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Characterization of the boron, lithium, and strontium isotopic variations of oil sands process-affected water in Alberta, Canada



Jennifer S. Harkness^a, Nathaniel R. Warner^b, Ania Ulrich^c, Romain Millot^d, Wolfram Kloppmann^d, Jason M.E. Ahad^e, Martine M. Savard^e, Paul Gammon^f, Avner Vengosh^{a,*}

^a Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, NC 27708, United States

^b Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA 16802, United States

^c Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB, T6G 2W2, Canada

^d BRGM, French Geological Survey, Laboratory Division, Orléans, France Orléans Cedex 2, F-45060 France

^e Geological Survey of Canada, Natural Resources Canada, Québec, QC G1K 9A9, Canada

f Geological Survey of Canada, Natural Resources Canada, Ottawa, ON K1A 0E8, Canada

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ABSTRACT

Oil sands operations in Alberta, Canada generate large volumes (> $840 \times 10^6 \,\mathrm{m^3}$) of oil sands process-affected water (OSPW) that contains contaminants that are toxic to aquatic life. OSPW is stored in open tailings ponds and leakage from the ponds presents a potential long-term environmental risk. However, the presence of naturally occurring saline water in the oil sands region in Alberta presents a challenge for delineating the impact of OSPW in cases where OSPW is leaked to the environment. Here, we characterize the inorganic chemistry and isotopic variations of boron (δ^{11} B), lithium (δ^{7} Li), and strontium (ϵ_{s}^{SW}) of OSPW from tailings ponds in order to evaluate the source of salinity in OSPW and the potential utilization of these isotope ratios as forensic tracers of OSPW migration in the environment. In addition to generating new data, we compiled published data to build a comprehensive dataset of the geochemical composition of different water sources in the oil sands region of Alberta. OSPW is brackish (TDS ~ 1800 mgL^{-1}), with elevated chloride (392 ± 184 mgL^{-1}), boron $(2.2 \pm 0.4 \text{ mg L}^{-1})$, and lithium $(0.12 \pm 0.11 \text{ mg L}^{-1})$ concentrations relative to the Athabasca River that is used for bitumen extraction. OSPW is characterized by narrow ranges of $\delta^{11}B$ (23.7 ± 1.8‰), $\delta^{7}Li$ (16.3 \pm 1.7%), and ⁸⁷Sr/⁸⁶Sr ratios (ε_{Sr}^{SW} = -3.9 \pm 19.2). The geochemical and isotope ratios in OSPW reflect mixing of residual, saline formation water from Lower Cretaceous units with fresh surface water that has been modified by interactions with the solid oil sands. The elevated boron and lithium concentrations and $\delta^{11}B$, $\delta^{7}Li$ and ε_{Sr}^{SW} variations we observed are distinct from the compositions of a shallow freshwater aquifer in the area $(8.1 \pm 5.0\%, 11.3 \pm 0.9\%$ and 9.7 ± 5.6 , respectively) and the local rivers $(15.6 \pm 4.7\%, 15.1 \pm 1.4\%)$ and 30.3 ± 16.0). However, groundwater and saline springs in the region presents a wider range of geochemical and isotopic values that are not always distinguishable from OSPW. The integration of boron, lithium, and strontium isotopes provides a potential monitoring tool for tracing OSPW release to local freshwater sources.

1. Introduction

The rapid growth of the Athabasca oil sands industry in Northern Alberta, Canada (Fig. 1) has triggered an intensive debate on the environmental effects of oil sands mining operations, including deforestation, direct contamination by wastewater, and atmospheric fugitive emissions of hazardous aerosols (Gosselin et al., 2010; Kelly et al., 2010; Savard et al., 2012; Abolfazlzadehdoshanbehbazari et al., 2013; Timoney and Lee, 2013; Brown and Ulrich, 2015). Recently, there has been increasing scientific and policy interests in the impact of fossil fuel development on water resources, and the overall water-energy nexus (Scott et al., 2011). Much of the research has focused on oil and gas extraction and coal combustion (Ruhl et al., 2012; Vidic et al., 2013; Vengosh et al., 2014). The vast bitumen reserves in the Alberta oil sands are the third largest oil reserves in the world, and processing of the bitumen has introduced a novel method for oil extraction that can have long-term effects on water quality and the environment.

The bitumen extraction process uses approximately 3 cubic meters of water per cubic meter of oil produced, which is generally a mixture of recycled process water (80–95%) and surface water (Allen, 2008).

E-mail address: vengosh@duke.edu (A. Vengosh).

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^{*} Corresponding author.

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Fig. 1. Location of Alberta oil sands deposits and extraction operations in the Alberta Oil Sands Region (AOSR). Triangles represent locations of samples analyzed in this study, and previous studies when the location was available.

Following extraction of the bitumen, the residual water, known as oil sands process-affected water (OSPW), becomes alkaline and slightly brackish with high levels of toxic organic acids (Renault et al., 1998; Abolfazlzadehdoshanbehbazari et al., 2013). The naphthenic acids that are abundant in OSPW are highly toxic (Jones et al., 2011; Tollefsen et al., 2012; Scarlett et al., 2013; Brown and Ulrich, 2015) and,

therefore, OSPW is subject to a zero-discharge policy (Allen, 2008). Currently, over 840 million cubic meters of OSPW and fine oil sands residues are stored in tailings ponds that cover a total area of about 130 km^2 in a region north of the city of Fort McMurray, Alberta (Gosselin et al., 2010; Jasechko et al., 2012; Holden et al., 2013). The coarse and fine grained residual oil sands settle during storage in



Fig. 2. Stratigraphy of the surface geology and major groundwater aquifers in the Alberta Oil Sands Region. Modeled after Lemay (2002).

tailings ponds and the clear water at the surface of the ponds is removed and reused for further bitumen extraction (Allen, 2008).

Recent studies have addressed the potential environmental impact of wastewater-associated contaminants in the Athabasca oil sands region (AOSR) (Kavanagh, 2009; Jasechko et al., 2012; Savard et al., 2012; Abolfazlzadehdoshanbehbazari et al., 2013; Ahad et al., 2013; Headley et al., 2013; Holden et al., 2013; Frank et al., 2014). In particular, the naphthenic acids found in OSPW (Headley et al., 2013) are one of the main environmental concerns related to tailings ponds and OSPW storage (Headley, 2004; Savard et al., 2012) because they are highly toxic to fish and other wildlife (Jones et al., 2011; Tollefsen et al., 2012; Scarlett et al., 2013; Brown and Ulrich, 2015). While direct disposal of OSPW to surface water or shallow groundwater is not regularly practiced, the seepage of OSPW from tailings ponds to underlying groundwater and subsequent migration to the Athabasca River is a potential long-term risk in areas of oil sands operations (Holden et al., 2011).

