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ARTICLE

Evidence of discharging saline formation water to the Athabasca River in the oil sands mining region, northern Alberta

J.J. Gibson, J. Fennell, S.J. Birks, Y. Yi, M.C. Moncur, B. Hansen, and S. Jasechko

Abstract: This paper summarizes various lines of evidence, including new geophysical and geochemical surveys indicating the discharge of naturally occurring saline formation water from Cretaceous and Devonian formations to the Athabasca River downstream of Fort McMurray — an active oil sands extraction area. The following features are indicative of saline water discharge: (*i*) the hydrogeological setting of the reach which is situated near the western, up-dip, and subcropping, edge of the Western Canada Sedimentary Basin; (*ii*) springs and seepage along area rivers and tributaries that have been observed and reported in previous studies; and (*iii*) a significant increase in dissolved solids in the river, particularly chloride, occurring in a downstream direction from Fort McMurray. Further evidence of the saline groundwater discharge was obtained from electromagnetic surveys conducted along a 125 km reach from the Clearwater River to the Firebag River. This technique was used to map the distribution of saline water in the riverbed hyporheic zone, and revealed broad zones of generally high terrain electrical conductivity values in deeply incised Cretaceous- and Devonian-aged subcrop areas, but with numerous point-source and lineal anomalies attributed to occurrence of saline water discharge in less incised areas. Porewater sampling using drive-point piezometers was then used to confirm the presence of saline water in selected zones. Depth-wise gradients in chemical parameters observed in the riverbed porewaters in these zones are interpreted as evidence of upward movement of saline formation water mixing with the Athabasca River. Geochemical properties of the porewater are consistent with natural sources of groundwater flow from the Cretaceous- and Devonian-aged formations discharging along various reaches of the river.

Résumé : Le présent article résume diverses observations, incluant de nouveaux levés géophysiques et géochimiques, indiquant une décharge naturelle d'eau saline de formations datant du Crétacé et du Dévonien vers la rivière Athabasca en aval de Fort McMurray — un secteur actif d'extraction de sables bitumineux. Les caractéristiques suivantes indiquent une décharge d'eau saline : (*i*) l'environnement hydrogéologique du tronçon situé à proximité de la bordure ouest, en amont-pendage et en affleurement masqué, du bassin sédimentaire de l'Ouest canadien; (*ii*) des sources et des suintements le long des rivières et des tributaires du secteur ont été observés et signalés dans des études antérieures et (*iii*) une augmentation significative de solides dissous dans la rivière, surtout des chlorures, en aval de Fort McMurray. D'autres évidences de décharge d'eau souterraine saline ont été obtenues de levés électromagnétiques effectués le long d'un tronçon de 125 km entre la rivière Clearwater et la rivière Firebag. Cette technique a été utilisée pour cartographier la distribution de l'eau saline dans la zone hyporhéique du lit de la rivière et elle a révélé de vastes zones de valeurs élevées de conductivité électrique sur le terrain dans les secteurs d'affleurements masqués, fortement encaissés, datant du Crétacé et du Dévonien mais avec de nombreuses anomalies ponctuelles et linéaires attribuées à l'occurrence de décharge d'eau saline dans des secteurs moins encaissés. L'échantillonnage de l'eau interstitielle au moyen de piézomètres enfoncés a par la suite confirmé la présence d'eau saline dans les zones choisies. Les gradients des paramètres chimiques en fonction de la profondeur, observés dans l'eau interstitielle du lit de la rivière dans ces zones, sont interprétés en tant que preuve du mouvement ascendant des eaux des formations salines et de leur mélange avec l'eau de la rivière Athabasca. Les propriétés géochimiques de l'eau interstitielle concordent avec des sources naturelles d'écoulement souterrain à partir de formations datant du Crétacé et du Dévonien qui se déchargent le long de divers tronçons de la rivière. [Traduit par la Rédaction]

Introduction

The oil sands of northern Alberta represent an important oil reserve to Canada and the world, containing an equivalent of over 170 billion barrels (or 2.7×10^{10} m^3) of oil. Currently, production is ~1.8 million barrels per day (mBPD), with planned expansion to 3.9 mBPD by 2020 (McLinden et al. 2012). These hydrocarbon deposits are located beneath a vast area of boreal forest located in northern Alberta and have been exposed along the flanks of the river valleys via long-term erosion of the Athabasca River and its tributaries. Additionally, the dissolution of salt deposits by freshwater influx during the Pleistocene (Grasby and Chen 2005) and previous dissolution phases (Broughton 2013) has led to the col-

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J.J. Gibson and Y. Yi. Alberta Innovates – Technology Futures, 3-4476 Markham Street, Victoria, BC V8Z 7X8, Canada; Department of Geography, University of Victoria, P.O. Box 3060, STN CSC, Victoria, BC V8W 3R4, Canada.
J. Fennell. Integrated Sustainability Consultants Ltd., 610, 633 – 6th Ave. S.W., Calgary, AB T2P 2Y5, Canada.
S.J. Birks. Alberta Innovates – Technology Futures, 3608 33rd Street N.W., Calgary, AB T2L 2A6, Canada; Department of Geography, University of Victoria, P.O. Box 3060, STN CSC, Victoria, BC V8W 3R4, Canada.
M.C. Moncur. Alberta Innovates – Technology Futures, 3608 33rd Street N.W., Calgary, AB T2L 2A6, Canada.
B. Hansen. WorleyParsons, Infrastructure and Environment, 500 – 151 Canada Olympic Road S.W., Calgary, AB T3B 6B7, Canada.
S. Jasechko.* Alberta Innovates – Technology Futures, 3-4476 Markham Street, Victoria, BC V8Z 7X8, Canada.

Corresponding author: J.J. Gibson (e-mail: jjgibson@uvic.ca).

*Present address: Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA.

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lapse of strata in various locations (primarily on the east side of the Athabasca River) and subsequent development of potential pathways for cross-formational flow between the Devonian, Cretaceous, and surficial environment (Mahood et al. 2012; Schneider et al. 2012; Broughton 2013). This evolution has led to a complex hydrogeological system, which features numerous potential connections between surface and subsurface water resources. At the same time, the presence of large ponds constructed to contain mine tailings, and in particular, to manage oil-sands-process waters used in the separation of bitumen and sand, have come under increasing scrutiny as a potential source of industrial input to the surface water environment. Transport and fate of oil-sands-related constituents in the regional aquatic ecosystem is a major environmental and health concern, with potential for great social and environmental impact. However, the debate about whether industrial-related effects are responsible for observed changes in the groundwater or surface water quality of the region continues, as the question of relative contributions from natural sources has not been thoroughly investigated and quantified. Knowledge of natural sources of salinity and organics is particularly important for design of monitoring strategies for industrial impact, as their presence may lead to downstream evolution of water chemistry that needs to be accounted for and understood.

The Athabasca River, from Fort McMurray to Old Fort (Fig. 1), is characterized by significant increases in electrical conductivity (EC), total dissolved solids (TDS), and various other analytes, such as chloride (Cl). Potentially toxic compounds such as naphthenic acids (NA) are also prevalent, and these have been identified both in natural sources and industrial process waters (Gibson et al. 2011). Given the hydrogeologic setting of the area, situated along a topographically driven groundwater flow gradient (Barson et al. 2001; Adams et al. 2004), the known hydraulic gradients between formations, occurrence of subsurface brines (Hackbarth and Nastasa 1979), and observed changes in water quality along the river (Jasechko et al. 2012), it is reasonable to suspect that the Athabasca River is actively receiving saline water discharge. Considerable observations have also been made that document the occurrence of bitumen fountains and saline springs along the Athabasca and Clearwater rivers (see Hitchon et al. 1969; Grasby and Chen 2005; Gue 2012).

To further understanding of the natural setting of groundwater seepage, its variability and characteristics, and to assess the potential for oil-sands-development impacts, a geophysical reconnaissance of a 125 km reach of the Athabasca River from Fort McMurray to the confluence with the Firebag River was conducted using an electromagnetic method (see Butler et al. 2004). Our hypothesis was that we should be able to locate saline water in the hyporheic zone of the Athabasca River that is mixing with river water in zones of active groundwater seepage. Locations exhibiting elevated terrain electrical conductivity in the riverbed hyporheic zone were identified as potential locations of groundwater seepage, which were then further assessed using drive-point piezometers (DPPs) to facilitate collection of porewater samples from various depth horizons (up to 3 m below the riverbed) for geochemical characterization. Results from these natural seepage zones provide previously unavailable context on the setting of groundwater–surface-water interaction along the lower Athabasca River.

Athabasca River hydrology

The Athabasca River sub-basin forms a major headwater tributary of the northward draining Mackenzie River basin. The Athabasca River headwaters are situated in the Rocky Mountains, with the river flowing northeastward toward the city of Fort McMurray, then northward into Lake Athabasca at the Peace–Athabasca Delta (Fig. 1). The river is the primary source of make-up water for oil sands mining and processing in the Athabasca oil sands region north of the city of Fort McMurray (56.7°N, 117.4°W).

