) is located within the Boreal forest ecozone in an area with sporadic permafrost (<10%). The Athabasca River sub-basin is situated at the southern extent of the northward draining Mackenzie basin, and is one of two major headwater tributaries of the Mackenzie River system. Athabasca River headwaters are located in the Rocky Mountains; the river flows NE toward the city of Fort McMurray then flows north into Lake Athabasca at the Peace-Athabasca Delta (Fig. 1). No dams are constructed along the Athabasca River, and consumptive divergences of water are small due to the lack of extensive agricultural development in the northern portion of the basin. However, the Athabasca River is the primary source of water for oil sands mines north of the city of Fort McMurray (56.7°N, 117.4°W).

Mean monthly temperature for Fort McMurray is −19 °C for January and 17 °C for July, with a mean annual temperature near 0 °C. Total annual precipitation is close to 450 mm, with 60% falling during the warmer months of May through August. Relief is subdued with the exception of large river incisions. Extensive ombrogenous bogs (precipitation-fed) and geogenous fens (continual input of shallow groundwater) control hydrology and infiltration at the surface (Vitt et al., 1994). Beneath surface peatlands and mineral soil uplands are sequences of glacio-fluvial, glacio-lacustrine and diamict sediments exceeding 300 m thickness in certain areas that overlie extensive paleochannels.

Regolith hydrostratigraphy is made up of sediments of varying levels of consolidation and permeability. Cretaceous aged rocks subcrop in northeastern Alberta, notably the McMurray Formation that is a complex set of shales and sandstones of fluvial, floodplain and estuarine origin that now contains bitumen (Mossop, 1980), saline groundwater (10–35 g L^{-1}) and some relatively dilute brines (>35 g L^{-1}). The McMurray Formation and other Cretaceous-aged strata lie sub-parallel to the land surface and unconformably overlie southwesterly dipping Paleozoic carbonates and evaporite horizons containing halite, sylvite, carnallite and gypsum group minerals.

Isopach estimations for ice sheet thickness during the last glacial maximum suggest that more than 4 km of ice resided above the study area (Bense and Person, 2008). Previous work suggests that large quantities of pressurized subglacial water recharged aquifers during the Pleistocene from geochemical (Grasby et al., 2000; Clark et al., 2000) and hydrogeologic modelling evidence (Lemieux et al., 2008). In northeastern Alberta, Paleozoic carbonates acted as permeable conduits, likely receiving large amounts of subglacial meltwater in comparison to endogenous rocks of the Canadian Shield to the NE, and deformable Mesozoic-aged rocks to the SW (Grasby and Chen, 2005). Pleistocene input of subglacial waters changed the groundwater advection pathway towards the SW, a reversal from both the modern and long-term geologic flow paths (Anfort et al., 2001; Grasby and Chen, 2005; Lemieux et al., 2008). Grasby and Chen (2005) also review collapse breccia distribution and describe geologic evidence for dissolution of the Prairie Evaporite formation by subglacial meltwaters during the Pleistocene. Evaporite dissolution may have created fractures in carbonates that acted as important macropore conduits for reflux of subglacial waters towards the surface. The Na-Cl end member waters are known to occur as seeps along the Clearwater and Athabasca Rivers (Ozoray, 1974).
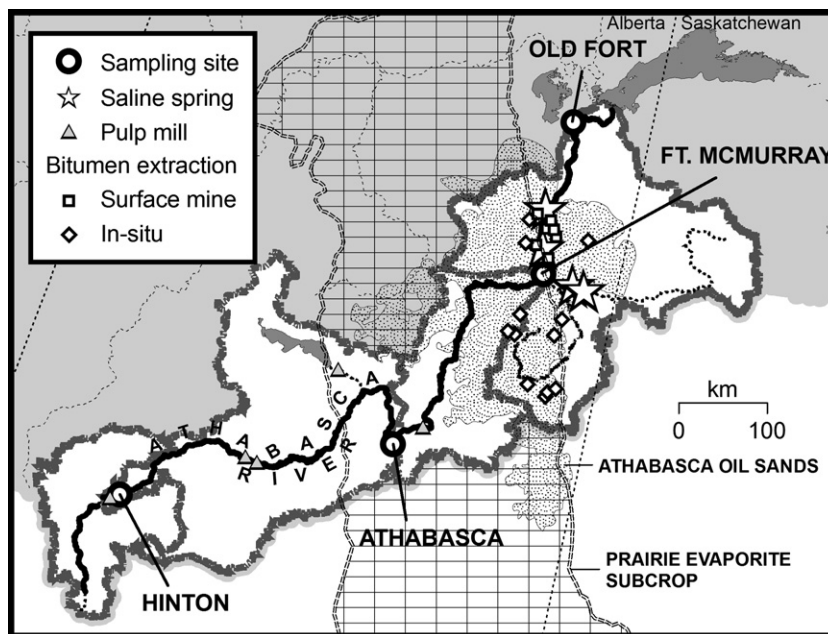

Fig. 1. Sampling sites, hydrographic, geologic and industrial developments in the Athabasca River basin. Locations of discharge measurement and chemistry sampling stations are shown as white circles. Industrial developments such as pulp mills (gray triangles), oil sands mining (white squares), and oil sands *in situ* production sites (white diamonds) are shown. Known locations of saline springs are marked as white stars. Drainage basins for each reach of the river are marked by a thick gray outline. The extent of the Athabasca oil sands deposit (stipple) and approximate subcrop boundary of the Prairie Evaporite group (cross-hatch; extent from Grasby and Chen, 2005) are delineated. Large lakes are delineated in dark gray.

