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The stable isotopes of site wide waters at an oil sands mine in northern Alberta, Canada

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ABSTRACT

Oil sands mines have large disturbance footprints and contain a range of new landforms constructed from mine waste such as shale overburden and the byproducts of bitumen extraction such as sand and fluid fine tailings. Each of these landforms are a potential source of water and chemical release to adjacent surface and groundwater, and consequently, the development of methods to track water migration through these landforms is of importance.

The stable isotopes of water (i.e. ^{2}H and ^{18}O) have been widely used in hydrology and hydrogeology to characterize surface water/groundwater interactions but have not been extensively applied in mining applications, or specifically to oil sands mining in northern Alberta. A prerequisite for applying these techniques is the establishment of a Local Meteoric Water Line (LMWL) to characterize precipitation at the mine sites as well as the development of a 'catalogue' of the stable water isotope signatures of various mine site waters.

This study was undertaken at the Mildred Lake Mine Site, owned and operated by Syncrude Canada Ltd. The LMWL developed from 2 years (2009/2012) of sample collection is shown to be consistent with other LMWLs in western Canada. The results of the study highlight the unique stable water isotope signatures associated with hydraulically placed tailings (sand or fluid fine tailings) and overburden shale dumps relative to natural surface water and groundwater. The signature associated with the snow melt water on reclaimed landscapes was found to be similar to ground water recharge in the region. The isotopic composition of the shale overburden deposits are also distinct and consistent with observations made by other researchers in western Canada on undisturbed shales. The process water associated with the fine and coarse tailings streams has highly enriched ^{2}H and ^{18}O signatures. These signatures are developed through the non-equilibrium fractionation of imported fresh river water during evaporation from cooling towers used within the raw water process circuit. This highly fractionated surface water eventually becomes part of the recycled tailings water circuit, and as a consequence it undergoes further non-equilibrium fractionation as a result of surface evaporation, leading to additional enrichment along local evaporation lines.

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1. Introduction

The oil reserves in northern Alberta are estimated to be in the order of 1.7×10^{12} barrels of oil (McLinden et al., 2012), 20% of which may be extracted through surface mining with a final disturbance footprint of approximately 4800 km^2 (Government of Alberta, 2008). Oil sands mining involves stripping and salvaging surface organic and underlying mineral soils, such as glacial till or alluvium, for future use in reclamation. This is followed by the removal and stockpiling of the bedrock overburden within mined out pits or on surface in overburden dumps. The oil sands are crushed and hydraulically transported to a mill/upgrader for extraction using a combination of hot water and diluent extraction. The waste streams from extraction are comprised of coarser sand tailings and fluid fine tailings (FFT) which contain a mixture of finer particles (silts, clays) as well as residual bitumen. These tailings are hydraulically transported back to disposal areas using recycled process water also known as oil sands process water

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(OSPW). The transport of mined ore, processing, and tailings transport requires large volumes of water. The Mildred Lake Mine, operated by Syncrude Canada Ltd., recycles approximately 1.5×10^8 m^3 of OSPW through the extraction/upgrading plant annually. This volume represents about 80% of the total water requirement for production (Zubot, 2010). The remainder of the water requirement is provided by freshwater imported from the Athabasca River. Approximately 2.5 m^3 of freshwater import is required for every 1 m^3 of bitumen produced. The main use of this freshwater is for steam generation (RSC, 2011) associated with extraction and bitumen upgrading.

Oil sands mines are designed to operate as 'zero release' facilities, meaning that the sites retain all water associated with dewatering, mining and extraction on site during operations. As the mine site moves towards closure, there will need to be release of site waters back to the Athabasca River. An evaluation of the magnitude and quality of these site waters will require that the rates, pathway and volume of water moving through the various closure landforms such as overburden and tailings be characterized.

There are relatively few cases in which stable isotopes of water have been measured for mining waste. Sracek et al. (2004) collected a limited number of water samples from a full scale waste rock pile (30–35 m) using suction lysimeters and a well in the underlying saturated zone. They were able to show that there was an equal contribution of snow melt water and spring rainfall to the stored water within the waste rock. Allen and Lepitre (2004) and Allen and Voormeij (2002) also utilized stable isotopes of water in a relatively small number of samples (n = 32) to characterize meteoric water as well as sources and mixing of mine site waters at the Sullivan mine in British Columbia, building on some similar work undertaken by Ghomshei and Allen (2000) at the Nickel Plate mine, British Columbia. Gibson et al. (1998) and Gibson and Reid (2010, 2014) used isotopes to estimate the water balance of tailings ponds and natural lakes over a 20-year period at sites in Yellowknife and in the central Arctic. Hydrogeological studies at mine sites using stable isotopes have been more numerous (e.g., Douglas et al., 2000; Fracflow Consultants Inc., 1998). A recent study by Barbour et al. (2016) undertook high resolution profiling of stable isotopes of water through waste rock piles associated with coal mining in southern British Columbia and were able to identify seasonal cycles of winter and summer recharge over depths of up to 85 m.

