Influence of saline groundwater discharge on river water chemistry in the Athabasca oil sands region – a chloride stable isotope and mass balance approach

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Abstract

A chloride mass and stable isotope ($\delta^{37}Cl$) balance approach was employed to calculate the effect of saline groundwater discharge into the Athabasca and Clearwater rivers in the Athabasca Oil Sands Region (AOSR) in north-eastern Alberta, Canada. Saline groundwater affected by halite, carbonate, and anhydrite dissolution discharges Na-Cl type water with total dissolved solids (TDS) up to 51,700 mg/L from exposed Devonian and Cretaceous units in the river valleys in this area. In this study, nine springs of groundwater with median Cl concentration of 9800 mg/L were sampled and chloride stable isotope ratios were determined, with $\delta^{37}Cl$ values ranging from 0.2 to 1.0‰. In contrast, river waters had historical monthly median Cl concentrations between 5.9 and 49.5 mg/L and $\delta^{37}Cl$ values between -2.2 and -1.4‰. The discharge rate of saline groundwater was calculated to be 100 ± 20 L/s into the Clearwater River and 134 ± 68 L/s into the Athabasca River. The chemical composition and discharge rates of saline groundwater were used to estimate its contribution to the mass fluxes of major ions, metals, and PAHs in the Athabasca and Clearwater rivers. Overall, saline groundwater contributed less than 0.2% of river discharge, but 0.04 to 39% of major ion concentrations in the rivers, with highest contributions under winter low-flow conditions. In the Clearwater River, saline groundwater contributed 23-39% of average monthly Cl flux and 18-32% of average monthly Na flux. For the same major ion fluxes in the Athabasca River, saline groundwater contributed 12-18% and 6-12%, respectively. The influence of saline groundwater discharge on the mass flux of trace elements in the rivers was found to be negligible, contributing less than 1% of river fluxes of Cu, Ni, Pb, and Zn. Similarly, the influence on mass flux of PAHs in the rivers was found to be negligible (<0.03%) but quantifiable. These results provide important insights on the natural contributions of saline groundwater discharge to river chemistry in the AOSR, a necessary factor to consider when monitoring for anthropogenic effects of oil sands development on river water quality.

1. Introduction

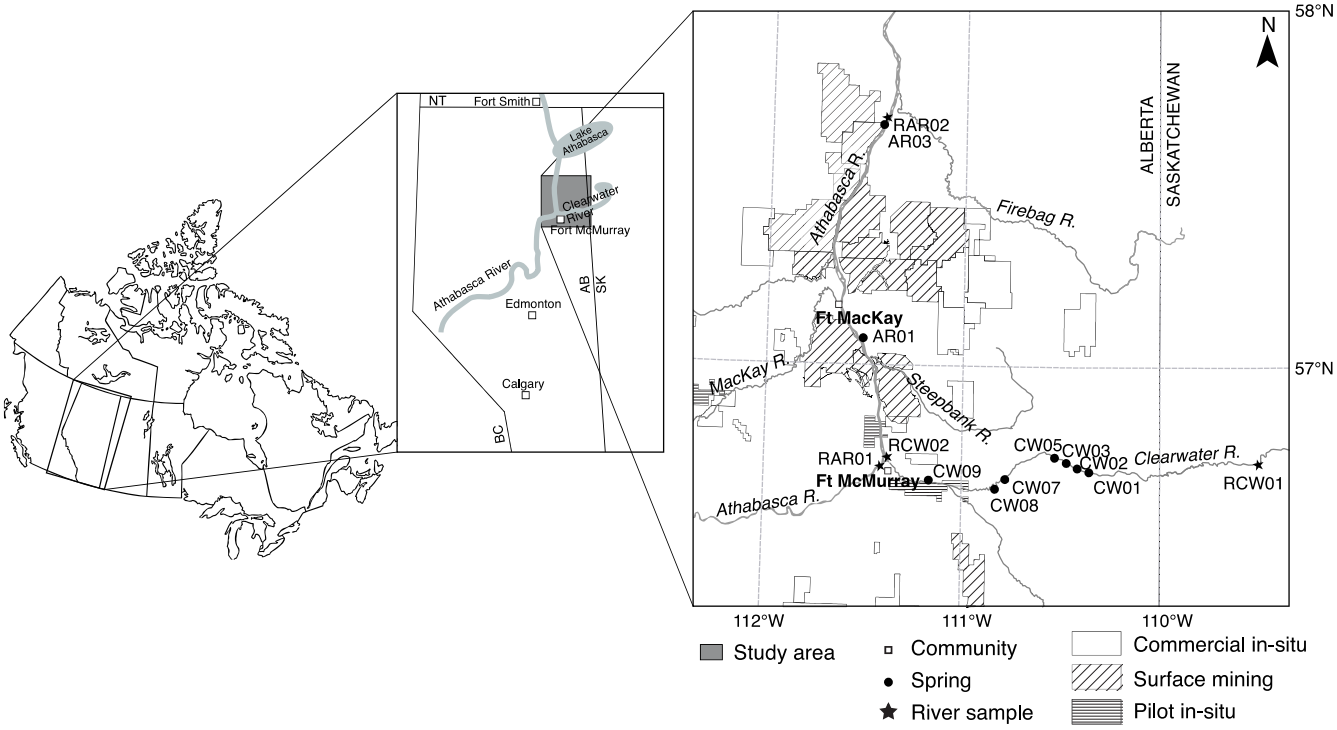
With remaining estimated reserves of 23.92 billion barrels (AER, 2016), the Athabasca oil sands region (AOSR) in north-eastern Alberta, Canada, is one of the world's largest proven crude oil reserves. Bitumen production in Alberta continues to increase (AER, 2016) and rapid development of this resource has raised concerns over potential negative impacts on water quality in the region (e.g. Kelly et al., 2009; Timoney and Lee, 2009; Kelly et al., 2010; Kurek et al., 2013). Of principal concern is the Athabasca River, Alberta's longest waterway, which flows north through several oil sands mining and in-situ developments in the AOSR and eventually discharges into the UNESCO World Heritage designated Peace-Athabasca Delta on Lake Athabasca. Also of concern is the Clearwater River, a Canadian Heritage River that lies south of the major oil sands mining developments of the AOSR and north of some in-situ developments. The Clearwater River joins the Athabasca River at the town of Fort McMurray (Fig. 1). Monitoring of surface water quality is a highly desirable component of responsible resource development in this region.

Within the AOSR, a simple comparison of upstream and downstream river water quality is not sufficient to identify effects of oil sands development, as natural changes in river water quality may result from saline groundwater input to the rivers. High permeability Devonian carbonate formations exposed at river level discharge naturally saline waters with total dissolved solids (TDS) reaching 72,000 mg/L via numerous springs (Gue et al., 2015; Hitchon et al., 1969; Ozoray et al., 1980; Grasby and Chen, 2005), riverbed seepage (Gibson et al., 2011; 2013), and fens (Stewart and Lemay, 2011). This discharge includes several known compounds of concern for human and environmental health such as As, Pb, Ni, Zn, phenanthrene, and naphthalene (Gue et al., 2015). Quantifying natural contributions of saline groundwater to the chemical load of the Athabasca River and its tributaries is an essential pre-requisite for determining true anthropogenic impacts to water quality related to industrial development

in the region. Effective tracer approaches are required to help elucidate these natural versus anthropogenic contributions affecting water quality of the riverine systems.