The Athabasca oil sands region (AOSR) has a climate that is seasonal, with monthly mean temperatures that vary from –19 °C in January to 17 °C in July, with a mean annual temperature of near 0 °C. Total annual precipitation is on the order of 450 mm, with 60% falling as rain during the warmer months of May through August. Relief is subdued with the exception of large river incisions. Ombrogenous (precipitation-fed) bogs and geogenous (groundwater-fed) fens govern hydrology and infiltration at the surface (Vitt et al. 1994). Beneath these peatlands and mineral soil uplands lie glacio-fluvial and glacio-lacustrine sediments that can exceed 300 m depth in areas overlying buried paleochannels (Andriashek and Atkinson 2007). These fine-grained soils, in combination with the climate, have resulted in the abundance of wetlands, bogs, and fens across the region.

River hydrology in the AOSR is strongly seasonal, with high flows associated with the snowmelt period in April–May–June, and low flows associated with ice-covered periods in November to March when inputs are mainly restricted to channel storage, groundwater inflows, and drainage of lakes and muskeg. The seasonal timing of Athabasca River discharge is shown in Fig. 2*a*, along with EC and Cl concentrations (Figs. 2*b*, 2*c*), which reveal more dilute discharge in spring and summer during high flow, and more concentrated discharge during the ice-on period. This observation is attributed to relative increase in the proportion of groundwater inflow during the low-flow period (January through March). Strong relationships are noted between discharge and various dissolved solids, including Cl as well as EC (Fig. 3), confirming that dilution during higher flow periods is the primary mechanism controlling river chemistry. It is also interesting to note that, at similar flow conditions, EC and Cl increase from Fort McMurray to Old Fort (Fig. 3), indicating that significant input of dissolved solids is occurring along the reach. While groundwater discharge is likely a primary natural source of increased dissolved solids on this reach, only a few studies have documented the nature of the seepage (Grasby and Chen 2005; Grasby 2006; Gue 2012). The geophysical reconnaissance performed as part of this study was used to target areas of potential saline groundwater seepage into the riverbed for subsequent verification sampling of the discharging porewaters.

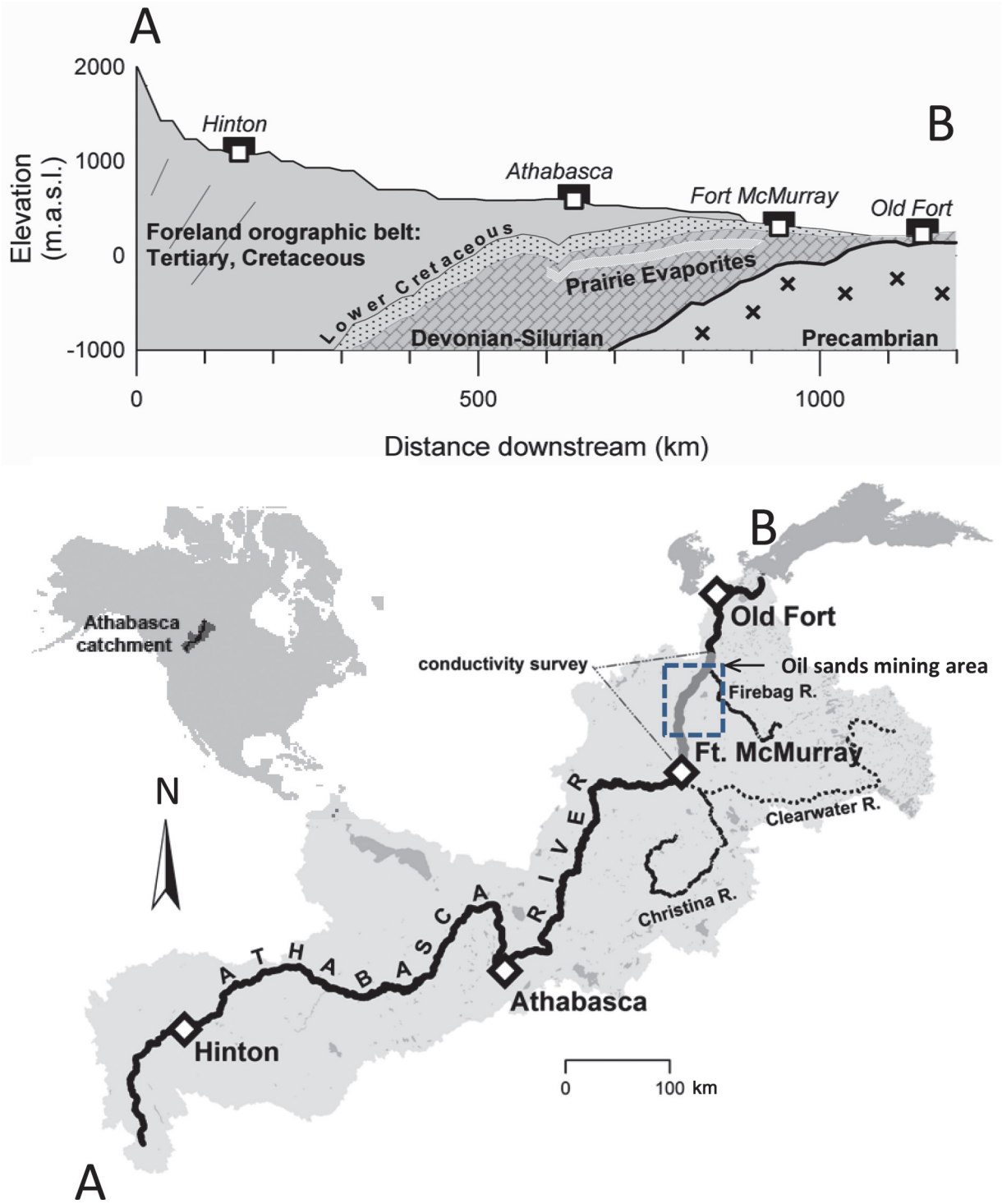
Hydrogeology

The 125 km reach of the Athabasca River from Fort McMurray to the Firebag River incises several geological formations, including the Cretaceous Clearwater and McMurray formations, and underlying Devonian formations. The Clearwater Formation is the youngest in the sequence and is exposed along the upper banks of the Athabasca River. This fine-grained shale-dominated formation overlies the McMurray Formation, which outcrops along most of the river from Fort McMurray to the Firebag River confluence. Devonian-aged carbonate rocks outcrop along the Athabasca River from Fort McMurray to 62 km north along the river and appear again at 99 km to the end of the study area. All formations are overlain by Quaternary-aged sediments comprising till, lacustrine clay–silt, and fluvial sands and gravels of glacial origin. Geological features of the study region are described in detail by Barson et al. (2001) and Hein et al. (2001). A brief overview of the important geological and hydrogeological characteristics is provided in the following subsections.

Waterways Formation (Devonian unit)

The Waterways Formation, part of the Devonian succession, underlies the McMurray Formation and comprises a series of carbonate aquifers separated by intervening evaporite deposits and shaly to marly aquitards. Devonian units in the area may have supported regional groundwater flow systems that originate from the Rocky Mountains overthrust belt and discharge in northeastern Alberta and Saskatchewan, although Grasby and Chen (2005) argue that the modern flow system is more localized. Groundwater is characterized by extremely high salinity (up to several

Fig. 1. Map showing Athabasca River basin, Alberta, highlighting the long-term river network (LTRN) monitoring stations. Inset shows position of the Athabasca River within North America. The electromagnetic terrain conductivity surveys and related sampling were conducted between the two downstream stations across the active oil sands mining area. Cross section A–B is a longitudinal profile along the river, showing the position of the Prairie Evaporite deposit and lower Cretaceous strata (including McMurray Formation) bearing the oil sands. m.a.s.l., metres above sea level.



hundred thousand mg/L of TDS, see Table 1), particularly in the vicinity of evaporitic beds.

McMurray Formation

The Upper McMurray Formation is disconformably bounded above and below by the Clearwater Formation and the Sub-Cretaceous unconformity, respectively (Wightman et al. 1995). The formation consists of interbedded sands, shales, and silts, and large areas of bitumen-impregnated sands that locally act as groundwater flow barriers (Bachu and Underschultz 1993). The McMurray Formation dips to the southwest. Groundwaters typically range from fresh to saline (Table 1).

Fig. 2. Monthly variation in (*a*) river discharge (*Q*), 1987–2009, (*b*) electrical conductivity (EC), and (*c*) chloride (Cl) concentration in Athabasca River at Old Fort. Note that winter months with ice cover (November to March, i.e., months 11, 12, and 1–3) tend to have the higher dissolved solids concentrations due to increase in proportion of groundwater inputs. Dilution during periods of higher flow is the predominant mechanism controlling concentrations in the river. Boxes denote 25th and 75th percentiles, with bars showing 5th and 95th percentiles, and solid circles denoting outliers. Months 1–12 represent January to December, respectively.