Gibson et al. (2011) undertook a broad survey of isotopic and geochemical tracers for natural waters (river and groundwater; n = 31) and tailings pond waters (n = 8) for sites along the Athabasca River in the oil sands mining region of northern Alberta. The tailings pond water appeared to fall along a local evaporation line (LEL) with a slope of approximately 4.5 when compared to the LMWL for Edmonton. The stable isotope of water composition of the process affected water in the tailings ponds also appeared to be strongly enriched relative to mean precipitation. The study by Jasechko et al. (2012) was focused on deeper groundwater in the same area associated with the discharge of deep saline waters into the Athabasca River. They report that freshwater lakes in the region appear to be recharged by water with an average isotopic composition of $\delta^{18}O$ of $-19.8‰$ and δ^2H of $-148.2‰$.

This study attempts to build on these earlier studies but with a particular focus on a single operating oil sands mine: Syncrude's Mildred Lake Mine. The objectives of the study are to establish a preliminary LMWL for the mine site; characterize the stable isotope of water signature of all mine site waters; and identify key processes responsible for the various isotopic signatures associated with mine site waters.

2. Study area

The Mildred Lake Mine operated by Syncrude Canada Ltd. (SCL) is located about 35 km north of Fort McMurray, AB within the North Athabasca Oil Sands Region (Fig. 1a). The bitumen rich ore at the site is primarily present in the Lower Cretaceous Wabiskaw-McMurray Formation and is overlain by shale from the Cretaceous Clearwater formation (Hein and Cotterill, 2006). The Mildred Lake Mine site covers approximately 200 km^2 and contains a variety of landforms including active mining areas, tailings sand structures, overburden dumps, above ground and in-pit tailings areas and freshwater reservoirs. An aerial image of the mine site is shown in Fig. 1b with the principle areas accessed for this study highlighted. These areas include: a reclaimed overburden dump comprised primarily of shale referred to as South Bison Hills (SBH); an above ground sand tailings area, Southwest Sands Storage (SWSS); a fluid fine tailings (FFT) and process water containment structure, the Mildred Lake Settling Basin (MLSB); an in-pit tailings basin containing mature fine tailings (MFT), West in-pit (WIP); and in-pit tailings basins containing composite tailings (e.g. mixtures of MFT and sand tailings), East in-pit (EIP); and Southwest in-pit (SWIP); as well as a freshwater reservoir which contains water pumped from the Athabasca River, the Mildred Lake (ML) reservoir.

The oil sands region of northern Alberta, Canada is located in the sub-humid region of the boreal forest and is marked by long, cold winters with approximately 450 mm of annual precipitation, of which 1/3 is snow, and with 500 mm of potential evapotranspiration (Huang et al., 2015a). The mean monthly air temperature within the region ranges from $-19\ ^{\circ}C$ during January to 17 $^{\circ}C$ for July, with a mean annual temperature near 1 $^{\circ}C$. Daily relative humidity also varies seasonally from 77% during the winter months of November to March to 65% during the evaporation months of April to October (RAMP, 2015).

3. Materials and methods

Field sampling programs were undertaken from 2012 through 2014 at sampling locations distributed across the various landforms at the site as described in Section 2. The sampling program included meteoric water (rain and snow pack samples), tailings pond water samples, and soil samples taken from the tailings (sand and FFT) as well as shale overburden.

3.1. Field sample collection

Rainfall was collected at three rainfall gauge stations located across the mine site including rainfall stations at the north-east end of SWSS (Cell 32), SBH (30 Top), and the south-west side of the MLSB (U-Cell) as shown in Fig. 1b. These samples were generally collected during non-freezing months (April through September) using collection samplers constructed with a funnel connected to a long tube which transferred the water to a 1 L collection bottle. These collection devices were based on a design similar to those described by IAEA (2014). The long tubing minimizes evaporative loss from the collected water between collection times. The rainfall collectors were sampled after significant rain events or were checked on a bi-weekly basis.