Previous studies have applied a range of geochemical and isotope techniques to identify naphthenic acids and other contaminants in the AOSR. Frank et al. (2014) used geochemical and organic analysis to profile OSPW mixtures and groundwater but found that those analyses alone were not able to distinguish OSPW in the environment. Gibson et al. (2011) used an array of isotopic methods (δ^{18} O, δ^{2} H, ³H, δ^{13} C, δ^{34} S, ³⁷Cl, ⁸¹Br, δ^{11} B, ⁸⁷Sr/⁸⁶Sr and ¹⁴C) to assess the release of OSPW to the Athabasca River through subsurface conduits. Their results highlight the complexity of the geochemistry of groundwater released to the Athabasca River and the limitations of using geochemical tracers

to identify OSPW migration in the environment (Gibson et al., 2011). Savard et al. (2012) applied carbon isotopes (δ^{13} C) of carboxyl (-COOH) groups in organic molecules and lead and zinc isotopes to identify dissolved organic and inorganic contaminants derived from OSPW ponds in the subsurface environment. The mining-related contaminants' levels decreased with distance from the ponds, which suggests they may only reach the Athabasca River in negligible amounts (Savard et al., 2012). In addition, δ^{13} C analysis of organic acids have been shown to successfully distinguish between OSPW derived contaminants and naturally occurring organic acids in preliminary studies (Ahad et al., 2012, 2013). However, these studies have been largely site-specific investigations rather than evaluations considering regional geochemical variations.

In this study new chemical and isotopic measurements were combined with previously reported data to evaluate the geochemical evolution and the potential monitoring tools of OSPW. The objective of this study is to evaluate the validity of these geochemical tools as reliable tracers for delineating OSPW in the environment. Our new analyses include boron (B), lithium (Li), and strontium (Sr) isotope variations that have been previously used to evaluate the geochemical evolution of global hydrocarbon sources, including oil and gas reservoirs, coal and stimulated oil sand reservoirs (Moldovanyi et al., 1993; Williams et al., 2001, 2015; Williams and Hervig, 2004; Millot et al., 2011). In addition, we evaluated the use of isotope systems to identify OSPW in freshwater resources and distinguish OSPW from naturally occurring saline water from local geological formations in the AOSR. These isotope tracers have been useful indicators in studying other energy-water related issues associated with shale gas and hydraulic fracturing (Warner et al., 2014) and coal ash disposal (Ruhl et al., 2014). We characterized the composition of OSPW for eight different tailings ponds and the variations in groundwater from a freshwater aquifer underlying the tailings ponds near Fort McMurray.

2. Materials and methods

2.1. Data sources

Samples were collected from three sources, (1) OSPW (n = 8); (2) fresh groundwater (n = 16); and (3) oil sands leachates (n = 5) and analyzed for major and trace elements and boron, lithium, and strontium isotopic compositions of water samples. OSPW was collected from eight different Athabasca oil sands tailings ponds in the surface mining region of the AOSR shown in Fig. 1. Two OSPW samples were collected from drainage systems, while the remaining six samples were collected directly from the ponds. Fresh groundwater was represented by seven groundwater wells from a freshwater aquifer, the Wood Creek Sand Channel, underlying a tailings pond north of Fort McMurray, and were sampled annually from 2010 to 2012 and analyzed for inorganic chemistry and isotope ratios. The hydrogeology of the aquifer is described in more detail in Holden et al. (2013). The hydrogeology underlying the AOSR consists of shallow surficial Quaternary aquifers and several Lower Cretaceous aquifers, including the bitumen-rich McMurray Formation, and deeper saline Devonian age carbonate aquifers (Fig. 2). Lastly, Oil sands leachates were generated from conducted leaching experiments of five unprocessed oil sands solids collected from open pit mines using deionized water.

OSPW geochemistry was compared to five different water types reported in the literature (1) Lower Cretaceous Formation Waters groundwater from Lower Cretaceous formations (Williams et al., 2001; Lemay, 2002; Gibson et al., 2011, 2013); (2) Devonian Formation Waters - formation waters from the Devonian formations in the Alberta Basin (Connolly et al., 1990; Eccles and Berhane, 2011), and Devonian Formations of the Canadian Precambrian Shield just northeast of the AOSR (Bottomley et al., 1999); (3) Saline Springs - saline groundwater discharging from Devonian carbonates to the Athabasca River (Gue et al., 2015); (4) Groundwater - groundwater from Quaternary aquifers from the Cold Lake region (Williams et al., 2001) and the Athabasca region south of Fort McMurray (Lemay, 2002), which range from low salinity to slightly brackish. Additional seeps along the Athabasca River were reported by Gibson et al. (2011); and (5) Surface Water surface water samples from the Athabasca and Peace rivers (Millot et al., 2003, 2010; Lemarchand and Gaillardet, 2006; Gibson et al., 2011). It is important to note that the river data for B and Li are limited to only a few river sites and likely do not represent all possible seasonal and spatial variations in the geochemistry of the river water in the AOSR.

In-situ oil sands operations involve deep steam injection that release bitumen, which is pumped back to the surface as produced water. Insitu mining accounts for 80% of the recoverable oil. The remaining 20% is mined at the surface and the bitumen is extracted by agitation with freshwater or recycled wastewater. The water used for agitation is 80–95% recycled OSPW (Allen, 2008); however, over 3 million m³ per year of Athabasca River water is allocated for use by the oil sands industry for bitumen extraction. While the in-situ operations do not pose the same environmental risks as surface mining, the geochemistry of high-temperature oil sands extractions can provide insight into the source of the isotope signatures in OSPW. Therefore, the geochemistry of OSPW was also compared to a sixth water type described in the literature; that is Thermal PW, which represents produced water from high-temperature (~200 °C) in-situ bitumen extraction reported by Williams et al. (2001). The sources and geochemical and isotopic data available for each water type are summarized in Table 1.

2.2. Leaching experiments

Solid, unprocessed McMurray Formation oil sands samples were provided by the Geological Survey of Canada and leached in the laboratory at Duke University. Ten grams of solid was mixed with 100 g of deionized water (> 17.8 Ω) and shaken for 24 hours at room temperature following the EPA Method 1316: Liquid-solid partitioning as a function of liquid -to-solid ratio in solid materials using a parallel batch procedure (Garrabrants et al., 2010). The leachate was then centrifuged and filtered for chemical and isotopic analyses and stored at 4 °C prior to analysis.

2.3. Analytical methods

Water samples were filtered in the field through 0.45 µm syringe filters for analysis of dissolved concentrations for major anions and isotopes. Samples for cations and trace metals were field filtered and preserved with nitric acid. Unpreserved samples were stored at 4 °C. All major dissolved elemental chemistry and boron and strontium isotope measurements were conducted at Duke University (Warner et al., 2014; Harkness et al., 2016). Lithium isotopes were measured at BRGM, France and Duke University (Millot, 2004). Major anions were determined by ion chromatography on a Dionex IC DX-2100, major cations by direct current plasma optical emission spectrometry (DCP-OES), and trace-metals by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometer (ICP-MS) at Duke University. The DCP and ICP-MS instruments were calibrated to the National Institute of Standards and Technology 1643e standard, which were measured at varying concentrations before, after, and throughout sample runs. Internal standards of In, Th, and Bi were spiked into all samples prior to measurement on the ICP-MS. The detection limit of the ICP-MS of each element was determined by dividing three times the standard deviation of repeated blank measurements by the slope of the external standard. Alkalinity as a proxy for dissolve inorganic carbon (DIC) was determined by titration with HCl to pH 4.5.