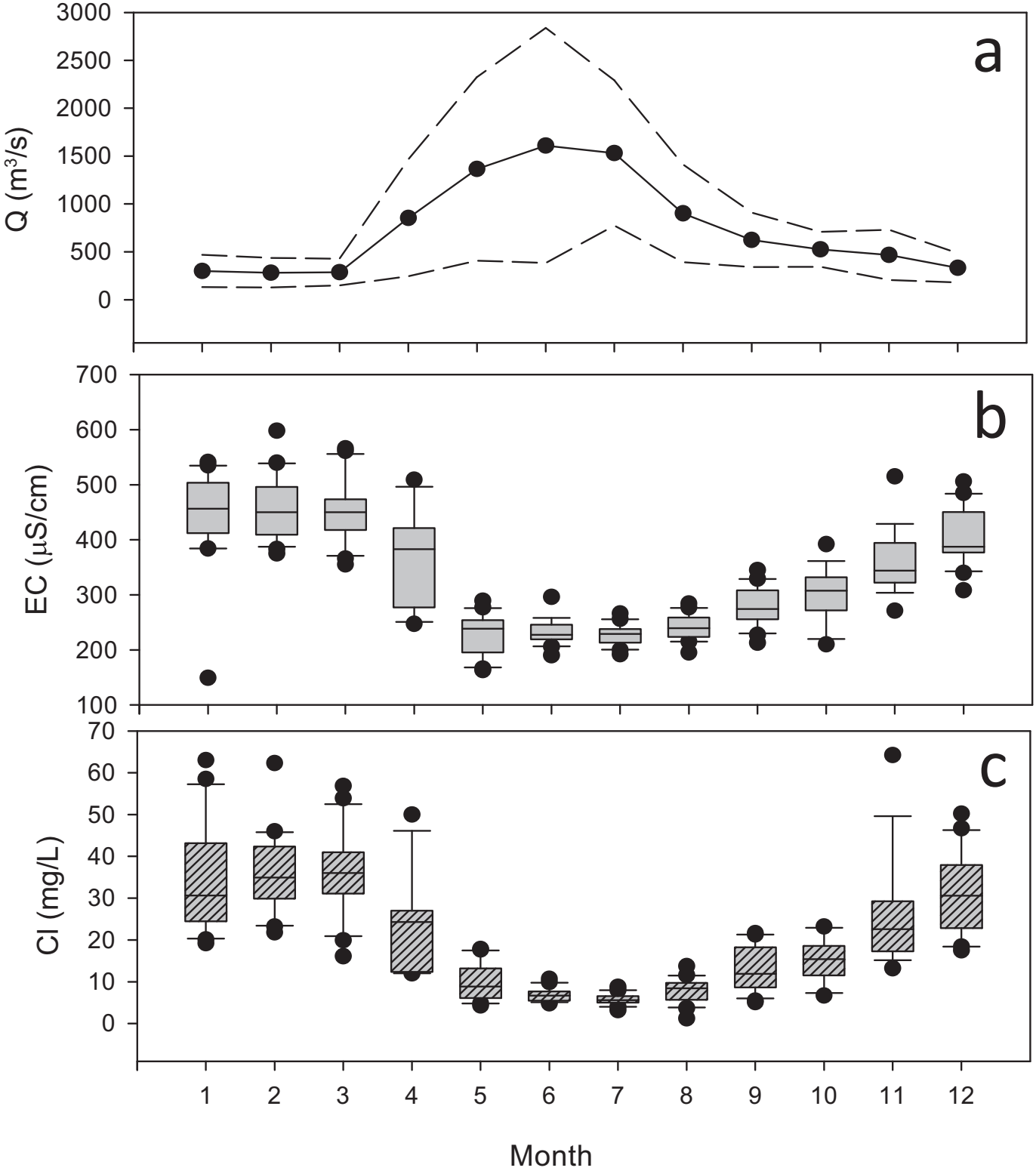


Fig. 3. Log–log plots of (*a*) electrical conductivity (EC) and (*b*) chloride (Cl) concentration versus instantaneous discharge (*Q*, m^3/s) in the Athabasca River upstream and downstream of study reach based on LTRN data. Note the consistent correlation between discharge and EC and Cl, suggesting a dilution mechanism during high flow. The apparent increase in dissolved solids along the reach is attributed primarily to saline groundwater input.

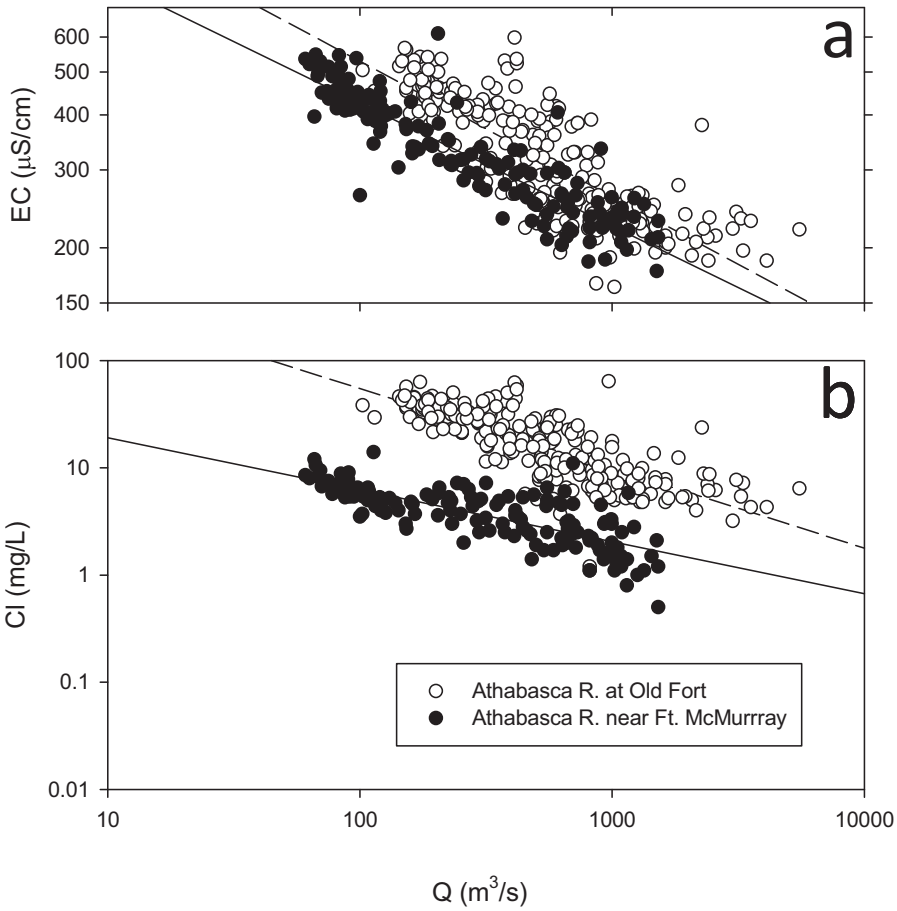


Table 1. Geochemical properties of selected water samples from groundwater, hyporheic zone, and river water.

	EC (μS/cm)		TDS (mg/L)		Cl (mg/L)		$\delta^{18}O$ (‰)		NA (mg/L)	
Location	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Groundwater[a]										
Quaternary	486–3680	1185	47–3740[b]	559[b]	12–1550[b]	72[b]	−19.7 to −17.1[c]	−18.6[c]	0–6.6[b]	1.4[b]
Clearwater Formation	1400–78000	7892	980–4005	2070	4–2000	483	−22.0 to −18.4[c]	−20.0[c]	0.50–5.0[b]	1.1[b]
McMurray Formation	79–78000	4560	196–278340	21000	1–171800	10409	−22.8 to −17.4[c]	−20.9[c]	1–160[b]	11.8[b]
Devonian	286–210000	31182	654–405587	73427	27–204000	41374	—	—	0–79[b]	10.6[b]
Hyporheic zone (porewater)										
Zone 1	71600–81300	76971	52736–64929	57489	29100–36100	31143	−20.6 to −20.5	−20.6	0.29–2.31	1.61
Zone 2	612–1130	831	535–1054	752	5–16	8	−17.6 to −17.2	−17.4	0.20–0.57	0.42
Zone 3	5190–71500	21381	3392–56409	15426	1240–31200	8126	−22.7 to −18.7	−20.4	0.77 −2.44	1.57
Zone 4	1460–1830	1701	1043–1281	1210	222–319	282	−18.6 to −18.4	−18.5	0.16–0.86	0.40
Zone 5	26200–41600	34043	16127–27889	21734	9530–15700	12490	−18.7 to −17.7	−18.2	0.12–0.16	0.15
Zone 6	799–834	815	732–795	766	19–25	22	−17.8 to −17.7	−17.8	—	—
Zone 7	1660–4550	3023	1126–2882	1924	328–1190	723	−18.8 to −17.2	−18.0	0.77–1.1	0.96
Athabasca River										
Fort McMurray	146–611	340	110–414	194	0.5–14	4.4	−16.6 to −18.8	−17.8	0.46–0.50	0.48
Old Fort	149–598	332	89–342	190	1.2–64	20.5	−16.9 to −17.5	−17.5	0.9[d]	0.9[d]

Note: EC, electrical conductivity; TDS, total dissolved solids; Cl, chloride; $\delta^{18}O$, oxygen isotope composition of water; NA, naphthenic acid concentration.
[a]From CEMA (2010*a*) except as noted.
[b]From CEMA (2010*b*), table A3-1.
[c]From Alberta Innovates – Technology Futures (AITF), unpublished data; note also that groundwater EC, TDS, and Cl are positively skewed datasets.
[d]Value measured at north end of survey reach near mouth of Firebag River.