3. Dataset

Physical and chemical data for both the Athabasca River and aquifers bearing saline fluids are utilized in this study. Athabasca River discharge and river levels are obtained from the Water Survey of Canada's database (Environment Canada). Monthly chemistry data for the Athabasca River is collected from the Long-Term River Network (LTRN; Alberta Environment). This chemistry database contains over 750 monthly analyses of Cl^- concentrations obtained from four stations along the Athabasca River between 1987 and 2010 (Table 1). The discharge and chemistry datasets are compiled at monthly intervals. In addition, a new dataset of monthly $^{18}O/^{16}O$ and $^2H/^1H$ ratios in Athabasca River waters have been established for the time period of 2005–2007 at four stations along the Athabasca River.

Two geographically-separate datasets were used to determine Cl^- concentrations in lower Cretaceous- and Devonian-aged formation waters. For the upper Athabasca River, stable isotope and Cl^- data for deep brine samples are compiled from data reported by Connolly et al. (1990) and Simpson (1999). For the Athabasca oil sands region, Cl^- concentrations and $\delta^{18}O$ and δ^2H values for well and seepage samples from Cretaceous- and Devonian-aged formations are compiled from the work of Ozoray (1974), Lemay (2002), Grasby and Chen (2005), Fennell (2010) and Gibson et al. (2011).

Chloride is a non-reactive, hydrophilic, and monovalent anion that is a constituent of soluble minerals such as halite, sylvite and carnallite. Chloride's conservative nature makes it a suitable tracer of the water it is dissolved in. Groundwater in the AOSR within Devonian- and some Cretaceous-aged aquifers have significantly elevated Cl^- concentrations (10^3–10^4 mg L^{-1}; Lemay, 2002; Fennell, 2010; Gibson et al., 2011) relative to regional precipitation (<1 mg L^{-1}; Munger and Eisenreich, 1983) and to surface waters (<10^0–10^2 mg L^{-1}; Halsey et al., 1997; Prepas et al., 2001; Scott et al., 2010) except where saline groundwater seepage is evident (10^3–10^4 mg L^{-1}; Stewart and Lemay, 2011). Saline water inputs to the Athabasca River were estimated by capitalizing on the one to three order of magnitude differences in Cl^- concentrations between surface-waters, and Cretaceous- and Devonian-aged formation waters using a mixing model described below.

4. Mass balance calculation

Along each reach of the river, the difference between the upstream (Q_{UP}) and downstream (Q_{DOWN}) discharge can be calculated as the sum of runoff and shallow groundwater input (R), and net groundwater input from lower aquifers (G), as represented by the following equation:

$$Q_{DOWN} = Q_{UP} + R + G \tag{1}$$

Direct precipitation is assumed to be small in comparison to basin runoff (mean annual precipitation for the Athabasca River basin is between 400 and 600 mm, corresponding to <1% of river discharge). Likewise, evaporation from the river itself is presumed to be negligible in comparison to other fluxes for this basin (mean annual evaporation ranges from 390 to 460 mm; Bennett et al., 2008). Integrating tracer concentrations (C) to each flux, a mass balance for Cl^- is developed between two stations along a river as represented by Eq. (2) and Fig. 2.

$$Q_{DOWN}(C_{DOWN}) = Q_{UP}(C_{UP}) + R(C_R) + G(C_G) \tag{2}$$

The net contribution of saline groundwater is estimated by solving Eq. systems (1) and (2).

$$G = \frac{Q_{DOWN}(C_{DOWN} - C_R) - Q_{UP}(C_{UP} - C_R)}{C_G - C_R} \tag{3}$$

All values in the right hand side of Eq. (3) are measured at a monthly time step for the Athabasca River, with the exception of the concentration of runoff prior to groundwater input (C_R), and the concentration of saline groundwater prior to mixing with modern waters (C_G). Surface waters in continental regions have very few sources of Cl^- aside from groundwater input, which often entrains Cl^- from water–rock interactions. Potential anthropogenic Cl^- sources to the Athabasca River include inputs from pulp mills and municipalities in upstream reaches of the Athabasca River, use of minerals (halite, sylvite) and solutions ($MgCl_2$, $CaCl_2$) for road de-icing, and potential seepage from oil sands developments and tailings in the lowermost (northern) reach. Data for de-icing (Municipality of Wood Buffalo, pers. comm.) for the lowermost reach of the Athabasca are used to calculate appropriate concentrations for C_R, by assuming surface water inflows and shallow groundwater make up most of the observed discharge increase between Ft. McMurray and Old Fort. For 2004–2009, an average of 34,000 L of a 30 wt.% $CaCl_2$ solution and 3300 tonnes of road salt were applied as road de-icing agents in Ft. McMurray. Dividing these Cl^- loads by the change in discharge between Ft. McMurray and Old Fort for winter months (November through March), a Cl^- concentration for runoff (C_R) is calculated, thereby removing this influence on the calculation of saline water inputs. Eq. (3) is reiterated using these C_R values, that range from 0.5 to 15 mg L^{-1}, with an average of 3.9 mg L^{-1} (Table 2), to calculate saline water inputs to the lower Athabasca River.