Snow surveys over a number of the closure landforms are performed each spring by SCL personnel or their field consultants. During the surveys undertaken in March 2012, January/February 2013, March 2013 and 2014, snow pits were dug or cored to ground surface and a composite depth snow sample was placed into large Ziploc® freezer bags (26.8 cm × 27.3 cm). These samples were then allowed to fully melt at room temperature and the melt
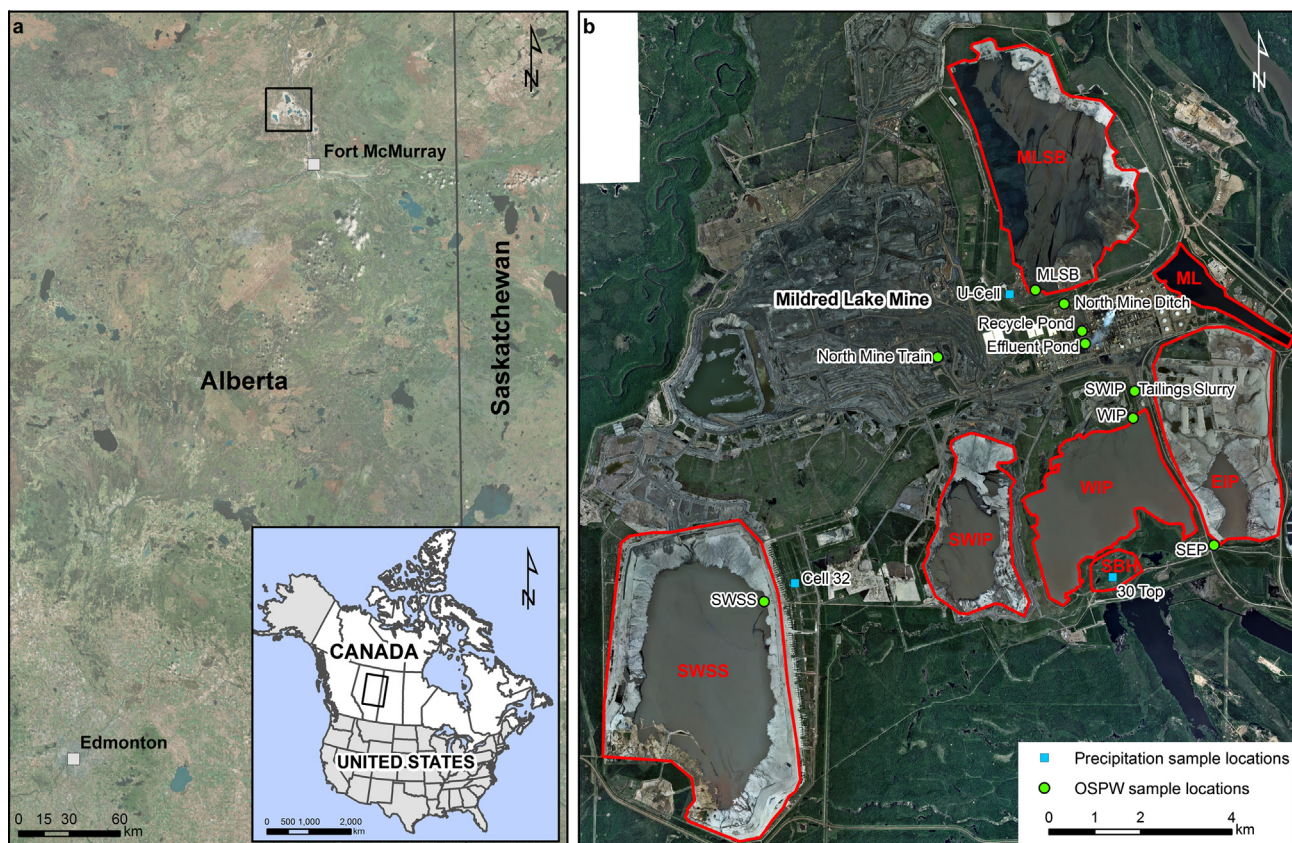
Fig. 1. (a) Map of northern Alberta showing the location of the Mildred Lake Mine (black box) and nearby Fort McMurray; (b) sampling areas at the Mildred Lake Mine site including: South Bison Hills (SBH) overburden dump, Southwest Sands Storage (SWSS), Mildred Lake Settling Basin (MLSB), West in-pit (WIP) tailings basin; East in-pit (EIP) and Southwest in-pit (SWIP) composite tailings containment; Mildred Lake (ML) fresh water reservoir. Also shown are the sampling locations for precipitation and OSPW.

water was poured into Exova 250 ml sample bottles and sealed. Precipitation data (rain and snow) collected for this study were combined with similar data on rainfall and snow samples collected by others during 2009 (Hilderman, 2011; Huang et al., 2015b).

Oil sands process water (OSPW) samples were collected from the surface of tailings basins and from select points along the process water circuit. Collection of OSPW from the surface of tailings ponds and along the recycle circuit was undertaken by a consultant working for SCL. Samples from tailings ponds surfaces were collected directly by dipping a sample bottle into the ponds with a telescoping metal arm. The sampled OSPW included the Recycle Pond, Effluent Pond, North Mine Ditch, North Mine Train, Tailings Slurry, WIP, SEP, MLSB, SWSS, and SWIP. The year and number of samples collected at each is given in Table 1, and the locations are shown in Fig. 1b.

A series of vertical profiles of the fluid fine tailings contained within WIP were sampled in the spring and summer of 2012 by a drilling contractor (ConeTec). ConeTec used a specialized pressurized piston sampler for fluid tailings to obtain discrete samples of fine tailings at specific depths. Following collection the piston is lifted above surface and the tailings sample discharged into a 3.78 L plastic pail which was sealed with a lid. The tailings samples were then centrifuged to obtain a water sample.

Surface water samples were taken from the Mildred Lake (ML) freshwater reservoir in 2012, 2013 and 2014, and from the perched ponds on SBH (Peat Pond, Golden Pond, Bill's Lake and Bison Lake) in 2012 by dipping a sample bottle just beneath the surface and filling to zero head space. Additional samples from the perched ponds were collected in 2003 and 2004, and in 2009 by Hilderman (2011).

Table 1
Year and number of samples at each OSPW sampling location, Mildred Lake (ML) and South Bison Hills (SBH) ponds and interflow.