Clearwater Formation

Regionally, the Clearwater Formation is considered an aquitard given its dominantly fine-grained texture and attendant low permeability (Hitchon et al. 1989, 1990). This Formation consists of a ~10 m shale unit in the upper portions. Although the Formation generally comprises shale, the unit grades into silt and fine-grained sands, suggesting that the shale unit may not be continuous (Bachu and Underschultz 1993). Along the northern section of the Athabasca River, exposures of Clearwater Formation unconformably overlie the McMurray Formation. Exposed outcrop is generally thin (<1 m) and is composed of fine-grained sediments (Hein et al. 2001). The Clearwater Formation contains natural gas and some accumulation of bitumen in certain locations, but not in the study area. Groundwaters are typically non-saline (Table 1).

Quaternary sediments

The surface of the bedrock underlying the Quaternary sediments represents one of the major unconformable surfaces of the Western Canadian Sedimentary Basin (WCSB) – the pre-Quaternary unconformity, which spans the period of erosion from Late Cretaceous – Early Tertiary to the onset of glaciation in the Early Quaternary. The most important features of these overburden sediments are isolated upland remnants and deep, broad relicts of paleo-river channel systems that formed during the Late Tertiary, but which were later modified by glacial and present-day fluvial processes. Remnants of buried fluvial channels provide a historical record of the erosion that has occurred on the bedrock surface from the Late Cretaceous to the Late Pleistocene. The lowermost unit of drift consists predominantly of coarse-grained sediment deposited by pre-glacial and glacial-fluvial systems. Basal fluvial sediments are present as thick sequences within the floors of the buried bedrock channels, and multiple overlying till units attest to multiple glacial and interglacial cycles during the Quaternary Period (Andriashek 2003). Groundwaters within this unit are typically fresh (Table 1).

Methods

Athabasca River geochemistry dataset

Water chemistry data such as EC and Cl measurements were acquired from Alberta Environment's long-term river network (LTRN) for stations at Fort McMurray and Old Fort. Additional data were reviewed from stations at Hinton and Athabasca (see Fig. 1).

Electromagnetic survey method

Waterborne electromagnetic (EM) terrain EC surveys were carried out over a 125 km reach of the Athabasca River from the city of Fort McMurray downstream to the confluence of the Athabasca and Firebag rivers (Fig. 1). A Geonics EM31 terrain EC meter coupled to a Trimble GeoXH differential global positioning system (GPS) was used to collect the data. The EM31, mounted in a 4.6 m inflatable jet boat, and operated in vertical-dipole mode, measures the combined electrical conductivity of the soil matrix and pore fluids, with a maximum depth of investigation of ~6 m below the water surface, and a peak response originating from a depth of 1.5 m below the water surface. Bathymetry data were collected using a Garmin GPS bathymetry unit, coupled to a data logging system. Positional information was collected using the Garmin GPS unit, which recorded to a data logger. Electrical conductivity along with bathymetry data were used to correct the terrain EC readings for varying water depth. As a result, the corrected EM31 data represent the terrain EC of the river bottom sediments and associated pore fluids. Throughout the field campaign, quality control was monitored continuously. The method has been described in detail elsewhere (Butler et al. 2004).

Two major field campaigns were conducted during this investigation. The first preliminary survey was conducted in June of 2009 (see Fig. 4), which covered the entire 125 km reach of the river. In September 2010, a high-resolution secondary survey targeted seven zones, defined as areas where significant terrain EC anomalies were found in the preliminary survey (see Fig. 5). In total, ~339 000 EM31 terrain EC measurements were collected along the 125 km reach of the Athabasca River during these studies. All geophysical work was conducted by WorleyParsons Infrastructure and Environment located in Calgary, Alberta.

Porewater sampling

The porewater sampling was conducted after the electromagnetic surveys, and targeted areas of the hyporheic zone with high terrain EC identified along the 125 km reach of the Athabasca River (Fig. 6). This reach traverses the primary area of oil-sands-mining development. Porewater sampling was carried out in two campaigns by Alberta Innovates – Technology Futures (AITF) and WorleyParsons, with isotopic and geochemical analyses performed by AITF and a variety of external laboratories (see Table 2). Several groundwater wells from the Alberta Groundwater Observation Well Network (GOWN) were also sampled as part of routine water testing programs by Alberta Environment to provide additional context to the geochemical assessment process. Historical groundwater geochemistry data were obtained from Ozoray (1974), Lemay (2002), and CEMA (2010*a*, 2010*b*).

Porewater from the riverbed was sampled during both field campaigns using DPPs. Sampling occurred at targeted locations where elevated riverbed terrain EC was measured during the EM31 survey. Each piezometer consisted of a 1.9 cm (3/4 in.) 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 manually installed using a slide hammer. During the preliminary survey, these devices were driven 0.5–1 m below the riverbed surface. In the follow-up high-resolution survey, piezometers were installed to depths between 0.75 and 3 m.

Following installation, the DPPs were developed and purged for 15 min using a peristaltic pump. Measurements of pH, oxidation–reduction potential (Eh), dissolved oxygen (DO), electrical conductivity (EC), and temperature were made in a sealed flow-through cell until values were stable. This was followed by sample collection. A detailed account of geochemical sampling and methods for the preliminary survey is provided in Gibson et al. (2011). Similar methods were used for the follow-up survey. Some of the most informative results from both surveys are presented and discussed herein, including EC, Cl, TDS, NA, and stable isotope data for water ($\delta^{18}O$). Details of analytical methods and detection limits are provided in Table 2. Analytical uncertainties associated with concentration measurements from all sources are estimated to be <2%. $\delta^{18}O$, determined by isotope ratio mass spectrometry at AITF Victoria and reported in per mil relative to Vienna Standard Mean Ocean Water (V-SMOW), is accurate to within ±0.05‰.

Results and discussion

Observed discharge

Springs and seeps were observed in several locations along banks of the study reach, for example, between zones S04 and S05 within the McMurray Formation and near S10 situated in the Devonian Waterways Formation. Springs have also been reported along river courses in the region and described in detail by Grasby and Chen (2005), Grasby (2006), and Gue (2012). Seepage, where observed, produced bank instability in some locations, causing trees to fall over. Seepage potential through the riverbed was also directly observed in many locations that were sampled. Upward seepage potential was noted qualitatively as a positive hydraulic head relative to river water level in DPPs installed at the ~1–3 m depth within the riverbed sediments.

Athabasca River geochemistry evidence

Water chemistry data reveal considerable addition of ionic content on the reach from Fort McMurray to Old Fort (Fig. 3), attributed mainly to input of high-salinity water, likely groundwater

Fig. 4. Low-resolution electromagnetic (EM) survey of terrain electrical conductivity along the Athabasca River from north of Fort McMurray to the mouth of the Firebag River. Upper panel shows relative position of lower panels a and b along the river, as well as panel c (see Fig. 5). Reconnaissance sampling locations are shown. Note that yellows and reds are inferred to be areas of enhanced saline groundwater discharge. Please see online version for colour.