It is very difficult, if not impossible, to use a single value to represent the chloride concentration of groundwater (C_G) due to the broad range of concentration variability (Table 2). For the purpose of mathematical operations, a range of values for C_G spanning the 80th and 20th percentiles of Cl^- concentrations from well samples is proposed. For upstream stations, concentrations for brines sampled near Edmonton ($n = 43$; Connolly et al., 1990) produce 20th and 80th percentile concentrations of 21,000 mg L^{-1} and 66,000 mg L^{-1} (Fig. 3a). For the lowermost reach between Fort McMurray and Old Fort, C_G values are obtained from measurements of Cl^- in Cretaceous- and Devonian-aged formation waters ($n = 38$; Lemay, 2002; Fennell, 2010; Gibson et al., 2011). The 20th and 80th percentile of lower Cretaceous and Devonian groundwater Cl^- concentrations (C_G) are 2200 mg L^{-1} and

Table 1
Water sampling and discharge measurement locations along the Athabasca River.

| Location	Gauge I.D.	Latitude	Longitude	Altitude (m.a.s.l.)	Synoptic distance downstream (km)	Drainage area (km²)	Mean Q (m³ s⁻¹)	Mean (Cl⁻) (mg L⁻¹)
Hinton	07AD0110	53.42	−117.57	974	150	9780	164	0.9 ($1\sigma = 0.8$; $n = 116$)
Town of Athabasca	07BE0010	54.72	−113.29	530	640	73500	360	2.9 ($1\sigma = 1.8$; $n = 260$)
Ft. McMurray	07CC0030	56.78	−111.40	240	940	131000	400	4.3 ($1\sigma = 2.4$; $n = 152$)
Old Fort	07DD0010/ 07DD0105	58.37	−111.52	211	1150	156000	613	20.5 ($1\sigma = 14.0$; $n = 230$)
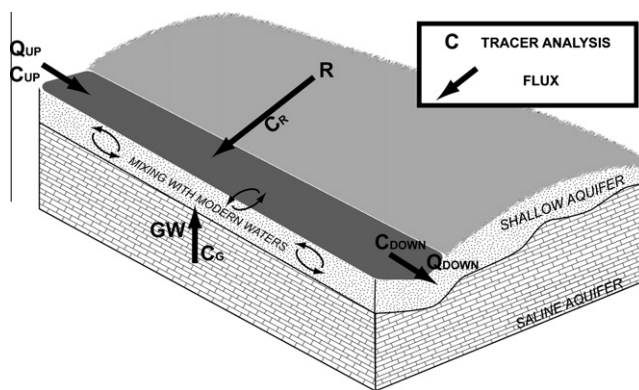
Fig. 2. Schematic of a hydrologic and chemical mass balance for two sampling stations along a river. Water transport fluxes and concentrations are represented by Q and C, respectively. Subscripts UP and DOWN represent an upstream and downstream stations where discharge and the concentration of a conservative tracer are measured. Runoff and net saline groundwater inputs between the upstream and downstream measuring stations are represented by the symbols R and GW, respectively.

15,000 mg L^{-1} for this lower reach. Distinct isotopic signatures in Cretaceous- and Devonian-aged formations for upstream and downstream reaches indicate that waters within these similarly aged formations have very different sources (Fig. 3b) and support the use of different Cl$^-$ concentrations for these two regions (Table 2).

Calculation uncertainty may also arise from the inexact measurement of river discharge (±20%), especially for data collected at Old Fort. For Old Fort (07DD011), only daily river elevation data is available for 1975 to present. Fortunately, river discharge was measured between 1977 and 1984 at another station only slightly downstream of Old Fort (07DD001; drainage area 0.6% larger than 07DD011). A second-order fit between discharge at 07DD001 and river level at 07DD011 allows a calculation of discharge from river level values, and captures 1975–1984 discharges within $2\sigma < 40\%$. Discharge is computed from Old Fort river level data applying this relationship for 1987 to the 2010 ($Q = 97.5649 L^2 - 40893.1 L + 4285066$; where Q is discharge in m^3 s^{-1} and L is river level in m.a.s.l.).

The upper Athabasca River flows over the Paskapoo Formation where Cl$^-$ forms a minor component of the total dissolved solids (Grasby et al., 2000; HCL, 2004). Chloride concentrations in 944 shallow groundwater wells located in the upper bedrock aquifers ranged from below detection limits to 463 mg L^{-1}, with 95% of the wells having Cl$^-$ concentrations <50 mg L^{-1} (HCL, 2004). 75% of the groundwater samples have Cl$^-$ concentrations less than 10 mg L^{-1} (median = 2 mg L^{-1}). The low Cl$^-$ concentrations in upper aquifers supports lumping shallow groundwater, interflow, and direct precipitation fluxes into single runoff (R) and runoff Cl$^-$ concentration (C_R) parameters in the mixing model.