Location	Year (number of samples)
Recycle pond	2011 (2); 2012 (5); 2013 (8); 2014 (5)
Effluent pond	2012 (5); 2013 (8)
North mine ditch	2012 (6); 2013 (3)
North mine train	2012 (6); 2013 (9); 2014 (6)
Tailings slurry	2013 (4); 2014 (2)
WIP	2011 (2); 2012 (4); 2013 (7); 2014 (6)
SEP	2011 (2); 2012 (5); 2013 (6); 2014 (4)
MLSB	2011 (2); 2012 (5); 2013 (8); 2014 (6)
SWSS	2011 (2); 2012 (5); 2013 (9); 2014 (7)
SWIP	2012 (1); 2013 (9); 2014 (7)
ML	2012 (1); 2013 (10); 2014 (8)
SBH ponds	2003 (10); 2004 (9); 2009 (10); 2012 (17)
SBH interflow	2003 (20): 2004 (18); 2005 (36); 2006 (7); 2007 (16); 2009 (56); 2012 (9); 2013 (26)

An interflow system, installed at the toe of the slope of the SBH overburden shale dump to measure lateral saturated groundwater flow along the reclamation cover and shale interface (Hilderman, 2011; Huang et al., 2015b; Kelln, 2007) was sampled from the collection barrels in 2012 and 2013 using a submersible pump. Additional samples were collected from the interflow system in 2003, 2004, 2006 and 2007, in 2005 by Kelln (2007) and in 2009 by Hilderman (2011). The number of samples collected each year from the ponds and interflow system are provided in Table 1.

Hilderman (2011) also collected a series of shale soil samples along vertical profiles below the reclamation cover at SBH. The samples were collected with a small tracked drill rig. Samples were

collected with a split spoon sampler and were taken from depths ranging from 0.95 to 9.1 m below ground. A reclamation cover comprised of glacial clay/till and peat covered the shale in the study area (Huang et al., 2015b).

Precipitation data are also compared to shallow groundwater data collected from a network of piezometers (0–5 m depth) installed in two natural watersheds situated within 60 km of Fort McMurray (Gibson et al., 2015). Shallow groundwater, which normally reflects a weighted mixture of snow and rain, provides an independent check on the derived local meteoric water line.

3.2. Laboratory analysis

The stable isotopes of water for soil and water samples were measured using the vapour equilibration method described by Wassenaar et al. (2008) and recently updated by Hendry et al. (2015). Approximately 10 ml of water or a few hundred grams of the soil sample was placed within a medium size Ziplock® bag and was inflated with dry air. The inflated bag was placed in a large Ziplock® bag which was evacuated and sealed. The sample was then left to equilibrate for three days. The vapour phase was then analyzed using a Picarro Cavity Ringdown Spectrometer L2130-I with the vapour isotope values corrected for equilibrium fractionation (vapour to liquid) and machine drift to obtain the corresponding pore-water/water values. The correction was undertaken using standard water samples of stable isotope concentrations that bracketed the composition of the core samples; Birsay, Saskatchewan glacial aquitard water (δ^2H and δ^{18}O of -178.7‰ and -22.86‰ respectively) and Saskatoon Tap Water (δ^2H and δ^{18}O of -130.2‰ and -15.96‰, respectively).

4. Results

4.1. Precipitation and shallow groundwater

The isotopic composition of rain and snow (Table 2 and Fig. 2) illustrate the temporal variation in precipitation at the site over the three year sampling period. Fig. 2 also includes results from a previously reported sampling campaign in 2009 (Hilderman, 2011; Huang et al., 2015b). The variation in δ^2H through the time period sampled for both rain and snow and for rain values with rain amount are also shown in Fig. 3a and b, respectively. Rainfall has the largest isotopic variance of all water sources at the mine site with an observed range of δ^{18}O from -26.2‰ to -9.1‰ and δ^2H from -201.6‰ to -75.7‰, with amount-weighted average values of -15.4‰ and -123.5‰, respectively. Snow has the most

depleted isotopic signature with values ranging from -31.5‰ to -21.8‰ for δ^{18}O and -243.3‰ to -172.8‰ for δ^2H (Table 2), with average values of -26.4‰ and -204.7‰, respectively. Snow forms a strongly linear pattern in δ^2H-δ^{18}O space plotting close to the Global Meteoric Water Line (GMWL), as compared to rainfall which forms a broader cloud and at times is found to be enriched below the GMWL (Fig. 2).

The volume of rainfall collected in 2009 and 2012 are comparable and the volume weighted isotope values of rainfall for the two years are relatively similar. The snow water equivalents (SWE) and isotope values for the snow pack from the spring of 2009, 2012, 2013 and 2014 are dissimilar and consequently the annual volume weighted isotope values for total precipitation vary from 2009 and 2012. Only one rainfall sample was collected in 2013, and while eight samples were collected in 2014, the amount of water collected was not recorded. Thus 2013 and 2014 rainfall results, while included in Fig. 2, are not presented in Table 2 and annual volume weighted isotope values for combined precipitation for 2013 and 2014 could not be calculated.