Strontium and boron isotopes were analyzed by thermal ionization mass spectrometry (TIMS) on a ThermoFisher Triton at the Duke University TIMS lab. $^{11}\text{B}/^{10}\text{B}$ ratios were measured as BO₂⁻ ions in negative mode and normalized to NIST NBS SRM-951 (Dwyer and Vengosh, 2008) and presented in $\delta^{11}\text{B}$ notation, calculated as:

 $\delta^{11}B = [({}^{11}B_{samples}/{}^{10}B_{sample})/({}^{11}B_{951}/{}^{10}B_{951}) -1] \ x \ 1000$

Long-term replicate measurements (n = 60) of NBS SRM-951 standard yielded a precision of 0.6‰. Lithium isotopes were measured on a ThermoFisher Neptune multi-collector inductively coupled plasma mass-spectrometer (MC-ICP-MS) at BRGM, France and on the TIMS at Duke University. ⁷Li/⁶Li ratios were normalized to the L-SVEC standard solution (NIST SRM 8545) or CIAWW IRMM-016 Li carbonate (Millot, 2004) and presented as δ^7 Li:

$$\delta^{7} \text{Li} = \left[\left(\frac{1}{\text{Li}_{\text{samples}}} \right)^{6} \text{Li}_{\text{sample}} \right) / \left(\frac{1}{\text{Li}_{\text{LiCO3}}} \right)^{6} \text{Li}_{\text{LiCO3}} - 1 \right] \times 1000$$

Long-term replicate measurements of NIST SRM 8545 by MC-ICP-MS and IRMM-016 by TIMS standard yielded a precision of 0.5‰ (Millot, 2004). Strontium in the samples was pre-concentrated by evaporation in HEPA filtered clean hood and re-digested in 0.6 mL of 3.5N HNO₃ from which strontium was separated using Eichrom Srspecific ion exchange resin. ⁸⁷Sr/⁸⁶Sr ratios were collected in positive mode on the TIMS and external reproducibility (0.710265 \pm 0.000006) was compared to standard NIST SRM 987. Strontium isotope ratios are presented as

$$\varepsilon_{Sr}^{SW} = [({}^{87}Srsample/{}^{86}SrSample)/({}^{87}SrSW/{}^{86}SrSW) - 1] \times 10000$$

2.4. Two-end members mixing model

Mixing-models were calculated assuming two end-members based

Table 1

Water types and the sources of data used in the study.

Water Type	Source ID	Data source	n	Data Available
Oil sands processed-affected water	OSPW	This study	8	Major ion, trace elements, $\delta^{11}B$, $\delta^{7}Li$, ϵ^{SW}_{Sr}
	OSPW	Gibson et al., 2011	5	Major ion, trace elements, δ^{11} B, ε^{SW}_{Sr}
Unprocessed oil sands (H ₂ O leaching)*	Oil Sands Leachates	This study	5	Major ions, trace elements, $\delta^{11}B$
Thermal produced waters	Thermal PW	Williams et al., 2001	8	Major ions, trace elements, $\delta^{11}B$
Wood Creek Sand Channel	Fresh groundwater	This study	16	Major ion, trace elements, δ^{11} B, δ^{7} Li, ϵ^{SW}_{Sr}
Quaternary groundwater	Groundwater	Williams et al., 2001	23	Cl, B, δ^{11} B
	Groundwater	Lemay 2002	35	Major ion, trace elements, $\delta^{11}B,\epsilon^{SW}_{Sr}$
	Groundwater	Gibson et al., 2011	2	Major ion, trace elements, $\delta^{11}B,\epsilon^{SW}_{Sr}$
Athabasca River	Surface Water	Gibson et al., 2011	4	Major ion, trace elements, $\delta^{11}B$, ϵ^{SW}_{Sr}
Alberta Oil Sands Region Rivers	Surface Water	Millot et al., 2003; Lemarchand and Gaillardet, 2006; Millot et al., 2010	6	Major ion, trace elements, $\delta^{11}B$, $\delta^{7}Li$, ϵ^{SW}_{Sr}
Saline Springs	Saline Springs	Gue et al., 2015	9	Major ion, trace elements, ε_{Sr}^{SW}
Seeps	Seeps	Gibson et al., 2011	10	Major ion, trace elements, $\delta^{11}B \epsilon^{SW}_{Sr}$
Canadian Shield Devonian brines	Devonian Brines	Bottomley et al., 1999	24	Major ion, trace elements, $\delta^{11}B$, ϵ^{SW}_{Sr}
Alberta Basin Devonian bines	Devonian Brines	Eccles and Berhane, 2011	18	Major ion, trace elements, δ^7 Li,
	Devonian Brines	Connolly et al., 1990,	13	Major ion, trace elements, ϵ_{Sr}^{SW}
Lower Cretaceous formation water	Lower Cretaceous Formations	Connolly et al., 1990	15	Major ion, trace elements, ϵ_{Sr}^{SW}
	Lower Cretaceous Formations	Lemay 2002	22	Major ion, trace elements, $\delta^{11}B$, ϵ^{SW}_{Sr}
	Lower Cretaceous Formations	Gibson et al., 2011	4	Major ion, trace elements, $\delta^{11}B,\epsilon^{SW}_{Sr}$
	Lower Cretaceous Formations	Williams et al., 2001	8	Cl, B, δ^{11} B



Fig. 3. Major ion chemistry of OSPW (circles) analyzed in this study. Published data on saline and fresh water sources in the Alberta Oil Sands Region are also plotted. Full data set is presented in Tables 2 and 3, OSPW typically has a Ca-Na-Cl-HCO₃-SO₄ water composition that is distinct from both the Ca-Mg-HCO₃ low salinity groundwater in the shallow groundwater and deeper Devonian and Cretaceous formation waters Ca-Na-Cl.

on Faure and Mensing (2005). Both the concentration and the isotopic ratio of the mixtures are determined as follows:

$$[C_m] = [C_A]f_A + [C_B](1 - f_A)$$

where:

 C_m = concentration in the mixture C_A = concentration in end member A C_B = concentration in end member B f_A = fraction of end member A in mixture

and

$$R_{m} = \frac{R_{A}(C_{A}f_{A})}{C_{m}} + \frac{R_{B}(C_{B}(1-f_{A}))}{C_{m}}$$

where:

 R_m = isotopic ratio in the mixture

 C_A = isotopic ratio in end member A C_B = isotopic ratio of end member B

Each mixture fraction for the mixing model was performed for individual elements, B, Li, Sr, and Cl using average concentrations and isotopic ratios of the end-members and then the corresponding lines generated using the mixture results for any given fraction (f) of OSPW (Faure and Mensing, 2005).