The conservative nature of chloride stable isotopes allows the fraction of Cl in the river water derived from groundwater to be determined through an isotopic mixing model. The natural sources of Cl to inland rivers are limited to precipitation and groundwater inputs (Jasechko et al., 2012) which have distinct δ^{37}Cl values. Fractionation of Cl isotopes does not occur biologically but only through physical processes such as brine evaporation and salt deposit formation (Clark and Fritz, 1997). Halites precipitated from seawater (δ^{37}Cl = 0‰), and their dissolution waters, are enriched in ^{37}Cl (Kaufman et al., 1984; Eggenkamp et al., 1995), with δ^{37}Cl values ranging from 0.4 to 0.6‰ or higher (up 1.0 ‰) given repeated cycles of evaporation and mineral precipitation (Eastoe and Peryt, 1999; Eastoe et al., 2007, Luo et al., 2014). The Cl in atmospheric deposition is largely sourced from marine aerosols, the acidification of which causes fractionation of Cl isotopes, resulting in δ^{37}Cl values of less than 0‰ (Volpe et al., 1998; Koehler and Wassenaar, 2010). If anthropogenic contributions of Cl are minimal, a two end-member mixing model of these two δ^{37}Cl sources can be employed to determine their relative contributions to riverine Cl flux.

The objective of this study was to use a novel chloride stable isotope and mass balance approach to estimate the discharge rates as well as mass fluxes of major ions, trace elements, and PAHs from naturally occurring saline groundwater into the Clearwater and Athabasca rivers. In conjunction with historical river discharge and water quality data, this approach allowed an estimate of the natural influence of saline groundwater on the water quality of the Athabasca and Clearwater rivers.



(page width) Figure 1: Location of the study area in northeastern Alberta, showing spring and river sampling locations, after Gue et al. (2015). Oil sands development extent of active and approved projects as of December 2013 is also shown (Alberta Environment and Parks (AEP), 2016).

2. Study Area

2.1. Geography

The study area is defined by the Clearwater River to the south, the edge of the Canadian Shield to the east, the Athabasca River to the west, and the Firebag River to the north (Fig. 1). The Athabasca and Clearwater river valleys incise 60 to 150 m below the boreal plains topography of north-eastern Alberta. Two settlements, the municipality of Fort McMurray and the hamlet of Fort MacKay, are located on the shores of the Athabasca River. A road connects Fort McMurray and Fort MacKay on the west side of the Athabasca River, but there is no road access along the Clearwater River beyond Fort McMurray.

The Clearwater River corridor is relatively undisturbed, though in-situ oil sands development occurs to the south. The Athabasca River, however, flows through several developed areas as it meanders 1375 km from the Columbia Icefields in the Canadian Rocky Mountains to Lake Athabasca. Conventional oil and gas developments, forestry, coal mining, municipalities, agriculture, commercial fishing, and trapping all occur upstream of the study area, and extensive oil sands mining operations are located along the river downstream of Fort McMurray (MRBB, 2004).

2.2. Hydrogeologic Setting

The study area is situated on the north-eastern edge of the Alberta Basin, within the Western Canada Sedimentary Basin (WCSB). Here, Cretaceous sediments lie unconformably over a wedge of southwest-dipping Paleozoic strata, which cover the crystalline Precambrian basement of Canadian Shield rocks. Pleistocene glacial drift overlies the entire area, which is in turn covered by muskeg and boreal forest (Carrigy, 1973).

The hydrostratigraphy in this region was described by Bachu et al. (1993) and includes three main aquifer systems (Fig. 2). The early- to mid-Devonian Elk Point Group is carbonate-dominated but includes beds of almost pure halite up to 76 m thick, that form the Prairie Evaporite Formation (Meijer-Drees, 1986). Stratigraphic evidence shows that salt units have dissolved since Devonian time, forming overlying dissolution collapse structures (Broughton, 2013). The saline springs of this study are generally located east of the modern dissolution edge (Fig. 1). The Elk Point Group as contains the Contact Rapids – Winnipegosis carbonate aquifer system, classified as a regional flow system driven by recharge in the Rocky Mountains (Bachu et al. 1993). The later Devonian Beaverhill - Cooking Lake carbonate karstic aquifer system, from which the springs investigated in this study emerge, was described by Bachu et al. (1993) as an intermediate to local flow system with underlying regional flow

patterns affected by local topography. Clastic-dominated Cretaceous sediments host the McMurray Wabiskaw aquifer/aquitard system, a local flow system completely driven by local topography.

Period	Group	Formation	Hydrostratigraphy
Quaternary		Pleistocene deposits	aquifer
Cretaceous	Colorado	Colorado shale	Colorado aquitard system
		2nd White Specks	
		Base of Fish Scales	
		Viking	
		Joli Fou	
	Mannville	Grand Rapids	aquifer
		Clearwater	aquitard
		McMurray	McMurray-Wabiskaw aquifer/aquitard system
	sub-Cretaceous unconformity		
Devonian		Wabamum	Winterburn-Wabamum aquifer system
		Winterburn	
	Woodbend	Upper Ireton	aquitard
		Grosmont	aquifer
		Lower Ireton	aquitard
		Cooking Lake	Beaverhill Lake - Cooking Lake aquifer system
	Beaverhill Lake	Waterways	
		Slave River	
		Fort Vermillion	Prairie - Watt Mountain aquitard system
	Upper Elk Point	Watt Mountain	
		Prairie Evaporite	
		Winnipegosis (Keg River)	Contact Rapids - Winnipegosis aquifer system
	Lower Elk Point	Contact Rapids	
		Ernestina Lake Upper Lotsberg Lower Lotsberg	Lower Elk Point aquitard - aquiclude system
		Basal Red Beds	Basal aquifer
Precambrian granitic bedrock			aquiclude

(1 column width) Figure 2: Generalized hydrostratigraphy in NE Alberta. Devonian carbonates that host the saline springs investigated in this study are shaded. Modified from Bachu and Underschultz (1993).

Other research has shown that the aquifer systems of the WCSB have never been fully flushed by meteoric water as would be expected from regional to local flow systems, but rather the apparent basin-scale flow regime in the WCSB is a transient response to deglaciation, and the basin has not yet reached equilibrium (Grasby et al., 2000; Grasby and Chen, 2005). Evidence based on stable isotope ratios shows that subglacial meltwater was forced into the subsurface in the AOSR area during the last glacial period and that it is the return flux of this water, having dissolved bedded evaporites in the subsurface,

that emerges as saline springs in the Clearwater and Athabasca river valleys today (Grasby and Chen, 2005; Gue et al., 2015).

2.3. Saline Springs

Saline springs in the AOSR have long been known, used as a source of salt by aboriginal peoples and later by voyageurs of the Hudson Bay Company. Bell (1884) wrote of cold mineral springs along the Clearwater River, and suggested that "copious" springs and seeps of varying sizes may have an effect on the river water chemistry. Bell (1884) also described the salt deposits at La Saline, a spring on the east bank of the Athabasca River labeled AR01 in this study. The saline springs in this region have been mentioned in several subsequent reports (Carrigy and Mellon, 1959; Norris, 1973; Hitchon et al., 1969; Grasby 2006). More recently, Stewart and Lemay (2011) reported on the general chemistry and isotopic composition of saline fens along Salt Creek, just south of the study area, which showed some similarities to the springs of this study. Gibson et al. (2011) reported on the geochemistry and isotopic composition of riverbed saline groundwater seeps along the Athabasca River within the study area, which were identified through a waterborne electromagnetic (EM) terrain conductivity (WorleyParsons, 2010). No EM imaging is available for the Clearwater River, but given the similar geologic and physical setting, it is reasonable to expect similar riverbed seepage in this river. Gue et al. (2015) demonstrated that the discharge of saline waters in the study area constitutes a previously unrecognized natural contribution of numerous compounds of concern to the surface water environment, including trace metals and PAHs.

The flow rate of saline groundwater into rivers in the AOSR is difficult to measure given the various forms of discharge (riverbed seeps, fens, springs). Jasechko et al. (2012) used a Cl mass balance approach to quantify the flow of all forms of saline groundwater seepage, from both Devonian and

Cretaceous formations, as 0.1 to 3% of the discharge of the Athabasca River over a reach extending north and south of the present study area. Here, we use stable chlorine isotope ratios in a novel approach to gain new knowledge about the discharge and influence of saline groundwater seepage on river water chemistry of the Athabasca and Clearwater Rivers in the AOSR.