The variability of annual volume weighted precipitation between 2009 and 2012 is comparable to precipitation data collected by Peng et al. (2004) between 1992 and 2001 for Calgary, AB. Over this 10 year time frame, annual average δ^2H values ranged from -149.5‰ to -112.3‰ and δ^{18}O values ranged from -19.4‰ to -15.5‰, highlighting the potential inter-annual variability in the stable isotope of water composition of precipitation. The annual volume weighted isotope values of precipitation at Mildred Lake for 2009 and 2012, averaging -18.2‰ and -16.8‰ in δ^{18}O and -151.3‰ and -131.8‰ in δ^2H, respectively, are similar to those observed for Calgary (10-yr volume weighted average δ^{18}O of -17.9‰, δ^2H of -136.1‰; Peng et al., 2004) and slightly more depleted than those observed for Edmonton (δ^{18}O of -17.1‰, δ^2H of -130.7‰; Birks et al., 2002). More depleted values for Mildred Lake than for Edmonton are not surprising considering the differences in latitude, and given that more northern, colder, regions tend to have more isotopically depleted precipitation (Rose, 1995). The cause of more enriched values for Calgary may be more complicated, but is possibly related to differences in southern air mass trajectories. Calgary and Edmonton are approximately 700 km and 500 km south of Fort McMurray, respectively.

The Mildred Lake Local Meteoric Water Line (LMWL) was developed using rainfall data from 2009 and 2012 collected over two to four week periods utilizing similar techniques to Peng et al. (2004) and Wassenaar et al. (2011). We calculate both an unweighted and weighted equation for the LMWL (Table 3), the latter based on a weighted least squares regression technique to account for

Table 2
Summary of collected precipitation samples and stable isotope of water results.

Sample	Total collected water volume (mm)[**]	Number of samples	δ^2H (‰)				δ^{18}O (‰)			
			Average[*]	Max	Min	Std Dev	Average[*]	Max	Min	Std Dev
2009 Rainfall (Hilderman, 2011)	220	26	−128.9	−88.5	−201.6	24.5	−14.9	−10.6	−26.2	3.8
2012 Cell 32 Rainfall	178	9	−119.7	−81.3	−130.6	17.9	−14.8	−10.3	−16.1	2.2
2012 U-Cell Rainfall	285	10	−123.2	−78.0	−143.5	23.5	−15.9	−9.1	−18.3	3.3
2012 30 Top Rainfall	328	13	−122.3	−75.7	−158.1	22.5	−15.7	−9.6	−20.5	3.1
2012 Rainfall Average	264	32	−122.0	−75.7	−158.1	21.1	−15.5	−9.1	−20.5	2.9
2009 March Snow (Hilderman, 2011)	93	14	−204.1	−173.4	−223.3	13.8	−26.1	−21.8	−28.8	1.9
2012 March Snow	41	11	−194.6	−172.8	−205.8	9.5	−25.0	−22.2	−26.9	1.4
2013 Jan/Feb Snow	–	11	−209.4	−187.0	−230.5	11.2	−27.3	−24.1	−30.3	1.5
2013 March Snow	102	10	−211.6	−197.3	−243.3	13.4	−27.4	−25.4	−31.5	1.8
2014 March Snow	59	2	−203.2	−201.4	−204.9	2.5	−27.0	−26.8	−27.3	0.3
2009 Precipitation	313	40	−151.3	−88.5	−223.3	39.7	−18.2	−10.6	−28.8	5.9
2012 Precipitation	305	43	−131.8	−75.7	−205.8	39.9	−16.8	−9.1	−26.9	5.4
2009/2012 Precipitation	618	83	−141.6	−75.7	−223.3	41.3	−17.5	−9.1	−28.8	5.8

[*] Rainfall and yearly average precipitation values are volume weighted averages.
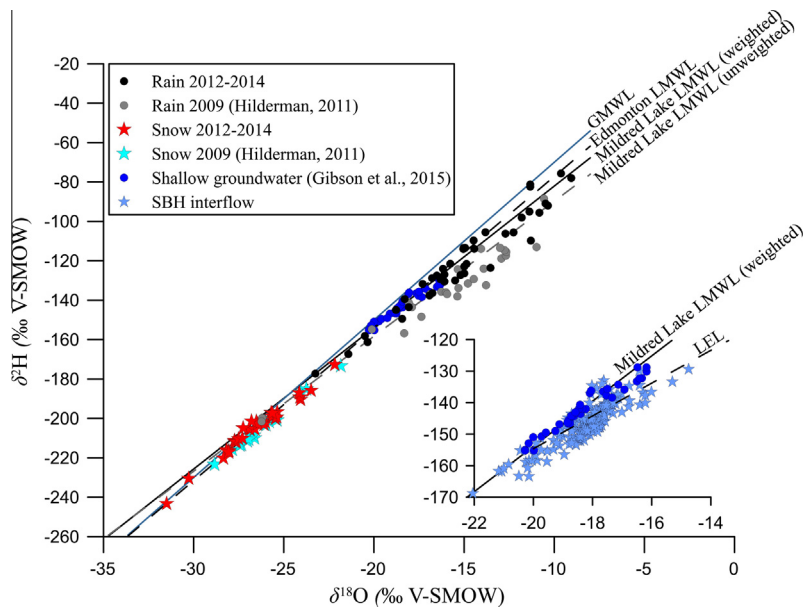[**] Snow depths given as average of snow water equivalent (SWE).