5. Results

Chloride (Fig. 3a) and $\delta^{18}O$ values (Fig. 3b) vary between 10^{-1} and 10^6 mg L^{-1} for Cl$^-$, and -25.1 to $+29.6\%$ for $\delta^{18}O$ values in Alberta's surface- and ground-waters. In the Athabasca River, Cl$^-$ concentrations increase progressively downstream, with long-term (1987–2010) average Cl$^-$ concentrations of 0.9, 2.9, 4.3 and 20.5 mg L^{-1} at Hinton, Athabasca, Ft. McMurray and Old Fort, respectively (Figs. 1 and 3a). The $\delta^{18}O$ values in Athabasca River waters increase downstream, with discharge-weighted values of -20.2%, -18.7%, -17.9% and -17.7% moving downstream along the four sampling stations. Deuterium excess ($\delta^2H-8\delta^{18}O$; Dansg-

aard, 1964) values decrease from 7.7‰, 4.3‰, 1.9‰ to 1.3‰ at each of the four stations moving downstream. This change in d-excess could reflect either inputs to the Athabasca River from modern surface waters that have undergone losses through evaporation, or/also inputs of evapoconcentrated brines bearing deuterium excess values as low as -130% (Connolly et al., 1990; Simpson, 1999). The input of evapoconcentrated brines is not thought to significantly modify deuterium excess values, as large increases in Athabasca River Cl$^-$ concentrations are not observed upstream of Fort McMurray, as would be the case if brines were the source of the deuterium excess decrease along these reaches.

$\delta^{18}O$ values in Cretaceous and Devonian formation waters range from -25% to $+30\%$, with deuterium excess values ranging from 10‰ to -130%. $\delta^{18}O$ values in these formations in the northeastern portion of the Athabasca River Basin range from -17% to -25% (average -19%; light gray box in Fig. 3), whereas groundwaters in formations of a similar geologic age located 400–600 km to the SE range from -15% to $+30\%$ (average of 4.3‰; stipple box in Fig. 3). These formation waters have been separated based upon distinct $\delta^{18}O$ values and by location (400–600 km between study sites). Distinct Cl$^-$ concentrations are applied for the saline groundwater end member in the mass balance calculation based on distinct isotopic data and well locations. Fig. 4 presents major ion geochemistry in a Piper (1944) diagram for the Athabasca River, Cretaceous and Devonian formation waters, and oil sands tailings. Chemical data for the lowermost reach of the Athabasca (at Old Fort) shows a clear mixing trend towards a Na-Cl type water, such as Cretaceous and Devonian formation waters, supporting use of the river-groundwater chemical mass balance used here.

The discharge of saline brines (G) has been calculated for each of the three reaches of the Athabasca River (Fig. 5). For the two reaches located between Hinton and Fort McMurray, the depth of Devonian-aged formations (>3 km; Simpson, 1999; Machel et al., 2000) and the presence of overlying aquitards suggest that there is little opportunity for significant saline groundwater discharge to the surface in the absence of faulting (Grasby and Lepitzki, 2002). Inputs of water from pulp mills, municipal discharges or shallow aquifers likely account for the small increases in Cl$^-$ between Hinton and the Town of Athabasca, and between the Town of Athabasca and Ft. McMurray. The calculated saline discharge values are treated as "control reaches," and are used to gauge noise in Cl$^-$ data in the Athabasca River associated with the Quaternary aquifer and anthropogenic discharges.

Calculation results for saline groundwater input along three reaches of the Athabasca River are shown in Fig. 5 at a monthly time step. The lowermost reach of the Athabasca River from Ft. McMurray to Old Fort receives the greatest flux of saline groundwater, with an average long term discharge between 500 and 3400 L s^{-1} (10^{-1} to 3%; Table 2). The range in estimates derives primarily from uncertainty in the Cl$^-$ concentration of the saline groundwater end member, but also from potential seasonality in saline groundwater discharges. The lower reach of the Athabasca River receives much more saline water than upper reaches and is best connected to lower Cretaceous- and Devonian-aged formations, likely as a result of subcrop exposure of these formations by the incision of the Athabasca, Clearwater and Christina Rivers. Each saline groundwater flux obtained is shown as a percentage of the monthly average discharge (Fig. 5a). Examination of the reach of the Athabasca River between Fort McMurray and Old Fort suggests that 10^{-1} to 3% of the Athabasca River's discharge is sourced from saline groundwater. A running mean of calculation outputs shows that average saline water discharges to the Athabasca River have remained near constant since 1987 for all reaches.

A new dataset of stable isotope ratios of O and H are reported for monthly water samples collected at four sampling stations

Table 2
Calculation inputs for saline water discharge to the Athabasca River. C_G ranges are the 20th and 80th percentile scenarios.

Reach	Number of monthly calculations	Average (Cl⁻): C_G (mg L⁻¹)	Average (Cl⁻): C_R (mg L⁻¹)	Average saline groundwater input (L s⁻¹)
1: Hinton to Athabasca	117	48000 (21000–66000)	0.5	10 (7–22)
2: Athabasca to Ft. McMurray	166	48000 (21000–66000)	0.5	9 (7–21)
3: Ft McMurray to Old Fort	76	7000 (2200–15000)	3.9 (winter months), 0.5 (summer months)	1080 (500–3400)