3. Results and discussion

3.1. Geochemical characterization of OSPW

OSPW is brackish (TDS = $1798 \pm 641 \text{ mgL}^{-1}$) with high Sodium (Na), chloride (Cl), sulfate (SO₄) and dissolved inorganic carbon (DIC), and low calcium (Ca) and magnesium (Mg) concentrations relative to the Athabasca River, the freshwater source used for bitumen extraction (Figs. 3 and 4) (Allen, 2008). Boron (mean = $2.17 \pm 0.48 \text{ mg L-1}$;



Fig. 4. Bromide (A), sodium (B) and sulfate (C) versus chloride concentrations in the different saline water sources investigated in this study. Circle symbols represent samples analyzed in this study, and other symbols represent data reported in the literature. Details on samples provided in Table 1. (A) Br/CI ratios in Devonian and Cretaceous formation water are elevated compared to OPSW and the saline springs have Br/CI ratios similar to OSPW despite overall higher salinity. (B) Na/CI ratios in Devonian and Cretaceous formation waters and produced waters were similar to saline springs and OPSW. (C) Sulfate in the saline springs and OSPW is significantly higher than Cretaceous and Devonian water to OSPW.

n = 9), Sr (0.93 \pm 0.47 mg L-1) and Li (0.11 \pm 0.11 mgL⁻¹) concentrations in OSPW are also enriched compared to freshwater (Table 2, Fig. 5). Based on our leaching experiments, B and Cl are both highly leachable by water from the unprocessed oil sands (1357 \pm 513 mgkg⁻¹ and 172 \pm 77 mgkg⁻¹, respectively), relative to lower concentrations of SO₄, Sr, and Li (54 \pm 18 mgkg⁻¹, 40 \pm 19 mgkg⁻¹ and 23 \pm 13 mgkg⁻¹, respectively) (Table 2).

The B isotope ratios in OSPW were enriched in the heavier isotope $(\delta^{11}B = 23.8 \pm 2\%)$, compared to the leachate of the unprocessed oil sands (14.0 \pm 2.0%; Table 2) and surface water (15.1 \pm 1.4%), and consistent with published values (a range of 22–25%) reported by

Gibson et al. (2011) (Fig. 6). The ε_{Sr}^{SW} ratios of OSPW measured in this study (-11.6 ± 2.8; n = 4) were near the lower end of the wide range of ε_{Sr}^{SW} ratios reported by Gibson et al. (2011) (-13.2 to +42.3; n = 4), and distinctly lower than surface water (+30.3 ± 16; n = 17) (Lemarchand and Gaillardet, 2006; Gibson et al., 2011) (Fig. 6). The Li isotope ratios of OSPW (δ^7 Li = 16.3 ± 1.7‰) on the other hand, were similar to that of surface water (15.1 ± 1.4‰; Fig. 6). To our knowledge, δ^7 Li values of Lower Cretaceous formation water were not reported in the literature and were not measured in this study.

3.2. Sources of salinity in OSPW

The high concentrations of dissolved salts observed in the brackish OSPW relative to the freshwater used in the extraction process could be the result of evaporative concentration of process water, mixing with saline formation water entrapped within the McMurray sand solids, or leaching during the thermal extraction process. Gibson et al. (2011) reported δ^{18} O and δ^{2} H values in OSPW that reflect evaporation, which supports the evaporation mechanism for contributing to salinity of the ponds. However, they also indicated that the stable isotope ratios in OSPW were found in process water prior to discharge to the tailings ponds. These enriched ¹⁸O and ²H ratios could arise from either using the evaporated recycled pond water for extraction or mixing with residual enriched ¹⁸O and ²H formation water trapped in the oil sands.

Trapped residual formation water can also be a source of salinity in OSPW. The Lower Cretaceous McMurray Formation that hosts the oil sands, can be highly saline due to the migration of underlying Devonian aged brines (Cowie et al., 2015). The Br/Cl ratios in OSPW $(1.0 \pm 0.5 \times 10^{-3})$ are significantly lower (p < .001) than Br/Cl ratios in Lower Cretaceous formation (3.8 \pm 1.3 \times 10⁻³) (Fig. 4). The Na/Cl ratios in OSPW (2.5 \pm 0.5) are also significantly higher (p < .001) than the Lower Cretaceous formation waters (1.2 \pm 0.8). The B/Cl (7.9 \pm 5.2 \times 10⁻³) in OSPW is significantly higher (p < .001) than the Lower Cretaceous formation water (1.2 \pm 1.8 \times 10 $^{-3}),$ and the Sr/Cl (4.0 \pm 4.4 \times 10 $^{-3})$ and Li/Cl $(0.6 \pm 0.4 \times 10^{-3})$ in OSPW are also significantly higher but at a lower confidence interval (p < .01) than those in the Lower Cretaceous formation water (3.2 \pm 2.0 \times 10⁻³ and 0.3 \pm 0.2 \times 10⁻³) (Fig. 4). ε_{Sr}^{SW} Values in OSPW (-11.6 \pm 2.8) are statistically the same (p = .64) as the Lower Cretaceous formation water (-3.8 \pm 14.5), while the δ^{11} B values (23.7 \pm 1.8‰) were significantly lower (p < .001) than Lower Cretaceous formation water (37.5 ± 6.8) (Fig. 6).

Results of our leaching experiments (Table 2) suggest that the solutes in OSPW are not solely derived from leaching of the unprocessed oil sands, nor do they result from concentrating the freshwater (e.g., the Athabasca River) used for oil extraction. Williams et al. (2001) analyzed whole rock samples of solid oil sands from the Cold Lake Region. They found that the primary source of B in oil sands is pumice, with likely lesser contributions from organic matter and clays. The $\delta^{11}B$ values in the solids ranged from -4‰ to +19‰, -28‰ to -11‰, and -4‰ to +1‰, respectively, across the region (Williams et al., 2001). Interactions of thermal waters with the oil sands would result in incorporation of the depleted ¹¹B source into the water, with a relationship between temperature and $\delta^{11}B$ value. Williams et al. observed this in the thermal produced water from the in-situ oil sands production in the Cold Lake region, with a negative correlation between temperature and $\delta^{11}B$ ratios in the produced water (Williams et al., 2001).

The higher overall salinity and relatively high δ^{11} B in OSPW cannot be solely from leaching or thermal extraction during processing. The leaching experiments we performed in this study were done with fresh DI water at room temperature, which represents only the leachable fraction in the final solutions. The δ^{11} B ratios of 12.9‰–16.2‰ of the leachable fraction (Fig. 6) were within the range that Williams et al. (2001) measured in the whole rock analyses. In contrast, the OSPW results from thermal extraction of the bitumen after mining. Thermal extraction of B from the oil sands during this process would lower the

Table 2

Chemistry and isotope ratios in water and solid oil sands collected in this study. All water chemistry reported in mgL^{-1} . All leachates of solids reported in $mgkg^{-1}$. All ratios are reported as molar ratios. Boron and lithium isotope ratios reported as per mil values (‰) while the Sr isotopes are reported as epsilon values, normalized to seawater ratio.