Fig. 2. Stable isotopes of water for precipitation (rain and snow), shallow groundwater (Gibson et al., 2015), and interflow. Mildred Lake LMWL (weighted and unweighted) calculated using 2009 and 2012 rain data only, and the local evaporation line (LEL) based on Gibson et al. (2015) for natural lakes in the oil sands region.
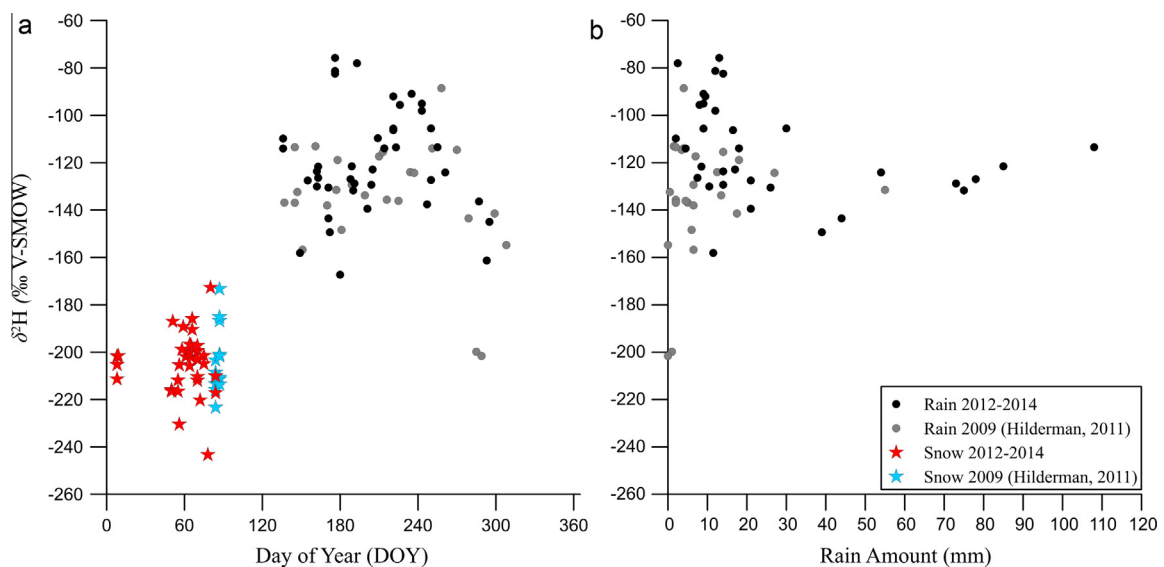

Fig. 3. (a) The range of seasonal variability in the precipitation samples collected at the site from 2009 to 2014 and (b) the amount effect in rainfall sampled in 2009 and 2012.

Table 3
Local Meteoric Water Lines (LMWL) for the Mildred Lake Mine site and other regional locations as well as the Global Meteoric Water Line (GMWL) and the Canadian Meteoric Water Line.

Location	Distance from mine	Years	LMWL
Mildred Lake Mine, unweighted	N/A	2009, 2012	$\delta^2H = 6.8\delta^{18}O - 21.3‰$
Mildred Lake Mine, amount-weighted	N/A	2009, 2012	$\delta^2H = 7.2\delta^{18}O - 10.3‰$
Global Meteoric Water Line	N/A	N/A	$\delta^2H = 8.2\delta^{18}O + 10.6‰$
Canadian Meteoric Water Line (Gibson et al., 2005)	N/A	1960–1997	$\delta^2H = 8.0\delta^{18}O + 8.5‰$
Calgary, AB (Peng et al., 2004)	700 km S	1992–2001	$\delta^2H = 7.7\delta^{18}O - 0.2‰$
Edmonton, AB (Hage et al., 1975)	400 km S	1962–1966	$\delta^2H = 7.7\delta^{18}O + 0.4‰$
Fort Smith, NT (Hage et al., 1975)	350 km N	1962–1966	$\delta^2H = 6.8\delta^{18}O - 20.9‰$

amount-effects associated with small volume events. The equation for the unweighted and weighted LMWL are $\delta^2H = 6.8\delta^{18}O-21.3‰$ and $\delta^2H = 7.20\delta^{18}O-10.3‰$ (see Fig. 2 and Table 3). As discussed in Section 5, the weighted equation is recommended as the appropriate input function for hydrological studies and it is shown to

intersect shallow groundwater, which is expected to comprise a mixture of recharge formed by rain and snow input.

The LMWL for the Mildred Lake Mine can be compared to other known LMWLs in the region as summarized in Table 3. Overall, the mine site LMWL seems reasonable when compared to the other

LMWLs. The mine site LMWL has a shallower slope and more negative intercept compared to the more southern LMWLs but a somewhat steeper slope and less negative intercept than the more northern Fort Smith LMWL. This demonstrates a general trend of decreasing slope with increasing latitude across northern Alberta.