3. Sampling and Methods

In this study, we sampled waters from saline springs and the Clearwater and Athabasca Rivers for chemical and isotopic analyses. The obtained results were augmented with chemistry data for the springs reported by Gue et al. (2015), as wells as publically available flow and water chemistry data to achieve robust mass and isotope balances for chloride.

3.1. Compilation of element fluxes in rivers

To determine the mass fluxes of elements in rivers, monthly flow and chemistry data were compiled from a series of publically available databases. These included historic river chemistry records from the Regional Aquatics Monitoring Program (RAMP) for station CLR-1 on the Clearwater River (RAMP, 2012) and from the Alberta Long Term River Network for the Athabasca River at Old Fort station (AB07DD0010) (AEP, 2013). Historic mean monthly river discharge for both rivers were derived from Water Survey of Canada records (Environment Canada, 2016) which were available for 2001 to 2011 for the Clearwater River at Draper (station ID 07CD001) and for 1971 to 1984 for the Athabasca River at the Embarras airport (station ID 07DD001). The locations for measurement of river water chemistry and flow were not consistent: on the Clearwater River, flow was measured 7 km upstream from the water quality sampling site; however, there are no major tributaries between the two locations allowing a reliable determination of mass fluxes of elements and compounds (Grasby et al.,

181 1999). This was also the case for the Athabasca River, where flow was measured 25 km upstream from
182 the water quality sampling site, with no major tributaries between the two locations.

183 **3.2. Sample collection**

184 To characterize the chemical composition of groundwater discharging into the river system, nine
185 springs were sampled in October 2010: seven in the Clearwater River valley and two in the Athabasca
186 River valley (Fig. 1). Springs were sampled as close to the source as possible. If the site was a seep, or
187 meadow with multiple pools, the pool with the highest electrical conductivity was sampled. River water
188 samples were taken upstream and downstream of the sampled springs on both rivers in October 2010
189 (Fig. 1) for chemical and Cl stable isotope analysis. The Clearwater River upstream site (RCW01) was
190 located on the south shore at the edge of the Canadian Shield in Saskatchewan, just before the river
191 begins to incise through Devonian carbonate rocks. The downstream site (RCW02) was located 165 km
192 (run-of-river) west, on the north shore of the Clearwater River just before the confluence with the
193 Athabasca River. The Athabasca River upstream site (RAR01) was located just before the town of Fort
194 McMurray and was accessed by road. The downstream site (RAR02) was located 114 km (run-of-river)
195 north, at the southern tip of an island. At river sites, a grab sample was taken by hand at about 20 cm
196 depth after wading from shore as far as possible into the main flow. Field measurements of temperature
197 and pH were taken on site directly in the springs and rivers at the sampling location. Samples were
198 filtered using 0.45 μm nitrocellulose membrane filters and preserved where necessary, then kept cool
199 during transport to the laboratory for subsequent chemical and isotopic analyses.

3.3. Chemical analysis

Full details on field sample collection, analytical methods, and results for isotope and chemical analysis of spring waters are reported in detail in Gue et al. (2015). Briefly, major ion analysis was conducted at the University of Calgary Applied Geochemistry Group (AGg) laboratory. Cation concentrations were determined by atomic absorption spectroscopy. Anion concentrations were determined by ion liquid chromatography for Cl and SO_4 and automated titration for HCO_3. For all major ion analyses the detection limit was 1 mg/L and measurement uncertainty was ±5%.

Trace element and PAH concentrations were analyzed at Environment Canada's National Laboratory for Environmental Testing (NLET). Trace element concentrations were determined using an inductively coupled argon plasma collision/reaction cell mass spectrometer (CRC-ICP-MS), with detection limits ranging from 0.0005 to 0.5 µg/L. PAH concentrations were determined after extraction and fractionation using single column capillary gas-liquid chromatography, with detection limits ranging from 2.95 to 24.1 ng/L.

3.4. Cl stable isotope determination

To isolate chloride for stable isotope analysis, silver chloride was precipitated from sample waters at the University of Calgary. This precipitate was converted to methyl chloride, from which $^{37}Cl/^{35}Cl$ ratios were determined at the National Water Research Institute (NWRI) in Saskatoon, Saskatchewan, using CF-IRMS as described by Wassenaar and Koehler (2004). An area-peak linear correction was applied to correct for preferential ionization of ^{35}Cl. Results are reported in the internationally accepted delta notation in per mil relative to standard mean ocean chloride (SMOC). Measurement uncertainty was ±0.1‰.

3.5. Cl stable isotope mass balance approach: groundwater contribution of Cl to rivers

Our Cl stable isotope and mass balance approach employs two end members: the Cl sourced from precipitation and the Cl sourced from subsurface halite dissolution. In this scenario, the $\delta^{37}Cl$ value observed in the upstream river sample is governed by the Cl isotopic composition of precipitation, surface runoff, and shallow groundwater exhibiting typically a negative $\delta^{37}Cl$ value similar to that of precipitation, the main source of Cl in the upstream watershed. The $\delta^{37}Cl$ value observed in saline groundwater is positive and similar to that of subsurface halites affected by dissolution. Hence, significant inputs of saline groundwater are expected to result in increasing Cl fluxes and increasing $\delta^{37}Cl$ values of chloride between upstream and downstream river sampling stations. The extent of Cl input from saline groundwater can be quantified using isotope and mass balances as follows:

The total Cl in the downstream river sample, F_{ds}, is the sum of the fractions of Cl in the upstream river sample (F_{us}) and in saline groundwater (F_{gw}) entering the river within the study area:

$$F_{ds} = 100\% = F_{us} + F_{gw} \quad (1)$$

Given conservative mixing and no Cl isotopic fractionation, the Cl isotope ratio in the downstream river sample ($\delta^{37}Cl_{ds}$) can be described by a stable isotope mass balance equation, where $\delta^{37}Cl_{us}$ is the stable isotope ratio of Cl in the upstream river sample, and $\delta^{37}Cl_{gw}$ is the isotope ratio of Cl in saline groundwater affected by evaporite dissolution entering the river over the study reach:

$$F_{ds}\delta^{37}Cl_{ds} = F_{us}\delta^{37}Cl_{us} + F_{gw}\delta^{37}Cl_{gw} \quad (2)$$

Combining Equations 1 and 2, the percent of Cl in the river sourced from evaporite dissolution over the study reach can be determined as follows:

$$F_{gw} = 100(\delta^{37}Cl_{ds} - \delta^{37}Cl_{us}) / (\delta^{37}Cl_{gw} - \delta^{37}Cl_{us}) \quad (3)$$

3.6. Discharge rate of saline groundwater

The Cl isotopic mass balance calculations enabled the estimation of the discharge rate of groundwater into the rivers over the study reach. First, the mass flux of Cl in the rivers (Q_{Cl}) was calculated from the median historical Cl concentrations in the rivers (Cl) and monthly average river flow (Q) (Equation 4) for the nearest available month to October, our isotope sampling month. This provides an estimate during river recession towards baseflow but prior to freeze-up when sampling is more difficult.

$$Q_{Cl} = Cl*Q \quad (4)$$

The discharge rate of groundwater (Q_{gw}) was then calculated by dividing the mass flux of Cl attributable to saline groundwater ($F_{gw}Q_{Cl}$) by the median Cl concentration measured in the spring waters (Cl_{gw}):

$$Q_{gw} = F_{gw}Q_{Cl}/Cl_{gw} \quad (5)$$

3.7. Major ion contributions from saline groundwater

The mass flux of Cl from saline groundwater was calculated from the groundwater discharge rate, Q_{gw}, and the median Cl concentration in the springs. The average monthly mass flux of Cl in the rivers was calculated from historical median concentrations and average monthly river discharge. The months which had publically available chemistry data for both rivers represented the annual water seasons: baseflow under-ice conditions (March), spring melt freshet (May), summer high flow (July), and autumn recession (September/October). The proportion of Cl flux in the rivers attributable to saline groundwater in these months was determined from the calculated mass flux of Cl from groundwater, assuming constant flow and chemical composition of groundwater discharge throughout the year. This is consistent with findings of Jasechko et al. (2012) who found that saline groundwater discharge to the Athabasca River from Cretaceous and Devonian units has remained near constant over the last 15 years.