(×10 ⁻⁵) (×10 ⁻⁵) (×	10 ⁻³)
OSPW	
TP1 366.6 24.2 15.6 364.1 0.1 1.7 0.8 -10.4 21.9 16.0 16.0 0.4 TP2 643.8 - 16.0 27.3 859.3 0.3 2.5 0.8 - 25.4 15.1 22.0 3.8 0.4 TP3 494.7 - 19.1 13.9 420.7 0.2 1.9 0.7 -13.0 24.0 15.5 16.0 3.9 0.4 TP4 549.1 - - 7.6 6.5 407.3 0.2 1.8 0.3 -14.5 21.2 15.2 20.0 3.3 0.3 0.3 TP4 318.0 0.18 0.6 456.8 2.2 45.5 24.0 236.8 0.2 2.2 1.1 - 16.8 11.0 7.1 0.6 TP5 387.2 0.34 0.9 642.6 2.6 49.1 27.0 0.2 2.0 1.1 - 1.68 11.0 7.1 0.6 TP6 147.1 0.29 2.0 352.0 <td>4 4 5 5 5</td>	4 4 5 5 5
Fresh Groundwater	
3B 747 34.3 0.02 92.3 4.1 90.2 23.5 56.6 481 0.04 0.2 0.8 10.8 4.0 5.0 1.3 (2010)	3
(2011) (2017) (2)
3B 203 44.5 0.06 66.3 2.3 92.5 26.3 15.9 0.04 0.2 0.6 2.0 1.2 10.8 3.0 3.6 0.5 (2012))
3A 708 43.0 0.02 68.5 2.5 95.8 27.6 17.7 496 0.03 0.2 0.5 2.0 3.6 0.8 (2010)	3
3A 696 43.3 0.02 68.3 2.4 89.1 25.9 17.8 493 0.04 0.2 0.4 9.3 11.0 10.7 2.0 3.7 0.8 (2011)	3
3A 203 45.2 0.06 64.4 2.2 92.5 26.5 17.0 0.01 0.04 0.1 9.3 3.0 10.5 1.0 0.9 0.2 (2012)	2
2D 145 7.7 0.04 27.3 5.4 84.1 25.0 3.6 0.04 0.2 0.5 14.1 2.0 19.5 4.9 (2012)0)
2B 148 11.1 30.9 4.3 82.5 25.5 5.1 0.03 0.1 0.4 2.0 12.5 3.0 (2010) ()
2B 600 9.1 0.02 28.6 4.9 82.2 25.2 3.3 456 0.03 0.1 0.4 2.0 15.3 3.6 (2011)<	5
2A 720 35.1 0.02 100.7 4.4 71.3 21.3 18.7 504 0.04 0.2 0.3 2.0 5.8 1.1 (2010) (2010	l
2A 702 34.0 0.02 89.4 4.0 74.0 22.3 17.1 495 0.04 0.2 0.3 2.0 5.6 1.0 (2011))
2A 201 31.9 0.03 83.4 4.0 76.0 22.6 14.4 0.04 0.2 0.4 18.1 13.3 12.4 2.0 6.1 1.2 (2012) <td>2</td>	2
1B 619 13.8 0.02 46.2 5.2 80.2 25.5 21.2 441 0.04 0.2 0.3 2.0 13.1 2.6 (2010) (2010	5
1A 662 40.1 0.03 87.1 3.3 71.5 24.4 24.8 451 0.03 0.2 0.3 2.0 4.6 0.8 (2010)	3
1A 750 21.3 0.01 46.9 3.4 101.9 31.9 62.0 504 0.03 0.2 0.4 12.6 11.9 12.5 2.0 8.5 1.6 (2011)	5
1A 253 27.8 0.01 62.8 3.5 94.0 29.2 63.1 0.04 0.2 0.4 10.3 2.0 6.6 1.3 (2012) (2012	3
Unprocessed Oil Sands	
OS-4A 255 79 39 1801 69 12.0 7.1 0.2	2
US-4p 204 /1 39 1727 58 13.0 6.8 0.2 OS-6A 173 15.6 47 21 1617 38 16.2 0.4 0.1	<u>د</u>
OS-6B 182 27 51 21 1593 30 14.6 8.8 0.1	[
OS-9A 86 14 38 9.9 714 28 8.3 0.1	l
OS-9B 79 6.5 35 8.9 691 18 8.7 0.1	L

 $\delta^{11}B$ signature of OSPW due to more intense water-rock interactions. We know this based on experimentally derived relationships between $\delta^{11}B$ and temperature and the lower ratios (3.1‰–14.1‰) observed in the in-situ thermal produced water (Fig. 6)(Williams et al., 2001). The higher $\delta^{11}B$ values of OSPW (23.7 \pm 1.8‰) must therefore derive from mixing of the leached or thermally-extracted B with a B source enriched in ^{11}B , most likely residual Cretaceous formation brines in the oil sands.

In contrast, Sr and Li have relatively lower contributions from leaching of the solid oil sands as well as lower concentrations in the thermal produced waters (up to 2 orders of magnitude lower) reported in Williams et al. (2001) (Table 2). The similarity of Sr/Cl and Li/Cl ratios of OSPW to the ratios in formation waters may likely be driven by a lower contribution of Sr and Li to OSPW from the thermal extraction or leaching of the oil sands (Fig. 5).

Combined, our results suggest that the high B concentrations found in OSPW with relatively high δ^{11} B values (23.7 ± 1.8‰) reflect mixing of B from residual entrapped fluids from Lower Cretaceous formations (δ^{11} B > 35‰) and B derived from leaching of oil sand solids during the thermal extraction process using the DI water leachates and thermal produced waters as a proxy (δ^{11} B < 15‰). The δ^{11} B values and B/Cl ratios in OSPW fall along a two-component mixing line (Faure and Mensing, 2005) between the Lower Cretaceous formation waters (mean = 37.5‰ and 5.2 × 10⁻³, respectively) and the thermal produced waters (mean = 7.8‰ and 54.3 × 10⁻³, respectively) used as a proxy for B leached during the thermal extraction process (Fig. 7). The mixing model shows that there must be a large



Fig. 5. Variations of boron, strontium and lithium concentrations with chloride concentrations. Circle symbols represent samples analyzed in this study, and other symbols represent data reported in the literature. Sources for different water types can be found in Table 1. OPSW has generally higher B/Cl ratios than both fresh and the different saline water sources, although some Lower Cretaceous formation waters had similar B/Cl ratios. Sr/Cl ratios were generally similar across all saline water types, while Li/Cl ratios showed a clear distinction between the Lower Cretaceous and Devonian formation waters. OSPW had Li/Cl ratios similar to the Lower Cretaceous water but elevated compared to saline springs and the Devonian waters.

contribution from the formation water to generate the isotope ratios measured in OSPW and that the extraction process alone is not a major contributor of solutes. Our calculations show that only about 3–5% of the thermally extracted boron can be added to OSPW to generate the $\delta^{11}B$ values from 21.3 to 26.3% (Fig. 7). We conclude the geochemical composition of OSPW is controlled by a complex mixture of residual formation water entrapped within the McMurray oil sands, coupled

with a small contribution from mobilization of solutes directly from the oil sands during thermal extraction and subsequence dilution by freshwater.