along the Athabasca between 2005 and 2007 (Fig. 6). Data for deep brines sampled near Edmonton (Simpson, 1999; Connolly et al., 1990) and saline seeps from Devonian formations are also plotted (Grasby and Chen, 2005). The intercept of a regression of available
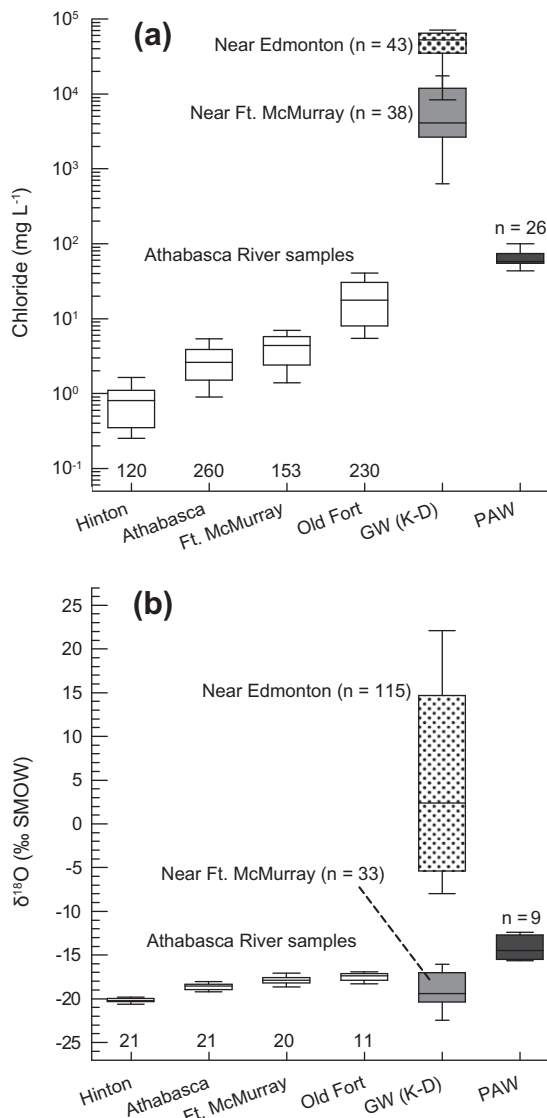
Fig. 3. Ranges of (a) Cl⁻ concentrations and (b) $\delta^{18}O$ values for sampling stations along the Athabasca River (Hinton, Town of Athabasca, Ft. McMurray and Old Fort), Cretaceous and Devonian-aged formation waters, and tailings waters from oil sands developments downstream of Ft. McMurray. Groundwater data for well samples in Cretaceous- and Devonian-aged formations (GW K-D) are presented for wells near Edmonton (stipple, Connolly et al. 1990; Simpson 1999), and samples near Ft. McMurray (light gray; Lemay, 2002; Grasby and Chen, 2005; Fennell, 2010; Gibson et al., 2011). Data for process-affected waters from oil sands operations (PAW) north of Ft. McMurray are collected from datasets of Fennell (2010), Gibson et al. (2011) and Abolfazlzadehdoshanbehbazari (2011). Boxes mark the 75th and 25th percentiles of each dataset and a black line within the box represents the median value. Whiskers represent the 90th and 10th percentiles.
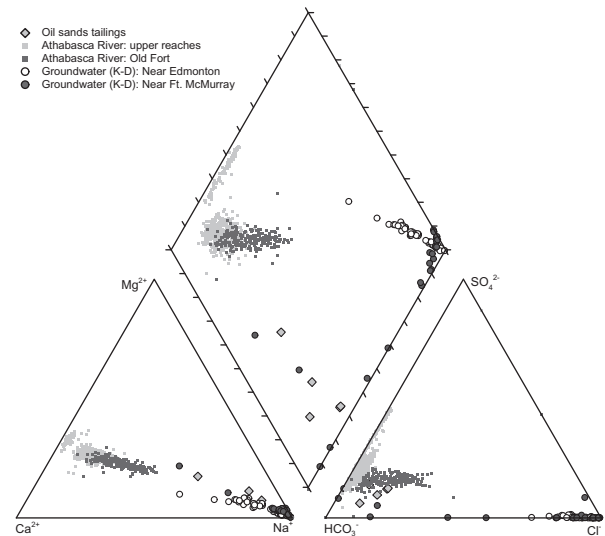

Fig. 4. Piper (1944) diagram showing major ion chemistry of waters in the Athabasca River basin. Three stations for the upper Athabasca River are represented by light gray squares (Hinton, Town of Athabasca and Fort McMurray). Samples of the Athabasca River collected downstream of oil sands developments are shown as dark gray squares. Also shown are Cretaceous and Devonian formation waters near Edmonton (white circles) and near Fort McMurray (dark gray circles), and results for oil sands tailings (gray diamonds).

lake data near Fort McMurray ($\delta^2H = 4.87 \cdot \delta^{18}O - 51.8$; data from Gibson et al., 2010) with the local meteoric water line occurs at a $\delta^{18}O$ value of −19.8‰, The amount-weighted $\delta^{18}O$ value of Edmonton precipitation is −18‰. $\delta^{18}O$ values of saline groundwater springs in the Athabasca oil sands region are as low as −25‰, and fall on the local meteoric water line in δ^2H–$\delta^{18}O$ space. The isotopic-signature of these deep groundwaters in the Athabasca oil sands region is too depleted in ^{18}O and ^2H to be of modern meteoric origin. These low $\delta^{18}O$ values are suggestive of groundwater that was recharged under cooler climate conditions than the present, consistent with a Pleistocene-aged meteoric recharge source (Remenda et al., 1996; Grasby and Chen, 2005; Birks et al., 2007).