The fraction of other major ions (Na, SO_4, Ca, Mg, HCO_3, and K) in the rivers attributable to saline groundwater discharge over the study area ($FM_{ds\text{-}gw}$) was calculated from the median molar ratio of the concentrations of the major ion (M_{gw}) to Cl (Cl_{gw}) in the spring waters, multiplied by the downstream molar concentration of Cl derived from saline groundwater ($Cl_{ds}F_{gw}$), and divided by the downstream molar concentration of the major ion (M_{ds}):

$$FM_{ds\text{-}gw} = (M_{gw}/Cl_{gw})Cl_{ds}F_{gw}/M_{ds} \quad (6)$$

3.8. Trace element and PAH contributions from saline groundwater

Mass fluxes of trace metals and PAHs from saline groundwater were calculated from Q_{gw} and the median concentrations of these compounds in saline springs reported in Gue et al. (2015). Average mass fluxes in the rivers were calculated from mean monthly river flow and median historic monthly concentrations where available. Historical data for only four of the metals measured in the springs (Cu, Pb, Ni, and Zn) were available for the Athabasca River (AEP, 2013); hence this set of metals was also examined for the Clearwater River (RAMP, 2012). Very little historical PAH data is publically available for the rivers, so concentrations in downstream river samples taken in this study were used with historical river flow to estimate mass fluxes in the rivers during recession.

4. Results

4.1. Spring Geochemistry

Most of the springs investigated in this study have been previously sampled by various researchers. Major ion concentrations of the saline spring waters over time are reported in Table 1.

Figure 3 illustrates that spring water geochemistry is consistent through time and therefore samples obtained in this study can be used to estimate the composition and effect of saline groundwater discharge to river waters over time in the AOSR.

Based on our sampling, discharging spring waters are characterized by low temperatures between 1.0 and 4.8 °C and near neutral pH values between 6.4 and 7.1. The spring waters are all Na-Cl dominated, with calculated total dissolved solids (TDS) ranging from 7,190 to 51,700 mg/L. The Na/Cl molar ratio of ~1 is consistent with dissolution of buried halite beds as a source of salinity (Gue et al., 2015; Grasby and Chen 2005). The spring waters also have appreciable Ca, Mg, and SO_4 concentrations suggestive of both carbonate and anhydrite dissolution in the subsurface (Gue et al., 2015).

(page width) Table 1: Major ion chemistry, temperature, and pH of spring waters through time. TDS was calculated as the sum of these major ions. Data sources: (1) Gue et al. (2015) (2) Grasby (2006), (3) Hitchon et al. (1999), (4) Alberta Research Council unpublished data.

ID	original ID	Year	Temp °C	pH	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	SO_4 mg/l	HCO_3 mg/l	Cl mg/l	TDS mg/L
AR01	La Saline[3]	1965	8.0	7.8	1,830	456	25,600	64	4,780	227	40,200	73,200
	RS96-19[4]	1996	9.8	6.6	1,820	491	26,000	82	4,860	625	32,900	66,800
	AR01[1]	2010	10.5	6.9	1,200	374	17,900	52	4,280	526	27,400	51,700
AR03	RS97-35[4]	1997	-	6.7	39	123	4,510	9	2,610	448	5,530	13,300
	A01-06[2]	2001	5.1	6.8	858	111	4,030	10	2,500	243	6,420	14,200
	AR03[1]	2010	1.7	6.7	867	130	3,990	13	2,500	206	6,170	13,900
CW01	RS94-01[4]	1994	5.0	7.3	190	86	2,460	12	378	388	3,560	7,070
	CW01[1]	2010	1.5	7.0	174	79	2,320	13	522	389	3,690	7,190
CW02	RS94-02[4]	1994	5.1	7.0	427	162	5,570	16	1,080	332	9,160	16,700
	CW02[1]	2010	2.0	6.8	375	147	4,800	17	1,080	332	7,500	14,300
CW03	RS94-03A[4]	1994	6.3	6.8	730	263	8,190	23	2,170	439	11,300	23,100
	A01-01[2]	2001	6.1	6.7	537	182	6,200	15	1,770	358	9,850	18,900
	CW03[1]	2010	2.8	6.8	577	207	6,720	23	1,760	505	10,400	20,200
CW05	RS94-05A[4]	1994	4.0	7.1	400	206	5,060	31	958	525	7,750	14,900
	A01-03[2]	2001	2.3	7.1	333	171	4,130	22	928	393	7,220	13,200
	CW05[1]	2010	1.0	7.1	396	204	5,390	32	1,130	486	8,090	15,700
CW07	RS94-07A[4]	1994	4.0	7.0	443	185	6,620	24	1,180	739	7,930	17,100
	CW07[1]	2010	1.5	7.1	408	177	6,310	26	1,290	752	9,830	18,800
CW08	CW08[1]	2010	4.8	6.9	555	233	8,340	29	1,760	565	12,600	24,100

CW09	RS96-20B[4]	1996	30.4	7.5	233	155	6,410	10	1,320	819	9,070	18,000
	CW09[1]	2010	4.6	6.4	607	245	7,280	22	1,680	538	10,700	21,100