The contribution of multiple sources and further alteration during processing and storage points to a complex geochemistry of OSPW that may differ between operations, as observed in previous studies (Gibson et al., 2011), as well as over time, as more OSPW is recycled and less freshwater is used. The contribution of secondary water-rock interactions during the thermal extraction process results in δ^{11} B values in OSPW that are significantly lower than the Lower Cretaceous formation water and significantly higher than the thermal produced water, which may distinguish them from saline groundwater migrated from these formation or in-situ oil sands operations. However, the Sr isotope ratios in OSPW fall within the range reported for Lower Cretaceous formation water in the region. There is limited literature data on Li isotopes in saline water from the region, but given lower contributions of Li from leaching of the solid oil sands and Li/Cl ratios similar to Lower Cretaceous waters, the Li isotopes in OSPW may not be different from saline groundwater. The wide variations in salinity of Lower Cretaceous formation water (TDS 680 to 113,000 mg L^{-1}) and isotope ratios (i.e. ε_{Sr}^{SW}) could likely explain some of the observed ranges in OSPW, particularly for the strontium isotope ratios. However, the wide range of isotope ratios also presents further challenges in attempts to establish a general geochemical framework for monitoring OSPW released and impact on the environment.

3.3. Implications for tracing OSPW in the environment

Previous studies have suggested that the geochemistry of OSPW could be modified by water-rock interactions during transport (i.e., leaking), particularly through transport in clay-dominated glacial till, which is typically underlying the OSPW ponds (Holden et al., 2011; Savard et al., 2012; Abolfazlzadehdoshanbehbazari et al., 2013; Holden et al., 2013). Although these water-rock interactions could also modify the isotope ratios of OSPW effluents, the high concentrations of B, Li, and in some cases Sr in OSPW, coupled with the distinct δ^{11} B, δ^7 Li, and $\epsilon_{\delta^T}^{SW}$ fingerprints that are different from those in regional groundwater (Fig. 8), could be used to delineate OSPW migration to groundwater and surface water. In this section we will combine previously reported literature data and the new results obtained in this study to evaluate regional variations in surface and groundwater resources as compared to the established OSPW geochemistry.

Freshwater sources in the AOSR, including groundwater and surface water, are impacted by the natural upflow migration of saline water primarily from Devonian age formations (Jasechko et al., 2012; Gibson et al., 2013; Gue et al., 2015). Devonian formation waters typically have lower B, Li and higher Sr than that of the Lower Cretaceous formations, which is the primary source of solutes for the OSPW chemistry (Fig. 5). Unfortunately, there is limited data on the B isotope signatures in Devonian formation waters in this region to compare the OSPW. The Sr isotope ratios in OSPW were statistically indistinguishable (p = .67)from Lower Cretaceous formation waters but were significantly lower than the Devonian formation waters (p < .01). There were two distinctly different Li isotope ratios for Devonian formation waters measured in the region (Fig. 6). The Devonian waters from southwest of the study area had significantly lower δ^7 Li values (p < .01) than that of OPSW, while Devonian waters from northwest of the study area had significantly higher δ^7 Li values (p < .01) (Fig. 6). The differences between the isotope ratios in OSPW and the Devonian age formation waters indicate that these isotope systems could distinguish OSPW contamination from migrated Devonian age formations waters that mixed with the shallow aquifers or discharge to surface water as springs.

Groundwater chemistry reported in previous studies for the Athabasca Region presented a wide range of salinity (TDS from 301 to 1770 mgL^{-1}). Lower salinity groundwater had a Ca-Mg-HCO₃ water type, while the more saline water had a Na-HCO₃ water type, both of



Fig. 6. Box-and-whisker plots of boron, strontium and lithium isotope variations in the different water types compiled in this study. The box represents the top 75th and lower 25th percentiles, with the thick black line representing the medium. The whiskers represent the range of data and the dots are outliers.

which are distinct from the geochemistry of OSPW (Na-Cl-SO₄-HCO₃) and formation water (Na-Ca-Cl) (Fig. 3). The variability in geochemistry of groundwater also resulted in wide ranges in the isotope ratios. $\delta^{11}B$ values ranged from +7 to 43‰ and ϵ^{SW}_{Sr} ranged from -16 to 107. $\delta^{11}B$ was positively and significantly correlated with chloride (r = 0.45, p < .01; Fig. 8). Strontium isotope ratios were correlated with Sr/Ca ratios (r = 0.74, p < .05; Fig. 8). These relationships indicate that the B isotopes in groundwater are likely due to varying degrees of contribution from deeper saline waters with higher $\delta^{11}B$, while the Sr isotope ratios reflect in-situ water-rock interactions that release Ca and Sr from the host aquifer rocks.

However, we find that the isotopes are not always distinct from the ratios reported in the literature for groundwater and saline springs in the region. The δ^{11} B values and B/Cl ratios in some of the saline groundwater (Cl > 50 mg L⁻¹) overlapped with the values in OSPW (23.7 ± 1.8‰), although saline groundwater samples also had with δ^{11} B values greater than values found in OSPW (> 30‰) (Fig. 8). While the B isotope ratios in OSPW may distinguish it from the Devonian saline waters, the variability of naturally saline groundwater in the region results in δ^{11} B that overlap with OSPW. While the OSPW has significantly higher S/Car ratios than most of the groundwater samples, some groundwater samples had similar Sr/Ca and Sr isotope ratios to



Fig. 7. $\delta^{11}B$ verus B/Cl of OSPW, thermal produced water, and Lower Cretaceous formation water from the AOSR. Circle symbols represent samples analyzed in this study, and other symbols represent data reported in the literature. Sources for different water types can be found in Table 1. Dashed line represents a two component mixing model between residual formation water in oil sands and leached boron, represented by thermal oil sands extraction. Note the difference between the $\delta^{11}B$ and B concentrations in OSPW relative to both thermal produced water and saline formation water.

OSPW. Sr isotope ratios in the higher salinity groundwater (Cl > 50 mg L^{-1}) overlap with the range found in OSPW (-3.9 ± 19.2) (Fig. 8). We found no values reported in the literature for Li isotope ratios in groundwater from the Athabasca region. Given the available data on the geochemistry of saline springs and groundwater throughout the AOSR, the individual geochemical tracers presented in this study may not always be sensitive enough to distinguish natural sources of saline water from OSPW impact in the subsurface.