6. Discussion

Discharge of saline waters from Cretaceous and Devonian aquifers is shown to significantly impact chemistry of the Athabasca River. Saline water inputs to the upper reaches of the Athabasca River (Hinton to Ft. McMurray) are 10–1000 times smaller than inputs downstream of Fort McMurray, and are more plausibly related to anthropogenic (i.e. municipal, industrial or road de-icing) or shallow aquifer inputs instead of deep formation water contributions. The influence of saline inputs on the Athabasca River is greatest between Ft. McMurray and Old Fort – the area of ongoing bitumen development – where 0.1–3% (500–3400 L s⁻¹) of Athabasca River's discharge is sourced from saline formation water discharge. These estimates are supported by seepage discharge measurements on the order of 10^{-1}–10^1 L s⁻¹ in the Athabasca
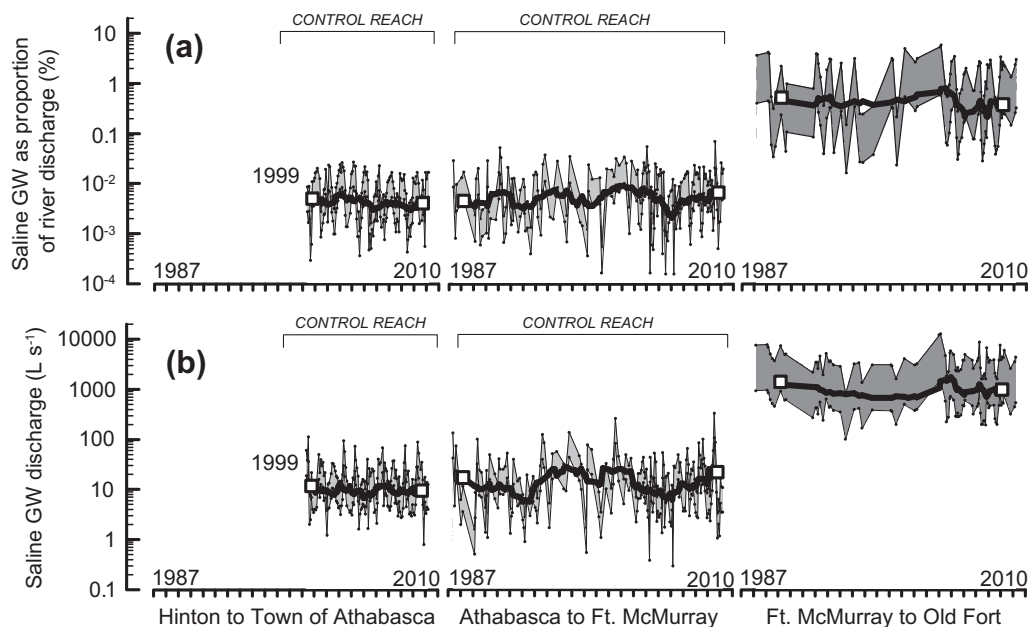
Fig. 5. Calculated saline water discharges along three reaches of the Athabasca River from 1987 to 2010. (a) Upper plots show this flux as a percentage of Athabasca River discharge. (b) Lower plots show saline groundwater discharge in m^3/s. All plots are semi-logarithmic, highlighting the order of magnitude difference between upstream reaches ("control reaches") and the lowermost reach between Ft. McMurray and the Peace-Athabasca Delta. A five-point running mean using the average Devonian- and Cretaceous-aged formation water Cl^- concentration (C_G) is marked by a thick black line and two white squares.
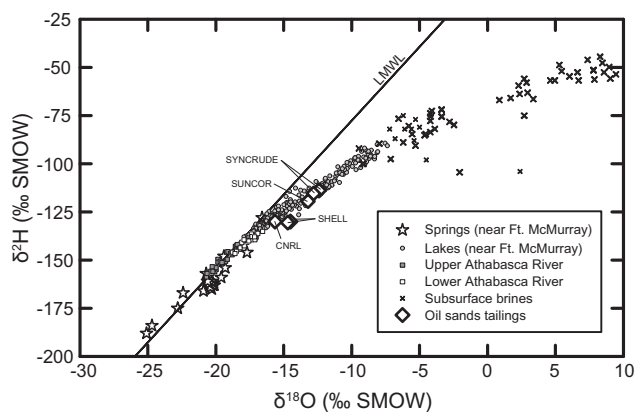

Fig. 6. Plot of stable isotope ratios of H and O ($\delta = [R_{sample}/R_{standard} - 1] \times 1000$; R: $^2H/^1H$ or $^{18}O/^{16}O$) in natural and process-affected waters within the Athabasca River basin. Data for the Athabasca River is divided into upper (dark gray squares, Hinton and Athabasca, $n = 42$) and lower Athabasca River stations (white squares, Fort McMurray and Old Fort, $n = 31$). Riverbank groundwater seepage data from the Fort McMurray area from Devonian formations are plotted as white stars (data from Grasby and Chen, 2005). Devonian brine samples from the Edmonton region from Connolly et al. (1990) and Simpson (1999) are represented by crosses. Data for 345 lake samples collected within 200 km of Fort McMurray between 2002 and 2008 are represented by small white circles (data from Gibson et al., 2010). Results for process-affected water samples are marked by white diamonds (data from Gibson et al., 2010 and Abolfazlzadehdoshanbehbazari, 2011).