For comparison, shallow groundwater results from a local study of natural watersheds (Gibson et al., 2015) along with shallow interflow collected from the reclamation cover at South Bison Hill are also shown in Fig. 2 inset. Naturally occurring shallow groundwater ranges from −16.2‰ to −20.3‰ in $\delta^{18}O$ and −155.2‰ to −128.8‰ in δ^2H, averaging −18.3‰ and −142.0‰, respectively, and is found to plot intermediate between average values of snow and rain, as expected where precipitation is the main source of subsurface recharge and evaporative losses are minor. This value is also very close to the mean isotopic composition of precipitation sampled during 2009 and 2012 (−17.5‰ in $\delta^{18}O$ and −141.6‰ in δ^2H; Table 2). The interflow water from the reclaimed overburden dump (South Bison Hill) plot over a similar range of isotopic value but remain in close proximity to the LMWL.

4.2. Mine site waters

In addition to meteoric water (snow, rain, and shallow groundwater) this study examined samples from representative source waters identified on the mine site including: fresh Mildred Lake make-up water, process-affected waters (OSPW) including the effluent pond and tailings ponds, north mine ditch water (fresh surface water runoff), WIP tailings profile and the SBH shale dump. Source waters are plotted along with the weighted LMWL for the Mildred Lake Mine in Fig. 4. The isotopic composition of Athabasca River water sampled at Fort McMurray on a monthly basis during 2002–2014 (Gibson et al., 2016), and the local evaporation line for natural lakes ($\delta^2H = 5.20\delta^{18}O$-50.6‰; Gibson et al., 2015) are shown for reference.

The mine water circuit begins with intake of Athabasca River water into Mildred Lake. The isotopic composition of Mildred Lake during 2012–2014 averaged −16.6‰ and −136.9‰ in $\delta^{18}O$ and δ^2H, respectively. The isotopic signature of the Mildred Lake water samples that plot near the LMWL in Fig. 4 generally overlay the overall seasonal range of the Athabasca River, which reflects

variations in streamflow sources including snowmelt, groundwater, surface water and rainfall. During 2002–2014, the Athabasca River varied seasonally from −20.2‰ to −16.5‰ in $\delta^{18}O$ and −158.1‰ to −133.8‰ in δ^2H, averaging −17.9‰ and −142.8‰, respectively, very close to that of Mildred Lake water. However, there are a few Mildred Lake samples that appear to plot out along a LEL and consequently reflect some seasonal enrichment of the Athabasca River water as a result of evaporation from the storage pond. Note that Athabasca River water plots close to the intersection of the LMWL and the local evaporation line (LEL) for natural lakes.

OSPW, including the effluent pond and tailings ponds (SWSS, MLSB, Recycle Pond, North Mine Train, WIP, SEP, SWIP, MLSB) are found to be enriched in $\delta^{18}O$ and δ^2H relative to Mildred Lake source water (Fig. 4). Tailings ponds varied from −16.1‰ to −9.6‰ in $\delta^{18}O$ and −135.1‰ to −99.7‰ in δ^2H, averaging −13.1‰ and −115.0‰ in $\delta^{18}O$ and δ^2H, respectively. The mean $\delta^2H/\delta^{18}O$ slope observed for tailings ponds is 4.3 with individual ponds ranging from 3.7 to 4.9. Tailings pond slopes are shallower and plot slightly above the local evaporation line for natural lakes (slope 5.2), and isotopic compositions tend to converge with natural lakes at more enriched values. This likely reflects apparent differences in the inflow composition of natural lakes and tailings ponds as well as the fact that the limiting isotopic enrichment for open-water bodies is atmospherically controlled and therefore likely similar for both tailings ponds and natural lakes. Tailings ponds enrich seasonally in response to the evaporation/inflow ratio of the reservoirs, typically being more depleted in spring at the time of snowmelt and becoming more enriched in summer as evaporation proceeds.

Mature fine tailings (MFT) porewater profiles from the West In Pit (WIP) show a similar pattern of variation to that of tailings ponds with a slope of 4.2. Values for MFT varied from −13.6‰ to −10.4‰ in $\delta^{18}O$ and −119.7‰ to −108.0‰ in δ^2H, averaging −12.5‰ and −115.8‰ respectively. While average values are similar to tailings pond OSPW, the MFT was sampled over a range of depths of FFT which had previously been dredged from the Mildred Lake settling basin and deposited in WIP. This might explain its more homogeneous composition relative to the tailings pond. The enrichment in MFT porewater is also more similar to that of
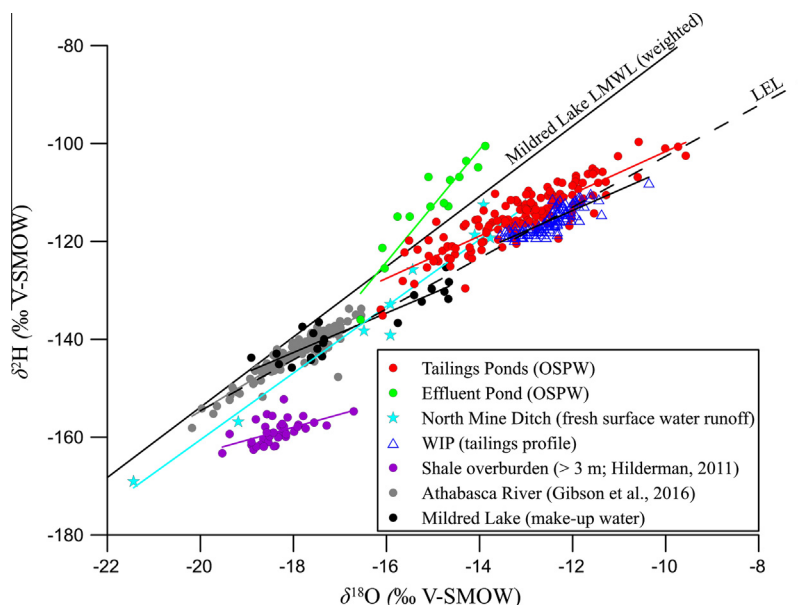