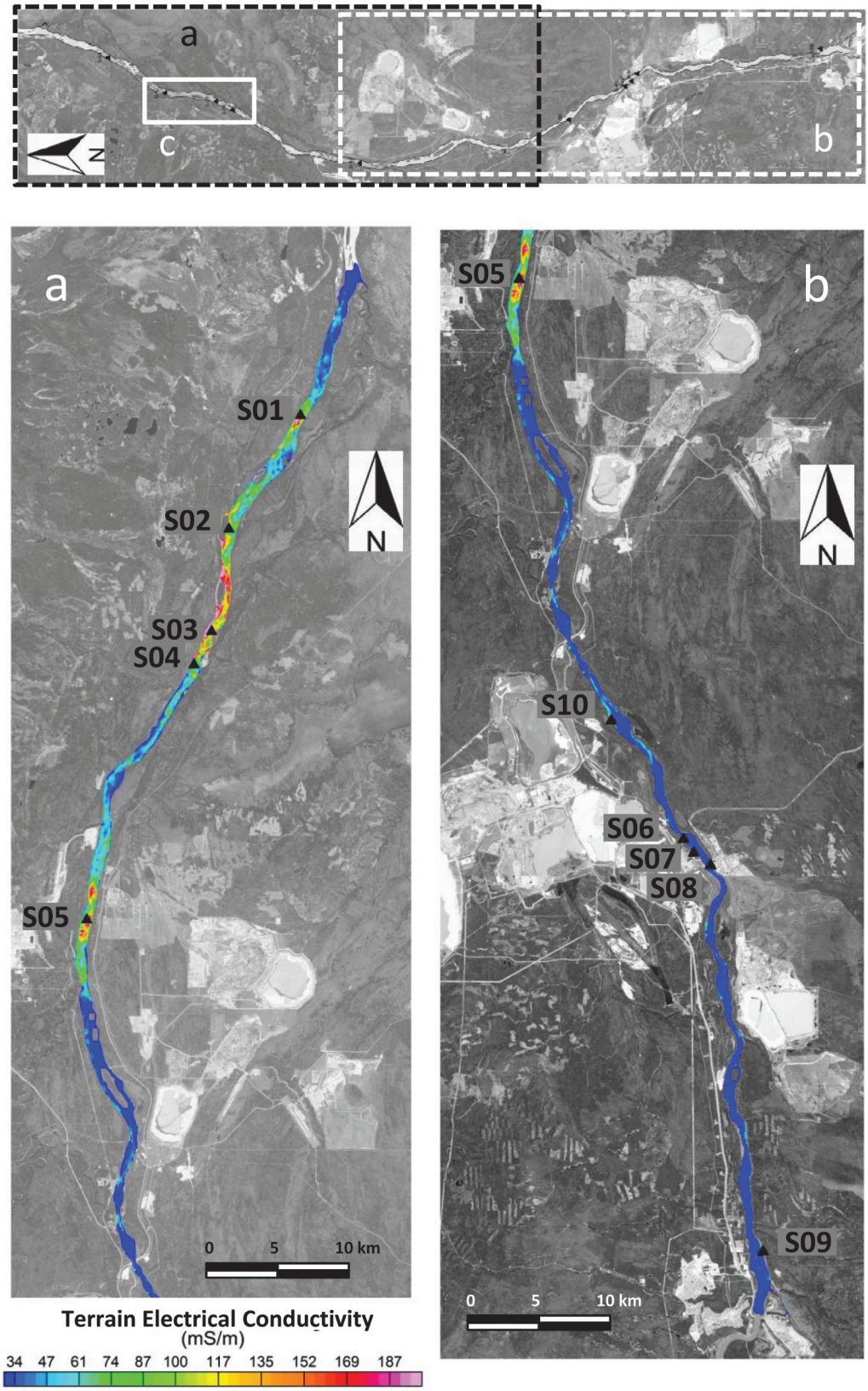


Fig. 5. Example of high-resolution EM survey of terrain electrical conductivity conducted along reach near Zone 1, S02 (see panel c, Fig. 4). Note that yellows, reds, and pinks are inferred to be areas of enhanced saline groundwater seepage. Please see online version for colour.

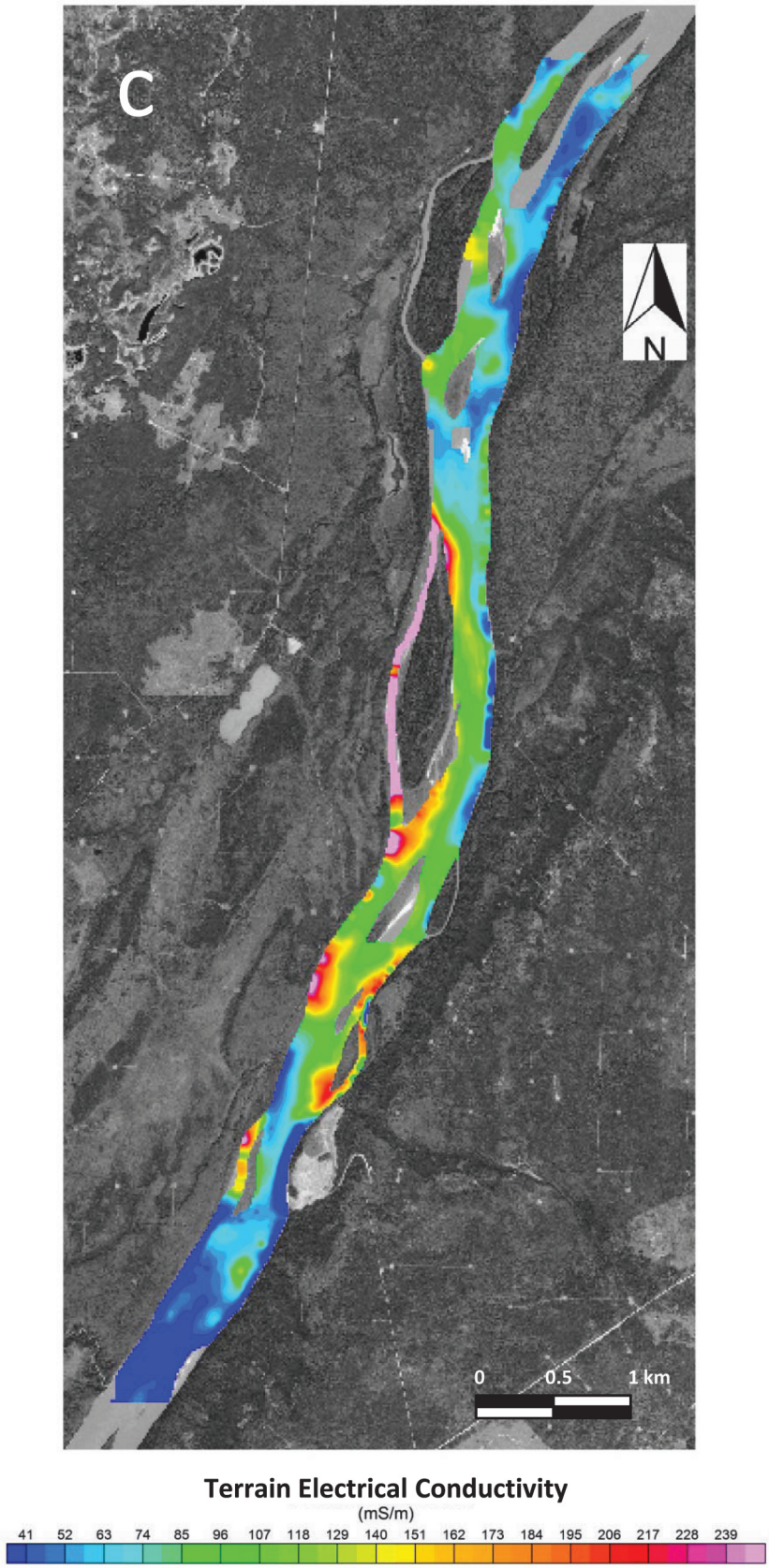


Fig. 6. Map showing zones of detailed investigation along with selected depth profiles of selected analytes. Circles denote porewaters and triangles denote river water sampled at the riverbed interface. Strong geochemical gradients in some areas suggest mixing between saline groundwater and Athabasca River water in the hyporheic zone. EC, electrical conductivity; Cl, chloride; TOC, total organic carbon; NA, naphthenic acids; $\delta^{18}O$, oxygen isotope composition of water. Please see online version for colour.