oil sands region (Ozoray, 1974; Gibson et al., 2011). Despite this seemingly small contribution of groundwater, the reach exhibits a fourfold increase in Cl^- concentration over 200 km, suggesting a profound impact of groundwater discharges on the chemistry of the Athabasca River. Fig. 7 highlights the seasonal variability of saline groundwater discharges as a proportion of Athabasca River discharge. The influence of saline groundwater discharges on Athabasca River chemistry is greatest in winter months when Athabasca River discharge is low (0.1–3%), whereas this impact is diluted in June and July during peak river discharge (<0.3%).

Other potential sources of salinity along the reach of the Athabasca River between Ft. McMurray and Old Fort include municipal discharges and process-affected water discharges from bitumen development. Process-affected waters are held in tailings compounds adjacent to the Athabasca River at elevations roughly 100 m above the Athabasca River. Ferguson et al. (2009) investigated potential water discharges from one tailings impoundment and calculated primary dyke water leakage to be in the range of $10^1–10^2$ L s^{-1}. Using this range in fluxes, and testing a hypothetical tailings source of Cl^- (50–500 mg L^{-1}; Fig. 3a) in a mixing model with the Athabasca River, it is calculate that total discharges from all ponds (~0.1 m^3/s, if rates of Ferguson et al. (2009) are applied to all ponds) correspond to at most a 1 mg L^{-1} increase in the Athabasca River's Cl^- concentration between Ft. McMurray and Old Fort, whereas Cl^- concentrations increase by 18 mg L^{-1}, on average. (Figs. 3a, and 8). Given this, and also the lack of a major ion mixing trend between river and tailings waters (Fig. 4), the latter is not considered to be more than a minor source of Cl^- added to the river on this reach.

This works lumps Cretaceous and Devonian formation waters in the Athabasca oil sands region into a single parameter, as Cl^- concentrations for these formation waters are similar. Decoupling contributions from these formations may be possible using other geochemical tracers, such organic tracers and stable isotopes of S. Bacterial SO_4 reduction has been shown to modify bitumen-bearing formation waters in the region ($\delta^{34}S_{SO4} = 25‰$; Hubert et al., 2011), although SO_4^{2-} derived from underlying evaporites is expected to carry high $\delta^{34}S_{SO4}$ values (Thode and Monster, 1965).

Dissolution of Devonian-aged evaporites by subglacial Pleistocene meltwaters is the most likely salinity source for lower Cretaceous and Devonian formation waters in the Athabasca oil sands region. This mechanism is supported by collapse breccias associated with evaporite dissolution in the region (see Grasby and Chen, 2005), and Na-Cl type groundwaters (Fig. 4). Ensuing pressurized groundwater advection during the Holocene likely emplaced these saline glaciogenic waters into overlying Cretaceous formations, an interpretation that is supported by the meteoric and ^{18}O-depleted
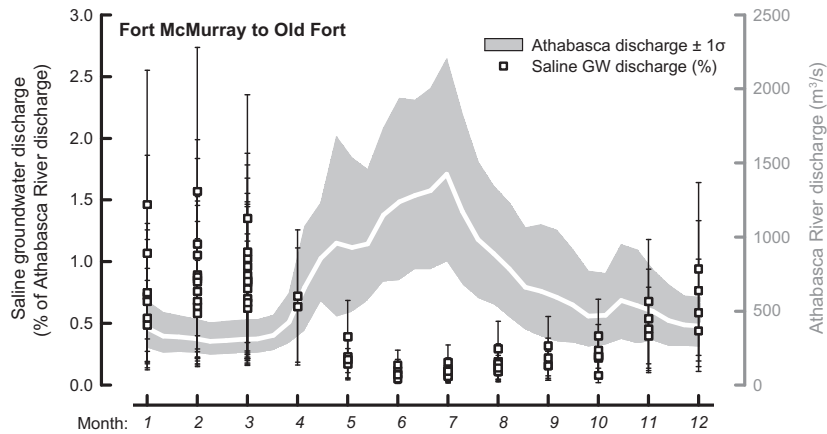
Fig. 7. Monthly saline groundwater discharges as a proportion of Athabasca River discharge (%) for the river reach between Ft. McMurray and Old Fort are shown as black squares and associated error bars (all data for 1987–2010 are plotted). The long-term mean discharge for the Athabasca River is represented by a white line (10 day bins). Shaded gray areas represent one standard deviation from the long-term mean discharge for each 10 day bin.
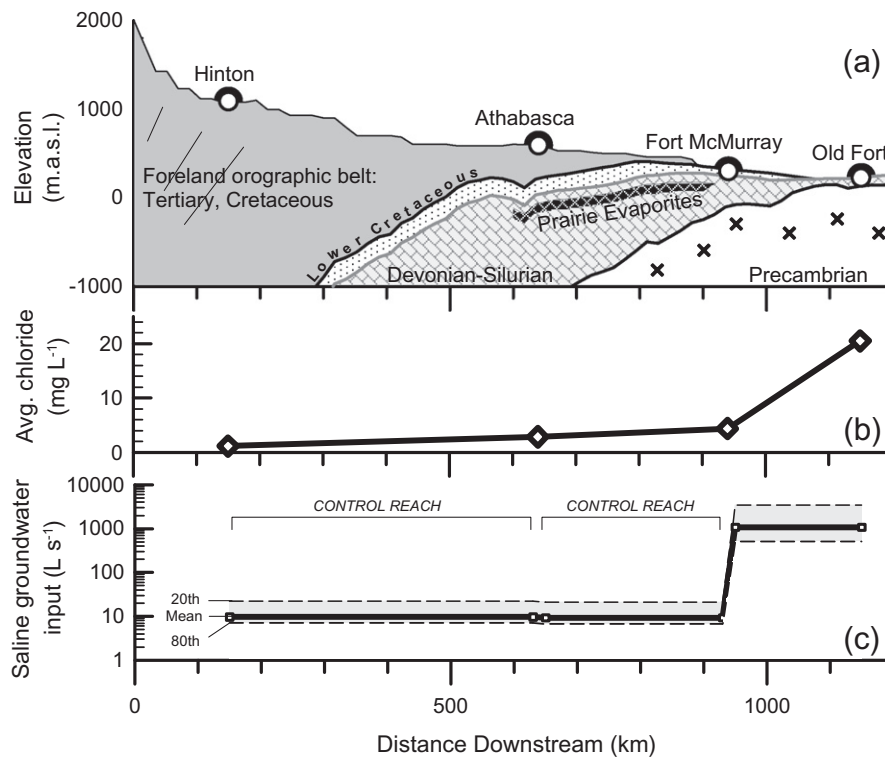