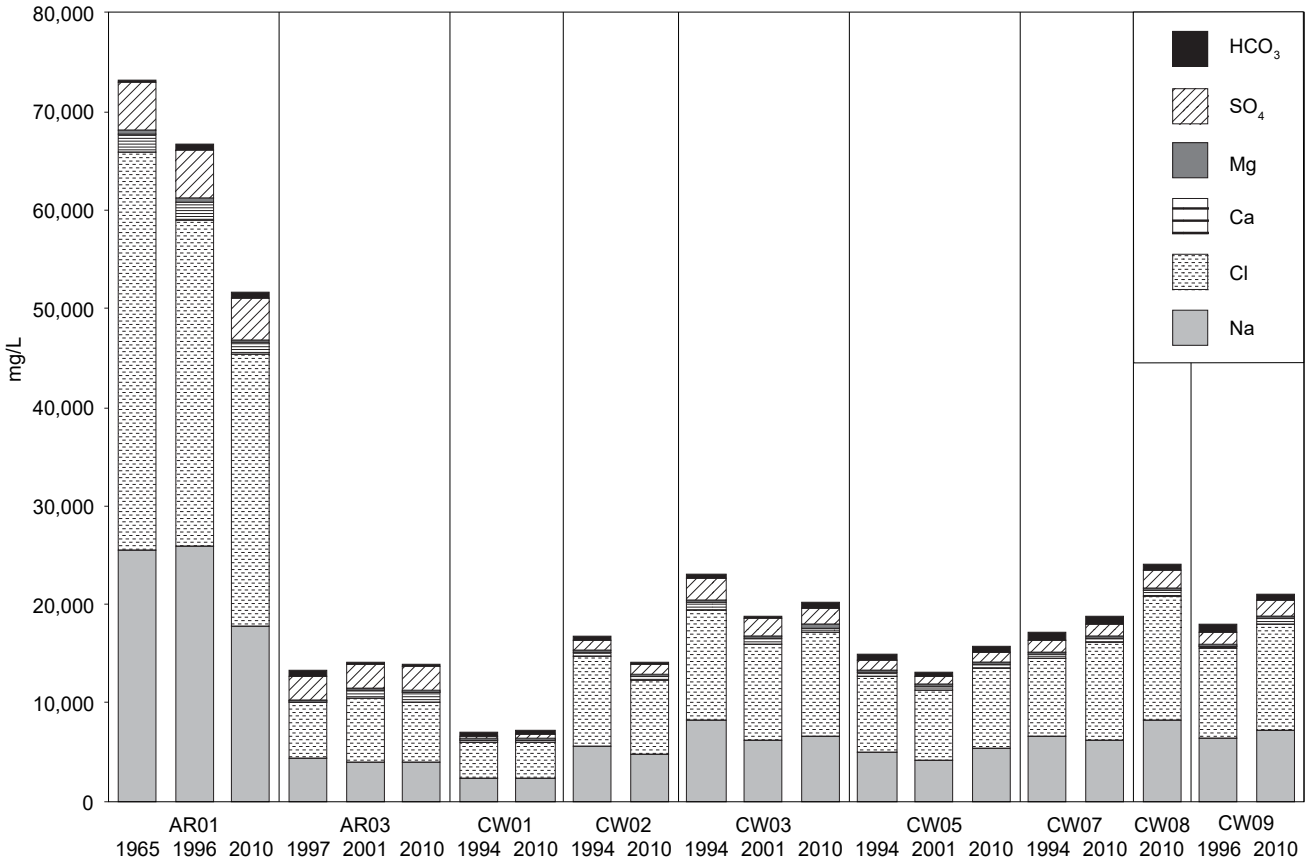


Figure 3: Major ion concentrations in spring waters over time. References are in Table 1.

4.2. River flow and mass flux

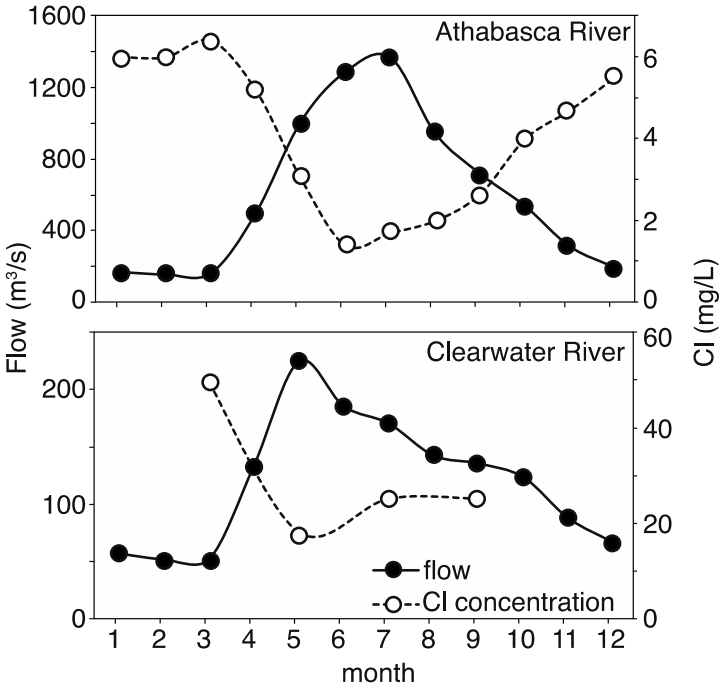
The mean monthly discharge of the Clearwater River at Draper ranged from 51 to 224 m^3/s over the period of 2001-2011 (Environment Canada, 2016). Mean monthly discharge in the Athabasca River at Embarrass ranged from 198 to 1640 m^3/s over the available period of 1971-1984 (Environment Canada, 2016). In both rivers, lowest flows were during under-ice conditions and highest flows were in early summer.

The monthly median concentrations and calculated mass fluxes of major ions in the rivers during baseflow, freshet, high flow, and recession months are listed in Table 2. Concentrations of major ions varied throughout the year, with the highest concentrations in March under baseflow conditions when the rivers are frozen and discharge is lowest. The lowest concentrations generally occurred in May during freshet when snowmelt and spring rains increase river discharge. This is illustrated by a plot of monthly average Cl concentrations in Figure 4. The mass flux of major ions was greatest in July during high summer flow when concentrations of dissolved ions are lower. This is typical of rivers in Alberta where the discharge rate exerts a dominant control over total riverine mass flux (e.g. Grasby et al., 1999). Similarly Grasby and Hutcheon (2000) show that significant drops in major ion concentrations (e.g. Cl as in Fig. 4) are related to spring snow melt and dilution of river discharge.

(page width) Table 2: Major ion contributions from saline groundwater to rivers over the study reach during baseflow (March), freshet (May), high flow (July), and recession (Sept./Oct.) based on median concentrations in saline springs (Gue et al., 2015); constant discharge rates of saline groundwater calculated in this study into the Clearwater River (CW) and the Athabasca River (AR); mean monthly discharge of rivers (Environment Canada, 2016); and monthly median concentrations of major ions in the rivers: [1]RAMP (2012) and [2]AEP (2013).

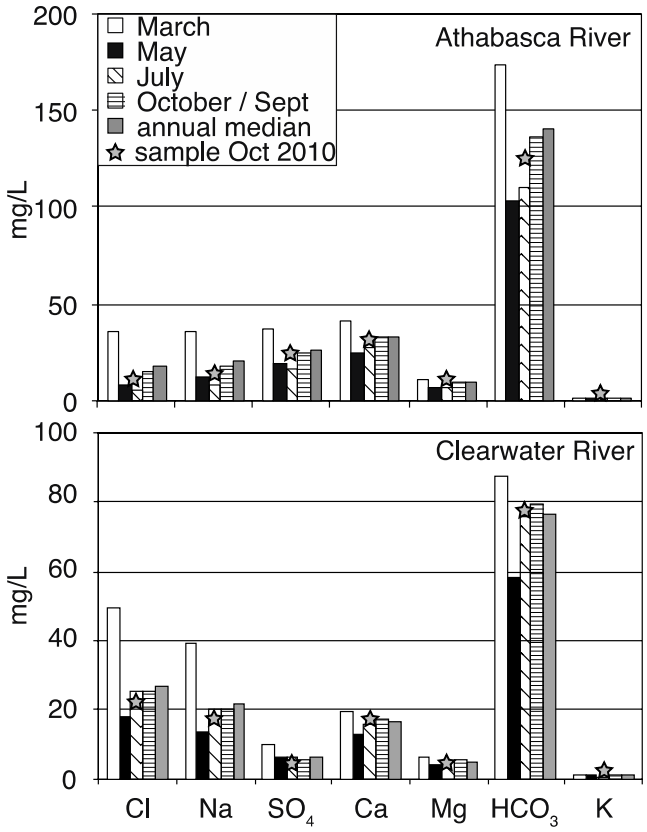
		Month	Cl	Na	SO_4	Ca	Mg	HCO_3	K	Discharge (m^3/s)
Springs	median concentration (mg/L)	all	9800	6310	168	555	204	505	23	CW 0.100 AR 0.134
	median ratio ion:Cl	all	1.00	1.00	0.05	0.04	0.03	0.03	0.00	
Clearwater River	median concentration (mg/L) [1]	Mar	49.5	39.0	9.8	19.9	6.7	87.5	1.4	
		May	18.0	14.0	6.3	12.6	4.0	58.0	1.2	
		July	25.0	20.5	6.4	16.0	5.2	75.5	0.9	
		Sept	25.0	20.0	5.5	17.3	5.7	79.7	0.9	
	downstream mass flux (g/s)	Mar	2.5	2.0	0.5	1.0	0.3	4.5	0.1	51.3
		May	4.0	3.1	1.4	2.8	0.9	13.0	0.3	224
		July	4.3	3.5	1.1	2.7	0.9	12.8	0.1	170
		Sept	3.4	2.7	0.7	2.3	0.8	10.8	0.1	135
	saline groundwater contribution	Mar	39%	32%	28%	4.7%	5.7%	1.1%	3.2%	0.19%
		May	24%	20%	10%	1.7%	2.2%	0.4%	0.8%	0.04%
		July	23%	18%	13%	1.8%	2.2%	0.4%	1.5%	0.06%
		Sept	29%	23%	19%	2.1%	2.6%	0.4%	1.8%	0.07%
Athabasca River	median concentration (mg/L)[2]	Mar	36.0	36.2	37.5	41.5	11.4	173.5	1.6	
		May	8.9	12.5	18.9	25.4	6.2	104.0	1.6	
		July	5.9	8.5	17.1	28.0	7.4	110.0	1.0	
		Oct	15.4	17.9	25.5	33.2	9.5	136.0	1.0	