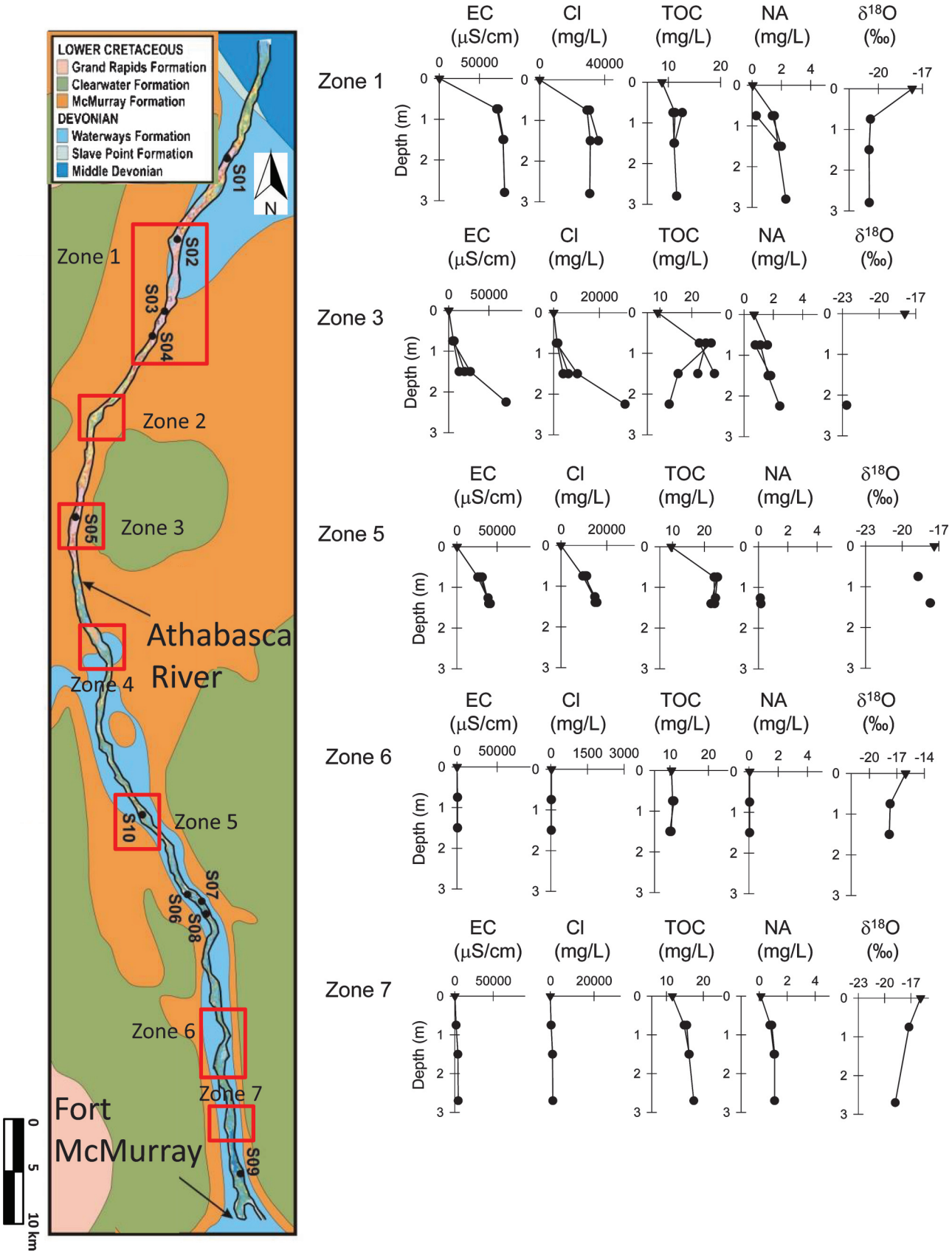


Table 2. Summary of analytical methods, detection limits, and laboratories used in this study.

Analyte	Unit	Detection limits	Analytical methods	Laboratory
pH	pH units	0.1	YSI multi-probe	Field parameters
Conductivity	μS/cm	0.2	YSI multi-probe	Field parameters
Total dissolved solid	mg/L	5–10	Calculated	AITF
Naphthenic acid	mg/L	0.01–0.1	GC–MS, FTIR	AITF, ALS
Bicarbonate (HCO_3)	mg/L	5	Alkalinity titration	AITF, ALS
Total organic carbon (TOC)	mg/L	1	TOC combustion analyzer	AITF, ALS
Chloride (Cl)	mg/L	0.5	Ion chromatography	AITF, ALS
Sulfate (SO_4)	mg/L	0.5	Ion chromatography	AITF, ALS
Calcium (Ca)	mg/L	0.5	ICP–OES	AITF, ALS
Magnesium (Mg)	mg/L	0.1	ICP–OES	AITF, ALS
Potassium (K)	mg/L	0.5	ICP–OES	AITF, ALS
Sodium (Na)	mg/L	1	ICP–OES	AITF, ALS
Ammonium (NH_4)	mg/L	0.05	Colorimetry	AITF, ALS
δ^2H	‰ V-SMOW	0.5*	Isotope ratio mass spectrometer	AITF, UofC
$\delta^{18}O$	‰ V-SMOW	0.05*	Isotope ratio mass spectrometer	AITF, UofC

Note: *Refers to analytical uncertainty. V-SMOW, Vienna Standard Mean Ocean Water; GC–MS, gas chromatography – mass spectrometry; FTIR, Fourier transform infrared spectroscopy; ICP–OES, induced coupled plasma – optical emission spectroscopy; AITF, Alberta Innovates – Technology Futures; ALS, ALS Laboratory Group; UofC, University of Calgary.

(see also Gue 2012; Jasechko et al. 2012). Taking Cl as an example, the average concentration increases from 4.3 mg/L at Fort McMurray to 20.6 mg/L at Old Fort. Jasechko et al. (2012) applied a monthly Cl mass balance between upstream and downstream river stations using LTRN data to estimate the volume of saline water added on the reach. They used monthly mean values of Cl in river water observed over a total of 76 months during 1990–2008 and an estimate of the Cl content of saline inflow sources, which were estimated to range between 2200 and 15 000 mg/L, with a mean value of 7000 mg/L. Jasechko et al. (2012) reported that saline groundwater input was likely between 43 000 and 294 000 m^3/day or 0.1%–3% (mean of 0.28%) of river discharge, values that take into consideration road-salt additions. Gue (2012), who conducted a similar analysis using a chlorine stable isotope mass balance, determined groundwater input on the Fort McMurray – Old Fort reach to be 8500 m^3/day, although only Devonian groundwater sources and a limited isotopic dataset were considered in the calculation. Gue (2012) concluded that lower flow rates calculated in her study relative to Jasechko et al. (2012) may reflect the fact that only saline water from Devonian carbonates was considered. She also cautions that small differences observed in upstream and downstream values of chlorine-37 and other assumptions used in the model lead to high uncertainty of 50%. Gue (2012) also presented evidence that saline discharge can be very localized, as three sampled springs were estimated to account for between 10% and 30% of total groundwater inputs on the reach. Jasechko et al. (2012) also tested a hypothetical tailings-pond leakage scenario and concluded that not more than 1 of 18 mg/L average Cl additions on the reach could potentially be related to tailings-pond sources.

Based on a more complete dataset of McMurray and Devonian formation groundwaters taken from CEMA (2010*a*), we obtain new estimates of the average Cl concentrations of formation water in the region. As shown in Table 1, McMurray and Devonian formation waters are found to have average Cl values of 10 409 and 41 374 mg/L, respectively. Applying the Cl mass balance model of Jasechko et al. (2012), data for Cl, and using these new groundwater values to constrain the range of saline input sources, we obtain an estimate of average saline groundwater inflow of between 16 000 and 62 000 m^3/day (0.05%–0.19% of river discharge) over a 76 month period, which is intermediate between estimates of Gue (2012) and Jasechko et al. (2012). However, caution should be used when interpreting these results, as Cl data for saline formations is significantly positively skewed. Overall, despite differences in amount of saline groundwater input predicted by these studies, there is consensus that significant saline groundwater discharge is occurring along the reach. Defining groundwater mixing end-members remains one of the principle challenges in application of such mass balance techniques.