Fig. 8. Synoptic profile of the Athabasca River showing (a) bedrock geology, (b) Athabasca River Cl⁻ concentrations, and (c) saline groundwater discharges to the Athabasca River. Lower Cretaceous- and Devonian-aged formations bearing saline waters subcrop between Ft. McMurray and Old Fort. Average Cl⁻ concentrations increase progressively downstream, with the largest concentration increase occurring between Ft. McMurray and Old Fort (average increase of 18 mg L⁻¹). Average saline groundwater discharges calculated for the period 1987–2010 are shown here. Discharges are shown for three groundwater salinity scenarios: 80th percentile, average, and 20th percentile of Devonian and Cretaceous formation water (Cl⁻). The largest groundwater discharges occur between Ft. McMurray and Old Fort (10³ L s⁻¹ ±half an order of magnitude). Upper reaches of the Athabasca are labelled as controls, as saline groundwater discharges for these reaches are expected to be near-zero. The lower groundwater discharges calculated for these upper reaches (~10 L s⁻¹) supports the calculation presented.

isotopic compositions of river seeps and groundwater samples relative to modern precipitation.

Advection of a denser, more saline groundwater to the surface requires a hydrologic gradient directed toward the surface. The mechanism for an "upward" hydrogeologic gradient could include relict subglacial pressures, or the regional topographically-driven flow system that recharges at higher altitudes in the Rocky Mountains. Moreover, the Athabasca, Clearwater and Christina river incisions expose aquifers bearing saline waters to the surface, thereby aiding the discharge of saline formation waters. Actual surface

seeps are likely to be a mixture of modern recharge, river water, and relict Pleistocene waters, supported by the presence of ^{3}H.

Subsurface–surface hydrologic connections are a primary water contamination concern for ecosystems in the lower Athabasca River basin as bitumen production continues. Natural sources of contaminants – notably naphthenic acids – include weathering of bitumen outcrops along river banks, and the seepage of water that has been in prolonged contact with bitumen. A standalone technology to quantitatively decouple natural contributions from those associated with bitumen development has remained elusive,

although recent use of multiple isotope tracers and Fourier transform ion cyclotron resonance mass spectrometry shows potential to label waters and organic compounds, including naphthenic acids (Gibson et al., 2011). The influence of saline groundwater seepage is shown to be a principle control on the inorganic chemistry of the Athabasca River; therefore, groundwater discharges should be prioritized as a target for new water quality monitoring networks in the AOSR. A variety of geophysical techniques are available to locate groundwater seeps, including electromagnetic surveys (Gibson et al., 2011), airborne infrared thermography (Schuetz and Weiler, 2011) and continuous thermal imaging via fiber optic instrumentation (Slater et al., 2010; Mwakanyamale et al., 2012). Establishing a baseline of natural discharges is the first step required to assess long-term water quality impacts of bitumen extraction in the Athabasca oil sands region.

7. Conclusions

A large gradient in Cl^- concentrations exists between surface- and ground-waters in the Athabasca oil sands region. Applying Cl^- as a conservative tracer, it is calculated that $500-3400\ L\ s^{-1}$ of natural saline groundwater discharges into the lower Athabasca River from Cretaceous- and Devonian-aged sedimentary formations over a 210-km reach. Similar rates of discharge per unit reach ($\sim 2.4-16\ L\ s^{-1}\ km^{-1}$) are expected to occur along the lower reaches of the Christina and Clearwater Rivers, as the lower portions of these tributaries incise into formations bearing saline waters. This provides a first approximation of the impact of saline groundwater on surface water quality in the region, important for improved groundwater and surface water management.

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