	downstream mass flux (g/s)	Mar	7.3	7.3	7.6	8.4	2.3	35.0	0.3	202
		May	9.8	13.9	21.0	28.1	6.8	115.4	1.8	1110
		July	9.7	13.9	28.0	45.8	12.1	180.4	1.6	1640
		Oct	10.9	12.7	18.1	23.6	6.7	96.7	0.7	711
	saline groundwater contribution	Mar	18%	12%	2.5%	0.8%	1.1%	0.2%	0.9%	0.07%
		May	13%	6%	0.9%	0.2%	0.4%	0.1%	0.2%	0.01%
		July	14%	6%	0.7%	0.1%	0.2%	0.04%	0.2%	0.01%
		Oct	12%	7%	1.0%	0.3%	0.4%	0.1%	0.4%	0.02%



(1 column width) Figure 4: Monthly average river flow and median Cl concentrations. References are in the text.

Major ion concentrations in downstream river samples collected in October 2010 are compared with historical median monthly river concentrations in Figure 5. For both rivers, the October 2010 samples had concentrations very similar to the historical median values during recession. Therefore, the water samples collected are representative of long-term average major ion chemistry in the river systems at this time of year, and are thus reasonable to use for Cl isotope and mass balance calculations (Section 4.3).



(1 column width) Figure 5: Historical median concentrations of major ions in the Athabasca River (AEP, 2013) and the Clearwater River (RAMP, 2012), plotted with concentrations for samples obtained in this study in October 2010 at downstream river sites.

4.3. Cl isotopes and stable isotope mass balance

The δ^{37}Cl values of dissolved chloride were positive in all spring waters, ranging from 0.2 to 1.0‰ (Table 3). The range of values though suggest Cl in different springs was potentially derived from dissolution of different salt beds, including primary and re-precipitated salts (e.g. Eastoe and Peryt, 1999; Eastoe et al., 2007, Luo et al., 2014). The δ^{37}Cl values of river water samples were negative, ranging between -2.2 and -1.4 ‰. In both rivers, the δ^{37}Cl values of river water increased between upstream and downstream locations. In the Clearwater River, δ^{37}Cl values in river water increased markedly by 0.8‰, from -2.2 to -1.4‰. In the Athabasca River, δ^{37}Cl values in river water increased by

0.3‰, from -1.8 to -1.5. This is consistent with influx of chloride from saline springs with $\delta^{37}Cl$ values greater than 0‰, which can be quantified via mass and isotope mass balance calculations.

(1 column width) Table 3: $\delta^{37}Cl$ values for dissolved chloride in spring and river water samples.

	Sample	$\delta^{37}Cl$ (‰)
springs	AR01	0.6
	AR03	0.3
	CW01	1.0
	CW02	1.0
	CW03	0.9
	CW05	0.2
	CW07	0.6
	CW08	0.7
	CW09	0.5
rivers	AR01 (Athabasca upstream)	-1.8
	AR02 (Athabasca downstream)	-1.5
	RCW01 (Clearwater upstream)	-2.2
	RCW02 (Clearwater downstream)	-1.4

The proportion of Cl in the rivers sourced from saline groundwater during recession, calculated using the median $\delta^{37}Cl$ value of all spring waters of 0.6‰ ($\delta^{37}Cl_{gw}$) in the Cl isotope mass balance (Equation 3) for both rivers, was 29 ± 5% in the Clearwater River and 12 ± 6% in the Athabasca River. Groundwater contribution to river Cl flux in other months was calculated using saline groundwater discharge (Section 4.4) and the median spring water concentration of 9800 mg/L. The resulting proportion of Cl flux in the rivers sourced from saline groundwater throughout the year ranged from 23 to 39% in the Clearwater River, and from 12 to18% in the Athabasca River (Table 2). In both rivers, the greatest contribution of Cl from saline groundwater was in March (Table 2), when the rivers are ice-covered and river flow is low.

4.4. Uncertainty Calculations

The estimated standard uncertainty in these isotopic and mass balance calculations differed by river. The largest source of uncertainty, which carried through all calculations, was the relative difference between upstream and downstream $\delta^{37}Cl$ values in the rivers compared with the measurement uncertainty for $\delta^{37}Cl$ values. In the Clearwater River, the difference between upstream and downstream $\delta^{37}Cl$ values was eight times the measurement uncertainty, and the standard combined uncertainty of the obtained discharge rate of groundwater (Q_{gw}) is ± 20%. In the Athabasca River, the relatively small change in $\delta^{37}Cl$ values in river water (three times the measurement uncertainty) resulted in higher relative combined uncertainty in the estimates of Q_{gw} (± 51% of reported values). The same combined uncertainties are estimated for the obtained values for the fluxes of major ions, trace elements, and PAHs from the springs in both river valleys due to their dependence on the calculated $Q_{gw.}$

Uncertainty is also introduced through the assumption made in Equation 1 of only two main sources of Cl in the rivers (atmospheric deposition and saline groundwater). For the Clearwater River, this assumption is valid as there are no point sources of industrial process water and few roads that may be a source of road salt. However, for the Athabasca River possible additional sources of Cl in the study area include road salt and potential seepage from tailings impoundments along the river. If present and relevant, these would result in an overestimate of saline groundwater input, as the $\delta^{37}Cl$ values of anthropogenic sources of Cl are often indistinguishable from those of halite dissolution in groundwaters (Koehler and Wassenaar, 2010). Conversely, the assumption in Equation 2 of a similar $\delta^{37}Cl$ value in the upstream sample as in precipitation and related Cl sources (tributaries, runoff, and shallow groundwater) may lead to an underestimate of groundwater input if, over the distance from the headwaters to the study reach, the $\delta^{37}Cl$ value of the river has been significantly increased by upstream Cl sources because the lower $\delta^{37}Cl$ values of runoff and tributaries within the study area would not be fully accounted for. This

is unlikely for the Clearwater River where the upstream sampling site is relatively close to the headwaters, but is possible for the Athabasca River where the upstream site is located far from the headwaters, increasing the likelihood of the upstream $\delta^{37}Cl$ value being altered from that of precipitation.

4.5. Discharge rate of saline groundwater

The discharge rate of the springs at the time of sampling was calculated based on the isotope mass balance (Section 4.3) and Equations 4 and 5. Using the median Cl concentration in springs of 9,800 mg/L, the discharge rate of saline groundwater to the Clearwater River was estimated to be 100 ± 20 L/s. Assuming constant groundwater discharge throughout the year, the proportion of monthly average flow of the Clearwater River attributable to groundwater input ranged from 0.04 to 0.19% (Table 2). The discharge rate of saline groundwater into the Athabasca River was estimated to be 134 ± 68 L/s and the proportion of monthly river flow attributable to groundwater input ranged from 0.01 to 0.07% (Table 2). In both rivers, the contribution of saline groundwater discharge to average river flow is inversely related to river flow.

4.6. Major ion contributions

The proportions of major ion fluxes in the rivers attributable to saline groundwater inputs are listed in Table 2. Results indicate that in the Clearwater River, approximately 40% of Cl, and 30% of Na and SO_4 were sourced from saline groundwater under baseflow conditions in March. During spring and summer high flow conditions, the proportion sourced from groundwater decreased to approximately 24% of Cl, 20% of Na, and 10% of SO_4. During recession, the proportions of Cl, Na, and SO_4 contributed by saline groundwater increased to 29%, 23%, and 19% respectively. In the Athabasca

River, approximately 18% of Cl and 12% of Na but only 2.5% of SO_4 were sourced from saline groundwater under baseflow conditions in March. During spring freshet, proportions of these ions attributed to saline groundwater decreased to 13%, 6%, and 1% respectively, and stayed relatively constant throughout the summer high flow and recession conditions (Table 2).