In contrast, the freshwater aquifer tested in this study did show a range of isotope ratios that are different from those of OSPW and could be useful in monitoring changes in fresh groundwater under or near tailings pond. The wood creek sand channel aquifer underlies tailings ponds near Fort McMurray and has low TDS (200-780 mgL⁻¹) with corresponding low concentrations of B (162.3 \pm 38.2 µgL⁻ ¹), Li $(34.7 \pm 7.4 \,\mu g L^{-1})$ and Sr $(429.9 \pm 158.6 \,\mu g L^{-1}; Fig. 4)$. Concentrations of Cl within the aquifer varied by up to 45% but over time an individual well did not vary by more than 15%. Concentrations of B, Li and Sr within the aquifer varied by 24%, 21%, and 37%, respectively, but individual wells varied by less than 10% over three years of observation, except for one well that had over 50% decrease in concentrations of all three elements. The $\delta^{11}B$ (8.1 ± 5.0%), ϵ_{Sr}^{SW} (9.7 ± 5.6) and δ^7 Li $(11.3 \pm 0.9\%)$ isotope ratios in the fresh groundwater were all significantly (p < .05) different from those in OSPW, with lower $\delta^{11}B$ and $\delta^{7}Li$ and higher ε_{sr}^{SW} in the fresh groundwater (Fig. 6). Lithium and Sr isotope ratios varied by less than 10% in the aquifer and over time, while B isotope ratios varied by as much as 60% in the aquifer and 100% in the same well over time. With the exception of the B isotopes, the geochemistry of the aquifer does not change much in space or time in the samples measured during this study period, and overall geochemistry is consistently different than OSPW. A two-component mixing model (Faure and Mensing, 2005) using the average isotope ratios and concentrations for B and Li suggest that as little as 5% OSPW contribution to the freshwater aquifer would be distinguishable, using B and Li isotope ratios as tracers for quantification of the amount of water contamination (Fig. 8).

The available data on the geochemical and isotope variations in surface water in the AOSR is limited. Gibson et al. (2011) collected 12 samples from the Athabasca River in the oil sands mining area, and two of those samples were resampled at a later date. Geochemistry from six surface waters sites (three on the Athabasca River and three on the Peace River) throughout the AOSR has been reported in a series of studies (Millot et al., 2003, 2010; Lemarchand and Gaillardet, 2006). The surface water is generally very low in salinity (TDS $< 420 \text{ mgL}^{-1}$), with low concentrations of Cl ($< 30 \text{ mgL}^{-1}$), sulfate ($< 32 \text{ mgL}^{-1}$), B $(< 0.02 \text{ mgL}^{-1})$, Li $(< 0.01 \text{ mgL}^{-1})$, and Sr $(< 0.3 \text{ mgL}^{-1})$ relative to OSPW and other saline water sources in the region (Table 3). The $\delta^{11}B$ $(15.6 \pm 4.7\%)$ and $\varepsilon_{Sr}^{SW}(30.3 \pm 16.0)$ in the surface water were significantly different from OSPW (p < .05), while the δ^7 Li $(15.1 \pm 1.4\%)$ values were not significantly different from OSPW (p = .28). The Sr isotope ratios varied up to 53% in surface water, even within the smaller stretch of the Athabasca River in the mining region (ε_{Sr}^{SW} =17–28). Boron isotopes also varied up to 30% across surface water in the region. However, despite this variation, the values remained distinctly different from OSPW through all the surface water sites (Fig. 6). This limited dataset does not likely capture all the variations in surface water throughout the region, but it can provide some insight into the possible ranges of concentrations and isotope ratios. Consequently, B and Sr isotope ratios, combined with geochemical variations may be able to identify direct release of OSPW to surface water (Fig. 8).

Discharge of OSPW effluents to the surface is currently prohibited and therefore it's unlikely that OSPW will be released directly to surface water. Rather, OSPW could migrate vertically beneath the storage ponds and then through subsurface conduits, before discharging to the rivers. However, natural saline water can also discharge to surface water and has been documented extensively in the AOSR (Jasechko et al., 2012; Gibson et al., 2013; Gue et al., 2015). Therefore, in order to detect OSPW migration to surface water, it's necessary to identify ways to distinguish OSPW from natural saline springs. Gue et al. (2015) measured the chemistry and Sr isotope ratios of Devonian age saline springs that discharged to the Athabasca and Clearwater rivers (Fig. 6). These springs had much higher salinity than observed in any of the OSPW samples (16911 \pm 5285 mgL⁻¹) and significantly lower Br/Cl and Na/Cl ratios (0.5 \pm 0.2 \times 10⁻³ and 1.00 \pm 0.03, p < .05; Fig. 4). The saline springs also had significantly (p < .05) higher concentrations of Li (0.4 \pm 0.2 mgL⁻¹) and Sr (12.7 \pm 5.2 mgL⁻¹), but not B $(1.7 \pm 0.6 \text{ mgL}^{-1}, \text{ p} = .25)$ (Fig. 5). The Sr/Ca (0.11 \pm 0.002) and ε_{Sr}^{SW} of the saline springs (-5.5 \pm 2.1) were not significantly different from the OSPW (p = .11; Fig. 8). Unfortunately, B and Li isotope values were not available in this study but the higher B/Cl and Li/Cl, and significantly different $\delta^7 L$ ratios in OSPW compared to the Devonian formation waters might indicate that these tracers could be useful. Gibson et al. (2011) analyzed seeps along the Athabasca River that were lower in salinity (TDS = $150 \text{ to } 2100 \text{ mgL}^{-1}$) relative to the saline springs but were also more geochemically diverse. The ε_{Sr}^{SW} values in these seeps (8.9 ± 11.6) were only significantly higher than OSPW at a 90% confidence interval (p < .1) although the saline seeps with Cl > 50 mg L⁻¹ had ε_{Sr}^{SW} greater (-1.1 to 20.2) than OSPW, with the exception of the one more radiogenic values reported by Gibson et al. (2011) with a ratio of 42.3 (Fig. 8). The δ^{11} B ratios in the seeps (25.3 \pm 12.0%) reported by Gibson et al. (2011) were not significantly different from OSPW (p = .4; Fig. 8). Like the shallow groundwater samples in the region, the seeps discharging to surface water have varied chemical compositions and isotope signatures, which complicates identifying OSPW migration to the subsurface and subsequent discharge to surface water (Fig. 8).

4. Conclusions

This study characterized and examined the ability of the inorganic geochemistry and the B, Li, and Sr isotopic ratios to distinguish OSPW contamination in a shallow freshwater aquifer, regional groundwater, and surface water in the AOSR relative to other natural contamination sources, such as Devonian and Lower Cretaceous formation waters and naturally occurring saline springs. The samples collected in this study are limited, and although combined with available literature data, are not intended to be comprehensive. Nonetheless, this study provides systematic evaluation of the available geochemical data.

The integration of new and reported geochemical and isotope data



Fig. 8. δ^{11} B vr B/Cl (A), δ^{11} B vs. chloride (B), ε_{Sr}^{SW} vs Sr/Ca (D), ε_{Sr}^{SW} vs. chloride (D), δ^7 Li versus Li/Cl (E), and δ^7 Li vs. chloride (F) of OSPW, groundwater, saline springs and seeps, and surface water from the AOSR. Circle symbols represent samples analyzed in this study, and other symbols represent data reported in the literature. Sources for different water types can be found in Table 1. Here we can see that the isotopes in groundwater and seeps throughout the Athabasca oil sands area are similar to OSPW. Surface water, however, has significantly different isotope ratios that OSPW.

revealed that the geochemistry of OSPW is derived from residue Lower Cretaceous Formation water with small contributions of B from leaching of the solid oil sands during bitumen extraction, followed by dilution with freshwater during storage in the tailings ponds. The combination of sources gives OSPW an alkaline, brackish-like chemistry with characteristic isotope signatures that differ from those of the high salinity McMurray Formation water and the low salinity Athabasca River water used in bitumen extraction. However, the geochemistry of OSPW is not necessarily distinct from that of saline groundwater or seeps that discharge to surface water in the region.