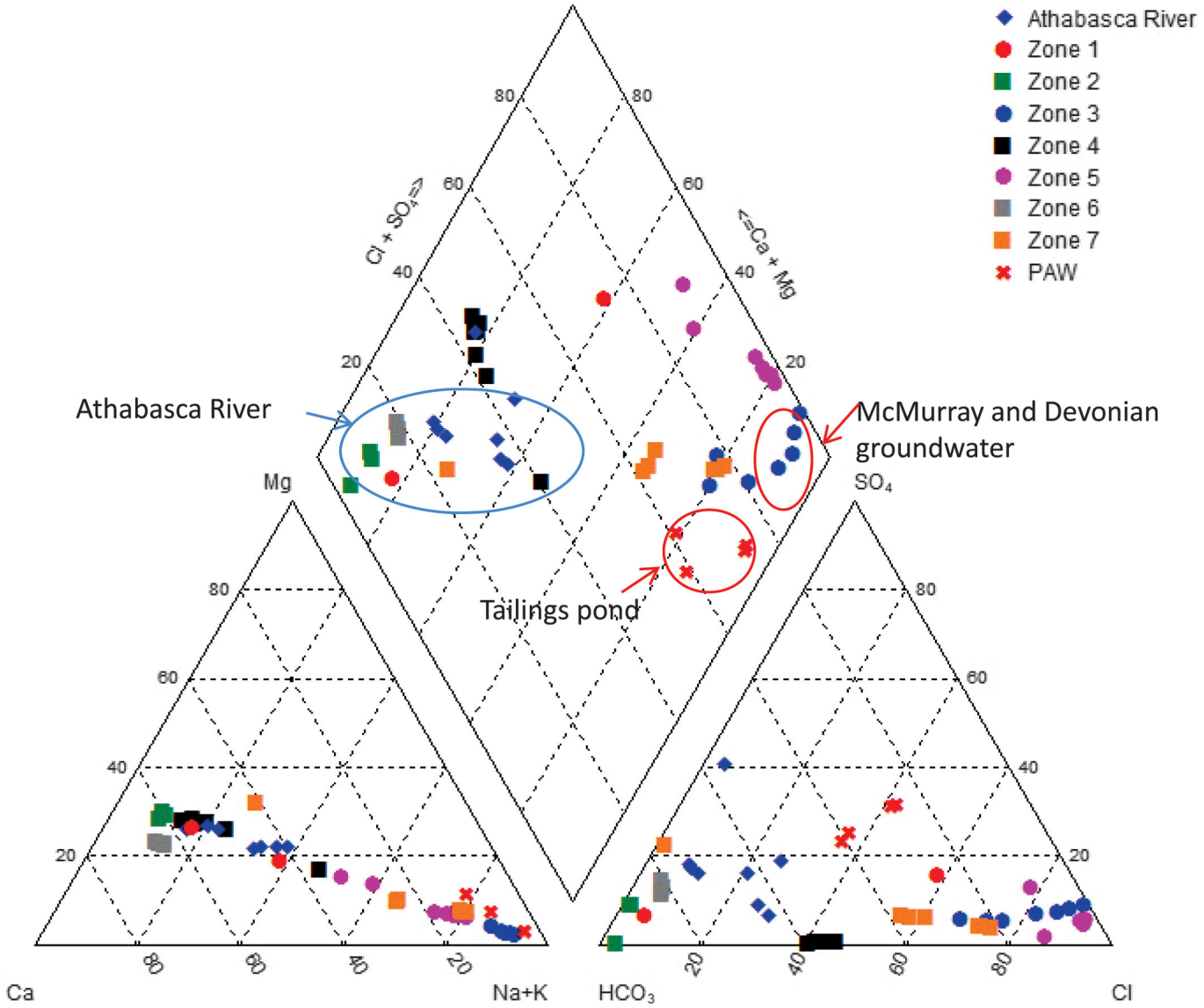
Electromagnetic survey evidence

The terrain EC in the riverbed generally ranges from <40 to >180 millisiemens per metre (1 mS/m = 10 × μS/cm). The results are presented as a colour gridded map with warm colours (yellows and reds) representing high terrain EC values while cool colours (blues) represent low terrain EC values (Figs. 4, 5). The electromagnetic surveys reveal considerable variation in the terrain EC of the riverbed along the survey reach. In general, background values are less than ~40 mS/m, as observed over most of the southern 70 km survey reach from S05 to S09, and in the 10 km reach north of S01, with slightly higher values of 40–60 mS/m observed over the ~10 km reach between S01 and S02 and the ~20 km reach between S04 and S05. High terrain conductivity values, >80 mS/m, were noted at sampling locations S01, throughout the interval between S02 and S04 (Zone 1 in the follow-up survey; see Fig. 6), and near S05 (Zone 3), as well as at more localized points along the river including locations S06 through S10, Zone 2 and Zones 4 through 7. Overall, high terrain EC is interpreted as an indicator of saline water in the hyporheic zone in the upper few metres below the riverbed.

The reach of higher terrain EC values noted between S02 and S04 (Zone 1) corresponds to subcropping of the Devonian Waterways Formation (Fig. 6) and as such is likely reflective of discharge of saline groundwater from this bedrock formation. Another broad zone of high terrain EC extending ~7 km in length is noted at S05 (Zone 3) where the McMurray Formation subcrops the Athabasca River (Fig. 6). Here, discharge from the McMurray Formation is inferred to be the source of the hyporheic zone water, although this is challenged to some extent later on when looking at the water chemistry. In contrast to the larger inferred saline groundwater seepage areas associated with the S01–S05 interval, including Zones 1 and 3, the geophysical anomalies associated with the S05–S09 interval, including Zones 4 through 7 are centred on isolated points or on lineal features attributed to locations of focused saline groundwater discharge along the riverbed. Given these patterns, the extent of groundwater seepage appears to be strongly influenced by the degree of incision into the lower Cretaceous and Devonian strata by the Athabasca River, with the most continuous zones of seepage seemingly occurring in northern reaches where McMurray and Devonian formations are most deeply incised.

High-resolution terrain EC surveys give a better perspective of the occurrence of the high-salinity water in selected areas, as shown for Zone 1 between S02 and S04 (Fig. 5).

Fig. 7. Piper plot showing major ion geochemistry of river water, hyporheic zone porewaters, and characteristic ranges for Athabasca River water (Jasechko et al. 2012), Cretaceous and Devonian formation waters (Ozoray 1974; Lemay 2002; CEMA 2010*a*, 2010*b*), and process-affected water (PAW) from oil sands tailings ponds (Gibson et al. 2011). Please see online version for colour.



The occurrence of saline water in the riverbed hyporheic zone is further verified by collecting porewater at selected locations, as described in the following section.

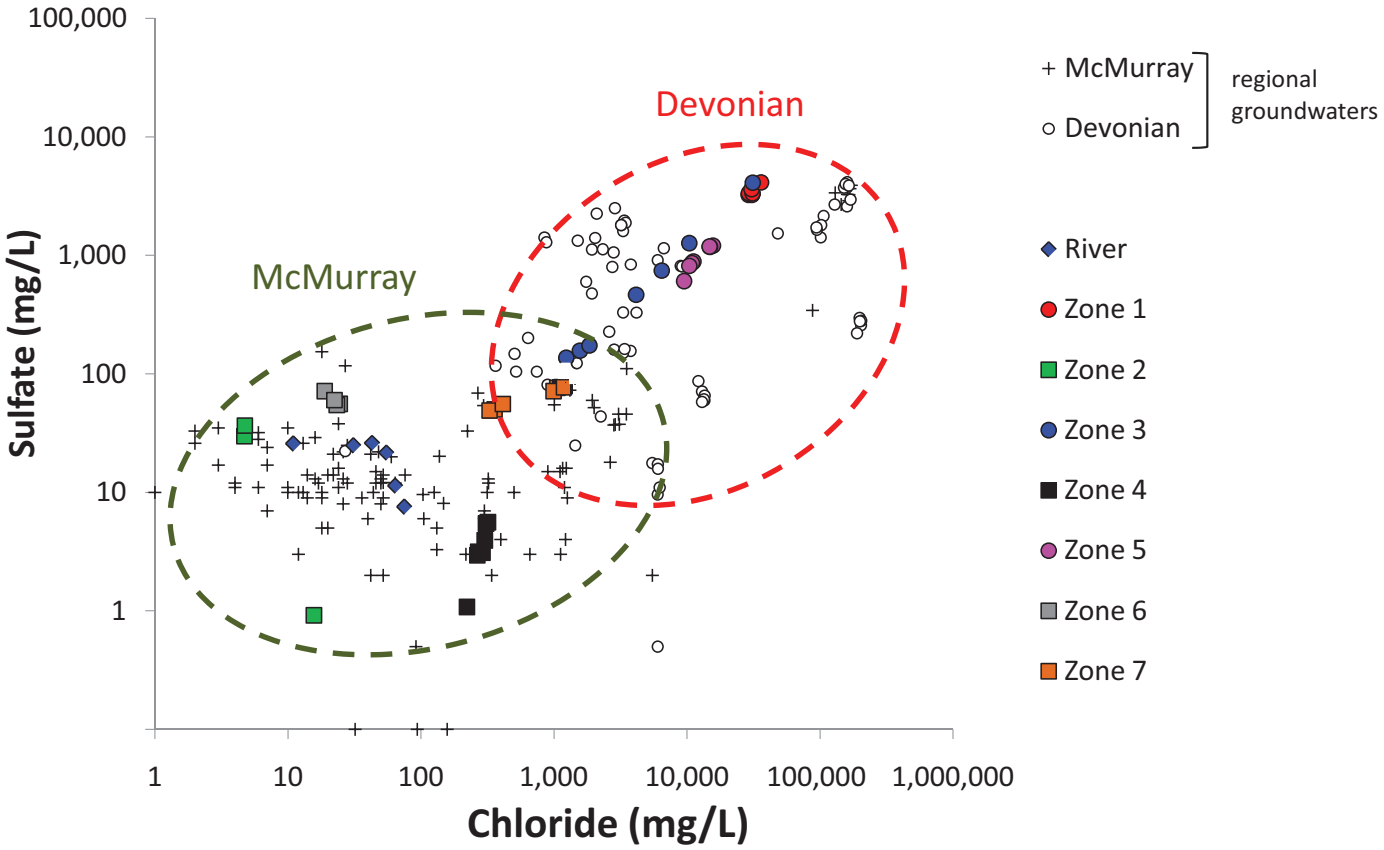
Porewater geochemistry evidence

Table 1 provides a summary of selected geochemical and isotopic data for river water, groundwater, and hyporheic zone (riverbed porewater) samples. A comprehensive summary of the geochemistry of porewater from this survey, along with a number of samples of river water, oil sands process-affected water, and new groundwater samples is provided as supplementary material.[1]

In general, porewater collected in areas of high terrain conductivity was found to have considerably higher EC values than the overlying river water (Table 1). While considerable variability is noted in porewater from zone to zone (Table 1), higher TDS (up to 65 000 mg/L), Cl (up to 36100 mg/L), and lower $\delta^{18}O$ values more typical of local formation water were noted for most profiles. The low $\delta^{18}O$ values and high salinities measured in these waters are fairly representative of formation waters of glaciogenic origin formed by dissolution of the Devonian-age evaporites by recharging meltwater during the last glaciation. This glaciogenic signature has commonly been observed in saline groundwater near the terminus of the Western Canada Sedimentary Basin (Grasby and Chen 2005). Glaciogenic waters are distinct from basinal brines, the latter having similarly high salinity values but enriched $\delta^{18}O$ values (~0 ‰) that are representative of seawater trapped during sedimentation (i.e., connate water). It is also important to note that naphthenic acids were also present in all hyporheic zone

[1]Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjes-2013-0027.