4.7. Mass flux of trace elements

The annual mass fluxes of trace elements into the rivers from saline groundwater (Table 4) were determined using the estimated saline groundwater discharge rate and median total concentrations of elements in spring waters reported by Gue et al. (2015). The highest annual flux from groundwater to the rivers was observed for Sr with 39,000 kg/yr to the Clearwater River and 52,000 kg/yr to the Athabasca River. The mass fluxes of B were 5,424 kg/yr in the Clearwater and 7,268 kg/yr in the Athabasca Rivers, and Li fluxes were estimated at 1,082 kg/yr in the Clearwater and 1,449 kg/yr in the Athabasca Rivers. The mass fluxes of Fe and Mn ranged from 218 kg/yr to 697 kg/yr in both rivers; while Al, Ba, Cr, Cu, Ni, Rb, Se, and Zn fluxes were between 2 and 119 kg/yr. Contributions of all other trace elements to the rivers from saline groundwater over the study reach were orders of magnitude lower.

The proportion of total metals attributable to saline groundwater input to the rivers was in general negligible throughout the year for the four metals with historical records of river concentrations (Table 4). In both rivers, the springs contributed the highest proportion of total river mass flux of Cu, Ni, Pb, and Zn under baseflow conditions in March. At this time of the year the groundwater contribution was as high as 0.26% of total Cu mass flux and 0.61% of total Ni mass flux in the Clearwater River. In the Athabasca River, the contribution of metals from saline groundwater at baseflow conditions remained below 0.02% of total mass flux for all four metals (Table 4). (1 column width) Table 4: Estimated mass flux of trace elements to the Athabasca and Clearwater rivers from groundwater discharge using median groundwater concentrations in springs (Gue et al., 2015) and calculated groundwater discharge rates.

	Clearwater springs	Athabasca springs
Q_{gw}:	100 L/s	134 L/s

	median springs (μg/L)	mass flux (mg/s)	annual mass flux (kg/yr)	mass flux (mg/s)	annual mass flux (kg/yr)
Ag	0.01	0.001	0.03	0.001	0.04
Al	13.7	1.4	43	1.8	58
As	0.15	0.02	0.5	0.020	0.6
B	1,720	172	5,424	230	7,268
Ba	28.2	2.8	89	3.8	119
Be	0.07	0.01	0.2	0.009	0.3
Bi	0.02	0.002	0.1	0.003	0.1
Cd	0.05	0.005	0.1	0.006	0.2
Ce	0.002	0.0002	0.01	0.0003	0.01
Co	0.06	0.01	0.2	0.008	0.3
Cr	1.15	0.12	3.6	0.15	4.9
Cs	0.01	0.001	0.02	0.001	0.03
Cu	1.02	0.10	3.2	0.14	4.3
Fe	165	16.5	520	22	697
Ga	0.07	0.01	0.2	0.009	0.3
La	0.01	0.001	0.04	0.002	0.05
Li	343	34.3	1,082	46	1,449
Mn	69.2	6.9	218	9	292
Mo	0.11	0.01	0.3	0.014	0.4
Nb	< 0.01	-	-	-	-
Ni	0.83	0.08	2.6	0.11	3.5
Pb	0.17	0.02	0.5	0.02	0.7
Pt	0.005	0.0005	0.01	0.001	0.02
Rb	17.7	1.8	56	2.4	75
Sb	0.07	0.01	0.2	0.009	0.3
Se	2.98	0.3	9	0.40	13
Sn	0.01	0.001	0.02	0.001	0.03
Sr	12,300	1,230	38,789	1,648	51,978
Tl	0.01	0.001	0.03	0.001	0.04
U	0.05	0.01	0.2	0.007	0.2
V	< 0.005	-	-	-	-
W	0.001	0.0001	0.004	0.0002	0.006
Y	0.005	0.0005	0.01	0.001	0.02
Zn	1.70	0.17	5.4	0.23	7.2

(page width) Table 5: Contribution to the mass flux of Cu, Ni, Pb, and Zn in the Athabasca and Clearwater rivers from saline groundwater discharge.

		Month	Cu	Ni	Pb	Zn	Discharge (m^3/s)
springs	median concentration (μg/L)	all	1.02	0.83	0.17	1.70	CW 0.1 AR 0.134
Clearwater River	CW springs mass flux (mg/s)	all	0.10	0.08	0.02	0.17	
	median concentration (μg/L)	Mar	0.8	0.3	0.2	10.5	
		May	2.7	2.0	0.7	15.0	
		July	0.8	0.8	0.4	7.1	
		Sept	0.7	0.7	0.3	2.7	
	mass flux (g/s)	Mar	0.04	0.01	0.01	0.54	51.3
		May	0.6	0.4	0.2	3.4	224
		July	0.1	0.1	0.1	1.2	170
		Sept	0.1	0.1	0.04	0.4	135
	saline groundwater contribution	Mar	0.26%	0.61%	0.21%	0.03%	0.19%
		May	0.02%	0.02%	0.01%	0.01%	0.04%
		July	0.07%	0.06%	0.02%	0.01%	0.06%
		Sept	0.11%	0.09%	0.04%	0.05%	0.07%
Athabasca River	AR springs mass flux (mg/s)	all	0.14	0.11	0.02	0.23	
	median concentration (μg/L)	Mar	3.7	4.6	1.8	10.8	
		May	4.0	7.0	3.0	15.9	
		July	5.1	10.0	1.9	17.2	
		Sept	2.3	4.2	0.9	12.3	
	mass flux (g/s)	Mar	0.7	0.9	0.4	2.2	202
		May	4.4	7.8	3.3	17.6	1,110
		July	8.4	16.4	3.1	28.2	1,640
		Sept	2.2	4.0	0.8	11.6	943
	saline groundwater contribution	Mar	0.018%	0.012%	0.006%	0.010%	0.07%
		May	0.003%	0.001%	0.001%	0.001%	0.01%
		July	0.002%	0.001%	0.001%	0.001%	0.01%
		Sept	0.006%	0.003%	0.003%	0.002%	0.01%

4.8. Mass flux of PAHs

The concentrations of PAHs measured in the spring waters were very low (Gue et al., 2015); nonetheless, the mass flux was calculated and the proportion of PAHs in the rivers attributed to saline groundwater discharge was estimated for the sampling month of October. The suite of detected PAHs differed in the Clearwater and Athabasca spring waters; therefore, the fluxes of PAHs in each river were compared only with those detected in springs found in its valley (Table 7).

The average mass flux of total PAHs in the Clearwater River during recession was approximately 40 mg/s. The mass flux of total PAHs from saline groundwater was estimated to be 1.7 μg/s, or 0.004% of the flux in the river. Of the 8 PAHs observed in the Clearwater River, only 3 were detected in the Clearwater springs. Saline groundwater discharge accounted for 0.02% of the fluxes of phenanthrene and 2-methylnaphthalene in the river and 0.004% of the flux of naphthalene in the river. The estimated annual mass flux of these compounds from saline groundwater ranged from 24-31 g/yr (Table 7).

In the Athabasca River, the average mass flux of total PAHs during recession was an order of magnitude higher at 164 mg/L. The mass flux of total PAHs from saline groundwater was estimated to be 19 μg/s, or 0.01% of the flux in the river and all but one of the 8 PAHs observed in the river in October 2010 were detected in the Athabasca springs (Gue et al., 2015). Saline groundwater discharge accounted for 0.01% of the average mass flux in the river of naphthalene; 0.02% of the mass flux of fluoranthene, fluorene, phenanthrene, and 2-methylnaphthalene; and 0.03% of the mass flux of chrysene, and 1-methylnaphthalene. The estimated annual mass flux of these compounds from saline groundwater ranged from 25-480 g/yr (Table 7).