While the isotope systems presented in this study may not be able to distinguish naturally occurring saline groundwater from OSPW

impacted freshwater in all cases, they may be useful for monitoring OSPW migration to fresh shallow aquifers and surface water adjacent to tailings pond. We found that the B, Li, and Sr isotope ratios in a freshwater aquifer located 10–15 m underlying a tailings pond are significantly different from OSPW, and thus, these isotopic tools could be used to identify even a small contribution (1–15%) of OSPW contamination in the aquifer. This aquifer is known to discharge to the Athabasca River, so the application of these isotopic tracers could be useful in identifying migration of OSPW to surface water via freshwater subsurface conduits. We conclude that more analysis and sampling is needed to characterize whether the isotope ratios are conserved during migration through such shallow aquifers. Additionally, the isotope

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 Table 3

 Summary of the geochemical data (mean values) reported from this and previous studies. All water chemistry reported in mgL⁻¹. All leachates of solids reported in mgkg⁻¹. All ratios are reported as molar ratios. Boron and lithium isotope ratios are reported as per mil values (‰), while the Sr isotopes are reported as epsilon values.

OSPW This study	C	l Br	Br/Cl (×10 ⁻³)	Na	Na/Cl	 Ca	SO4 J	E B	i Sr	D	IC B/C (×1	1 10 ⁻³)	Li/Cl (×10 ⁻³)	Sr/Ca (×10 ⁻³)	$\delta^{11}B$	8 ⁷ Li	εSr
	7 4 4 3 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	46.7 0.3 94.3 0.1	5 1.0 5 0.9	537.2 427.8	2.7	50.9 14.2	439.3 : 314.1 I	2.2 0 V/A 0.	.20 1.1 13 0.2	0 , N €	/A 6.1 86 NA		0.6 0.6	13.2 15.2	23.8 23.4	16.3 N/A	-11.6 3.7
Unprocessed Oil Sands This study Thermal Produced Waters Williams et	ر 1 عد ما., 2001 8	48.1 N/ <i>i</i> 588 N/ <i>i</i>	A N/A A N/A	N/A 6230	N/A 1.3	2384	57.5 (135.5 (0.9 0. 0.1 N.	.02 0. /A N/	Γ Ν Ν	/A N/A /A 16.6	1 5	N/A N/A	N/A N/A	14.0 7.8	N/A N/A	N/A N/A
WCSC aquifer This study Groundwater Uliliams et Groundwater Lemay 200 Groundwater Gibson et a	/ at al., 2001 1 1 1 1 2 2 1 1 2 2 2 2 2 2 2 2 2	0 N/ ₁ 56 N/ ₁ 7.31 0.0 69.9 0.2	A N/A A N/A 6 N/A 1 N/A	64 N/A 89.4 161	N/A N/A N/A N/A	35 4/A 12 12	24 (N/A (52 (51.1 P	0.0 0.0 0.4 0.0 0.0	.03 0. /A N/ 05 0.1	4 X 2 C	31 7.4 /A 32.6 11 400 /A N/A	ø -	1.6 N/A N/A 4.2	2.3 N/A 5.3	8.1 18 19.9 25.4	11.3 N/A N/A N/A	9.7 N/A 9.6 12.4
Athabasca River Gibson et a Athabasca and Peace Rivers Millot et al Gaillardet,	al, 2011 1 al, 2003; Lemarchand and 1 , 2006; Millot et al., 2010	4.2 N// 3.1 N//	A N/A A N/A	18.3 5.3	N/A N/A	37.8	28.4 (N/A (0.01 0.01	.01 0. .01 0.	3 12 N,	28 12.(/A 2.9	0	5.0 2.4	3.0 3.5	18 14.4	N/A 15.1	21.5 50.9
Saline Springs Gue et al., Seeps Gibson et a Canadian Shield Devonian Bottomley	, 2015 1 al., 2011 3 et al., 1999 7	0700 5.5 58.4 N/ <i>i</i> 7195 691	0.5 A N/A 1 8.5	7005 180.9 14522	1.0 2.8 0.4	573 [33.9 { 31834 \$	1778 81.3 397 2	N/A N N/A 0. 2.3 1.	//A 12 .04 1.0 .78 55	7 4, 0 N, 6.6 6(78 N/A /A N/A 5 0.2		N/A 1.0 0.04	11.0 4.0 8.2	N/A 25.3 N/A	N/A N/A 35.2	-5.5 8.8 48.1
Alberta Basin Devonian Eccles and Brines Eccles and Alberta Basin Upper Connolly et Devonian Brines	1 Berhane, 2011 1 et al., 1990 7	16875 27: 5992 405	2 2.1 5 5.1	53878 36385	0.7	10755	234 (680 E	0.1 6 55.9 2.	3.8 12 5 33	8.5 5(5.2 1()4 0) 0.7		0.5 0.03	N/A 23.0	N/A N/A	10.8 N/A	N/A 16.3
Lower Cretaceous Connolly e Formations Lower Cretaceous Lemay 200	et al., 1990 4 02 1	.7227 18{ 4284 58	3 4.0 3.4	26493 4593	0.9	3446	98 51.6	14.8 1 5.8 1.	4.5 22 .7 14	0.9 1 [,] .1 50	4 0.3 1.8		0.3 0.2	56.6 60.7	N/A 37.8	N/A N/A	1.0 - 9.2
Formations Gibson et a Lower Cretaceous Gibson et a Formations Williams et Formations	al., 2011 1	88 1.0 700 N//	8 5.7 A N/A	408 N/A	3.6 N/A	37 I	6.8] N/A 7	N/A 0 7.8 N	.2 0.' /A N/	76 N N,	/A N/A /A 2.2	-	1.0 N/A	20.2 N/A	N/A 36.8	N/A N/A	6.6 N/A

ratios in OSPW are distinguishable from surface water in the region, and thus accidental releases of OSPW directly to surface water can also be identified using B, Li, and Sr isotopes.

Overall, combining B, Li, and Sr elemental distribution and isotopic ratios can be useful tracers of OSPW contamination even at low mixing proportions (i.e., 1–5%) with different fresh water resources in AOSR, especially surface water and shallow fresh groundwater as illustrated in Fig. 8. They are especially likely to be useful when monitoring freshwater aquifers that are at risk for migration of effluents from ponds and that may be connected to regional surface water. B, Li, and Sr concentrations and isotopic ratios should therefore be included in future monitoring programs and baseline studies aimed at evaluating the overall impact of oil sands extraction on the environment. The data gaps identified in this study highlight the lack of comprehensive groundwater data in the region and the need for additional studies that can identify tracers that can better distinguish OSPW in the environment.

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