Fig. 8. Sulfate and chloride concentrations in seepage zones tested along the Athabasca River compared with regional groundwater. Groundwater data are taken from CEMA (2010*a*). Please see online version for colour.



porewaters, and naphthenic acid concentration in Athabasca River waters was found to increase along the survey reach (Table 1).

Depth profiles of geochemical parameters measured on porewater within the 3 m depth interval below the riverbed sediment – water interface confirm that saline water is present in the hyporheic zone in many locations including Zones 1, 3, 5, and to some extent Zone 7 (see Fig. 6), and we attribute this to upward seepage of saline groundwater and mixing with Athabasca River water. However, geochemical gradients observed at Zone 6 (also Zones 2 and 4, not shown) are less convincing of the presence of saline groundwater seepage. We attribute this either to weak gradients or to upwelling of more dilute groundwaters likely associated with late Cretaceous formation waters or shallower groundwaters, as some isotopic contrast is still maintained (Fig. 6).

Groundwater sources

There are several characteristics of these zones of groundwater seepage that strongly suggest natural sources from late Cretaceous and Devonian formation waters. These include the physical setting of the seepage zones, the broad occurrence of these zones especially along the northern reaches of the EM survey, and their location above saline water-bearing formations as opposed to being in close proximity to oil sands tailings ponds and other development features in the area. In fact, measured EC and TDS values of the porewaters collected from these seepage zones are greater than any of the tailings ponds that might be considered potential anthropogenic sources (e.g., see Gibson et al. 2011).

Groundwater in this area from the McMurray Formation has a fairly large range in TDS and Cl, with TDS ranging up to 280 000 mg/L and Cl ranging up to 170 000 mg/L (Table 1). Similar ranges were reported by Hackbarth and Nastasa (1979). The higher-TDS waters from this formation typically have a Na–Cl composition (Ozoray 1974; Lemay 2002), but some Na–HCO_3-type waters have also been described in more dilute samples. Groundwater from Devonian formations along this reach of the Athabasca River are characterized by higher TDS and Cl than the overlying McMurray Formation, with TDS ranging up to 400 000 mg/L and Cl ranging up to 200 000 mg/L (Table 1; see also Hackbarth and Nastasa 1979), and are typically Na–Cl-type waters. Relative abundance of major ions in the river waters and porewaters (see data provided as supplementary material[1]) are compared with reported ranges of Devonian and McMurray formation groundwaters (Ozoray 1974; Lemay 2002; CEMA 2010*a*, 2010*b*) to illustrate the relationship between waters that influence the hyporheic zone of the river (Fig. 7). As shown, porewaters collected during this survey from Zones 1, 3, and 7 plot clearly along a mixing line between river water (Ca–Mg–Na–HCO_3 type) and McMurray and Devonian formations (Na–Cl type), which provides further evidence that these formations are the source of water sampled in the hyporheic zone. Less influence from these formations is evident for porewaters collected in Zones 2, 4, and 6, which are found to be more similar to the ranges found in Athabasca River water in this study (blue triangles, Fig. 7 (colour can be viewed in online version)) as well as reported ranges from the LTRN for the Athabasca River at Fort McMurray and Old Fort (ellipse labeled Athabasca River, Fig. 7) (see also Jasechko et al. 2012, their fig. 4). Relative abundance of major ions in Zone 5, while showing significant trends towards McMurray and Devonian groundwater sources, appear to be unique in that they are typically more calcium-rich than expected due to simple mixing with Athabasca River water (Fig. 7). We attribute this to calcium buildup in the hyporheic zone possibly similar to the situation noted by Jin et al. (2010) for groundwater–surface-water mixing

zones in streams with geologic settings containing gypsum. We also note a distinction between formation waters and process-affected water (PAW) from local tailings ponds in that the former tend to have Cl as the dominant ion. The tailings pond waters differ from both the porewaters and formation waters in their more mixed anion compositions.

The Cl and sulfate (SO_4) concentrations can be used to further separate McMurray and Devonian groundwater sources. Figure 8 shows a cross-plot between Cl and SO_4 concentrations (in log–log scale presentation) for groundwater samples collected from regional monitoring wells across the study area (CEMA 2010*a*). Two relatively distinct groupings of groundwater are evident — one associated with the Devonian formations (i.e., comparatively higher Cl and SO_4 concentrations) and the other associated with the McMurray Formation of Cretaceous age (i.e., comparatively lower Cl and SO_4 concentrations). This may be explained by the difference in lithology of the two intervals, that is, the presence of extensive evaporite minerals (e.g., halite and anhydrite) in the Devonian compared with the clastic-dominated Cretaceous formations. Also shown are porewater and surface water samples collected at the various stations investigated as part of this study. Compared with these two distinct fields, water samples from the Athabasca River plot tightly in the centre of the McMurray field, as do porewater samples from Zones 2, 4, and 6, implying a link to waters originating from that formation or shallower Cretaceous-age formations with similar water chemistry. In contrast, porewaters from Zones 1, 3, and 5 plot within the Devonian field, implicating groundwater emanating from these deeper, more saline, formations. Of note are samples associated with Zone 7 and to some degree Zone 3, which plot in an area of overlap between the Devonian and McMurray fields. While Zone 3 overlies the McMurray Formation, this formation is apparently not the main source of saline water at this location. This configuration suggests the occurrence of mixing phenomena and further reinforces the complex character of the region with respect to cross-formational flow conditions.

Conclusions

Observed and reported springs and seeps, significant increase in dissolved constituents along the river between Fort McMurray and Old Fort, electromagnetic surveys, and porewater sampling all suggest that saline groundwater seepage is occurring along the Athabasca River in the oil sands mining region. The most prevalent areas of seepage occur slightly downstream (north) of active oil-sands development in areas underlain by McMurray and Devonian subcrop. Natural sources of groundwater input to the river, although relatively small from a volumetric perspective, could have a significant impact on surface water quality on the reach due to their high salinity and high organic content.

Apart from river deltas and low-lying coastal plains where saline water sources are commonly encountered due to seawater intrusion (see de Louw et al. 2013), there are many examples of large rivers where naturally occurring saline groundwater discharge has a significant impact on river water quality. Some examples include the Rio Grande (Moore et al. 2008), Murray (Mosley et al. 2012), Darling (Meredith et al. 2009), Jordan (Farber et al. 2004), and Swan-Avon rivers (Degens et al. 2012). Saline groundwater and brines are also common features of many oil fields which are primarily located in modern or ancient sedimentary basins where trapped seawater or evaporite deposits may be present (see Gupta et al. 2012). In most cases, input of saline groundwater leads to higher river salinity during low-flow periods as observed for the lower Athabasca River. It is important to note that the proportion of saline groundwater inputs in these studies was found to be susceptible to groundwater development, water management strategies, historic land use patterns, and climatic change. For the lower Athabasca region, contributions of saline groundwater may therefore be affected by river water abstraction for oil sands production, groundwater dewatering or development for in-situ oil sands extraction, or deep-well brine disposal.

There is considerable discussion and controversy raised at present over the role of anthropogenic sources of contaminants from oil-sands development on downstream river water quality and chemical conditions in the Peace–Athabasca delta. This study provides a refined description of the widespread occurrence of probable natural seepage from the bedrock formations that needs to be considered when discussing water quality management in the region. While this study provides significant evidence that natural sources of salinity are being added to the river (including both point and non-point sources), the ability to quantify and evaluate proportions of natural and anthropogenic sources of salinity and organics where they may co-exist is complicated and will require further development of more specialized geochemical and isotopic tracers, as well as geophysical methods. Ongoing work is aimed at further characterization of natural and anthropogenic constituents associated with oil-sands processing, including a more complete understanding of the flux and loading of constituents to the Athabasca River and ultimately the Peace–Athabasca delta. Further assessment of river seepage sources and mixing is also underway using an array of solute isotope and organic profiling data collected during this survey.

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