(page width) Table 7: Contribution to the mass fluxes of PAHs in the Athabasca and Clearwater rivers from saline groundwater discharge in the sampling month of October.

		total PAH	chrysene	fluoranthene	fluorene	naphthalene	1-methylnaphthalene	2-methylnaphthalene	phenanthrene
Clearwater River (mean October discharge 111 m^3/s)	springs median concentration (ng/L)	17.25	-	-	-	9.95	-	7.62	9.30
	springs mass flux (μg/s)	1.73	-	-	-	1.00	-	0.76	0.93
	springs annual mass flux (g/yr)	54	-	-	-	31	-	24	29
	river downstream concentration (ng/L)	363.5	4.3	17.7	22.1	227	18.7	29.9	38.6
	river mass flux (mg/s)	40.3	0.5	2.0	2.5	25.2	2.1	3.3	4.3
	saline groundwater contribution	0.004%	0%	0%	0%	0.004%	0%	0.02%	0.02%
Athabasca River (mean October discharge 711 m^3/s)	springs median concentration (ng/L)	189.8	5.8	11.6	14.0	113.4	12.7	14.7	26.9
	springs mass flux (μg/s)	25.4	0.8	1.5	1.9	15.2	1.7	2.0	3.6
	springs annual mass flux (g/yr)	802	25	49	59	479	54	62	114
	river downstream concentration (ng/L)	230.1	3.9	12.1	12.5	145	9.6	15.2	25.5
	river mass flux (mg/s)	163.6	2.7	8.6	8.9	103.1	6.8	10.8	18.1
	saline groundwater contribution	0.02%	0.03%	0.02%	0.02%	0.01%	0.03%	0.02%	0.02%

5. Discussion

The range of $\delta^{37}Cl$ values of dissolved chloride in spring waters (0.2 to 1.0‰) is consistent with values observed in evaporite deposits, supporting previous interpretation of these saline groundwater discharge sites deriving salts from halite dissolution (Gue et al., 2015). Given the conservative nature of Cl, the increase in $\delta^{37}Cl$ values of river water between upstream and downstream locations supports the underlying hypothesis of mass flux of dissolved salts from groundwater contributing to, and alerting, the

geochemistry of the river systems as they flow through Devonian outcrop belts in the Fort McMurray area. Based on this, we used our chloride mass and isotope balance approach to estimate that the annual groundwater flux to the Athabasca River throughout the AOSR is 134 ± 68 L/s, or only 0.01 to 0.07% of monthly mean river flow. In comparison, Jasechko et al. (2012) estimated groundwater discharge into a similar reach of the Athabasca River to be 500-3400 L/s, or 0.1 to 3% of river flow. One possible explanation for this discrepancy is likely their incorporation of Cretaceous groundwater with lower salinity into Cl mass balance calculations, which results in a higher groundwater flux estimate due to an overall lower salinity groundwater. This discrepancy points to a fundamental issue with such an approach as it difficult to determine the true average salinity of the total groundwater flux to the river system from all geologic units exposed in the river valleys. The Cl isotope mass balance approach used here avoids this problem as our estimates of the contribution of Cl over the study area to the rivers are entirely based on the stable isotope signatures and mixing relationships.

Despite the low volumetric groundwater flux to the rivers, we demonstrate that major ions in the rivers are sourced to a considerable extent from saline groundwater, especially Cl, Na, SO_4, and to a lesser extent Ca, Mg, and K. The contribution of groundwater to the overall mass flux of ions was greatest during the ice-covered season when river flow was lowest; in contrast groundwater contribution was lowest in the late spring and early summer when river flow was highest and when there is increased input of major ions from tributaries and overland flow. As river flows decrease in the fall, the influence of saline groundwater discharge on river chemistry gradually increases. Overall, the proportions of major ions sourced from saline groundwater over the study reach are much smaller in the Athabasca River than in the Clearwater River, consistent with the mean discharge of the Athabasca River being 6.5 times greater and the catchment being much larger.

In contrast to the major ion load of the river systems, groundwater contributions of trace elements to the rivers were minimal. For the trace elements with historical records available, Cu, Ni, Pb, and Zn, the mass flux was estimated to be between 2 and 7 kg/yr each, or less than 0.6% of the river mass flux at any time of year. This is an important finding, as Ni and Zn are also among the predominant trace metals in bitumen (Fairbridge, 1972; Allan and Jackson, 1997; Hitchon 1993) and are therefore of interest for monitoring efforts in the AOSR. Saline groundwater cannot be considered a major source of these elements to the river. By far the greatest trace element contribution from saline groundwater was Sr, at 39,000 kg/yr to the Clearwater River and 52,000 kg/yr to the Athabasca River. The high mass flux of Sr from saline groundwaters, and its $^{87}Sr/^{86}Sr$ ratio between 0.708 and 0.709, reflect the subsurface dissolution of Devonian carbonate and sulfate minerals (Gue et al., 2015), where Sr often replaces Ca in the mineral structure.

Groundwater discharge was also a negligible source of PAHs to river waters, contributing only 0.02% or less of the total PAH flux in the rivers in the month of October. Annually, the mass flux of total PAHs from saline groundwater was estimated to be 802 g/yr in the Athabasca River and 54 g/yr in the Clearwater River. A similar suite of PAHs was observed in the Athabasca River and springs in its valley, and the proportion of each contributed by groundwater, though very low, is similar. This suggests that the springs and the river are affected by the same source of PAHs. However, only 3 of the PAHs observed in the Clearwater River were found in the springs in its valley, suggesting different or additional sources of PAH to the river. The mass flux of each of these is negligible, ranging between 0.004 and 0.02% of river mass flux in October.

6. Conclusion

Historic records and oral tradition indicate that saline springs have discharged into the Athabasca and Clearwater rivers continuously for hundreds of years. Comparison of historic measurements of saline spring geochemistry shows that the compositions of these spring waters are consistent over time. Therefore, these springs can be used as an effective gauge of the overall saline groundwater contribution to the river systems in areas of oil sands development. As the springs represent individual point discharge sources, and not the overall groundwater contribution, geochemical tracers are required to discern the total mass flux from naturally occurring saline springs to the river systems. Our Cl stable isotope data show marked increases in δ^{37}Cl values between upstream and downstream reaches of the rivers that are consistent with groundwater contributions having distinct isotopic fingerprints with a median δ^{37}Cl value of +0.6‰. This enabled us to estimate total groundwater flux and total mass flux of major ions, trace elements, and PAHs to the river system.

This approach has the greatest certainty in areas with little to no anthropogenic activity, as is the case for the Clearwater River, where differences in the Cl stable isotope ratios far exceeded the measurement uncertainty. For the Athabasca River greater uncertainty exists due to potential anthropogenic input of Cl and the smaller change in river water δ^{37}Cl values. Nevertheless, our methods allowed a realistic estimate of natural groundwater contributions to river systems in areas of active industrial development. Our study demonstrates that natural groundwater discharge, although contributing less than 0.5% of river flow, has a marked impact on major ion river chemistry, but has only minute influence on the mass fluxes of trace elements and PAHs in the river systems. These results help to quantify the baseline contributions of naturally occurring saline groundwater discharge to the river systems in the AOSR, which is an important pre-requisite for delineating natural versus anthropogenic contributions to river water quality through areas of industrial development.

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Highlights

1. Discharge rates of saline groundwater were calculated using Cl stable isotope ratios.
2. Saline groundwater contributes <0.2% of the flow of the Athabasca and Clearwater rivers.
3. Saline groundwater contributes up to 40% of riverine flux of Cl in winter.
4. Negligible saline groundwater contributions to riverine trace element and PAH concentrations
5. The influence of saline groundwater on river chemistry is greatest in winter.

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