Fig. 4. Stable isotopes of water signature for mine site waters plotted along with LMWL. Local evaporation line (LEL) is based on Gibson et al. (2015) for natural lakes in the oil sands region. Athabasca River water is based on Gibson et al. (2016).

natural lakes than tailings ponds. Given that it contains relict wastewater produced decades ago, we believe that these subtle differences may reflect historical changes in OSPW and water management practices at the site.

The effluent pond varied from −16.6‰ to −13.9‰ in $\delta^{18}O$ and −136.0‰ to −100.5‰ in δ^2H, averaging −15.1‰ and −112.9‰, respectively, and is distinguished from other OSPW as it has a slope of 10.7 in δ^2H-$\delta^{18}O$ space (Fig. 4). Although the reason for this unusual composition is unknown, it may reflect re-condensation of boiler evaporate.

Samples collected from North Mine Ditch are generally considered to represent freshwater runoff and shallow groundwater at the mine site. These samples varied from −21.4‰ to −13.0‰ in $\delta^{18}O$ and −169.1‰ to −112.5‰ in δ^2H, with average values of −15.9‰ and −132.9‰, respectively. North Mine Ditch samples trend along a line with a slope of 6.9, sub-parallel to the LMWL, which indicates minimal evaporative modification of water originating mainly from rain, snow, and possibly shallow groundwater (Fig. 4).

The shale overburden samples (Hilderman, 2011) plot along a low-slope evaporation line (2.6) which appears to reflect static (rather than turbulent) diffusive transport often associated with soil-water evaporation (see Allison et al., 1983). Isotopic compositions were found to range from −19.5‰ to −16.7‰ in $\delta^{18}O$ and −163.3‰ to −152.3‰ in δ^2H, with average values of −18.4‰ and −158.9‰ for $\delta^{18}O$ and δ^2H, respectively. δ^2H values for deep shale dumps (>3 m) overlap the ranges reported for insitu shale

porewaters from South Saskatchewan and Alberta (Table 4). However, values for $\delta^{18}O$ are more enriched, reflecting an offset below the LMWL. This evaporative enrichment may signify that water losses by evaporation during both excavation and storage have modified the parent formation water signals.

Several small ponds at South Bison Hills were also sampled and analyzed for stable isotopes (Fig. 5). These are freshwater ponds formed on top of reclaimed, generally unsaturated, overburden dumps and consequently are considered perched ponds with little groundwater inputs. The isotopic compositions in these ponds varied from −20.2‰ to −6.5‰ in $\delta^{18}O$ and −164.9‰ to −90.2‰ in δ^2H. The main inputs into the ponds likely include snowmelt runoff and rainfall. Most interestingly, the isotopic composition of these small reclaimed ponds varies along the local evaporation line for natural lakes (LEL), which distinguishes them from tailings ponds. Fig. 5 also presents typical data for water collected from interflow drains located at the base of slope beneath the reclamation cover at South Bison Hill. The interflow was found to range from −22.0‰ to −14.8‰ for $\delta^{18}O$ and −168.8‰ to −129.4‰ for δ^2H, with average values of −18.2‰ and −146.7‰, respectively.

In summary, we have documented and summarized the variation and average isotopic values for various water types identified at the Mildred Lake Mine. A summary table showing average values and standard deviations of the major mine site waters is provided (Table 5). While some waters display overlapping ranges in either $\delta^{18}O$ or δ^2H, the waters are generally distinct when viewed in δ^2H-$\delta^{18}O$ space (Figs. 2, 4 and 5) and often vary along distinct

Table 4
Measured stable isotope of water signature for overburden shale (>3 m) as compared to literature values for undisturbed Cretaceous shale from Western Canada.

| Region	Range of stable isotope values of water in shale		Reference
	δ^2H (‰)	$\delta^{18}O$ (‰)	
Mildred Lake Mine	−163 to −152	−19.5 to −16.7	Hilderman (2011)
South Saskatchewan-shale/till interface 80 m below ground	−163 to −144	N/A	Hendry and Wassenaar (1999)
South Saskatchewan- shale/till interface approximately 12 m below ground	−158 to −145	N/A	Hendry et al. (2011)
Alberta- between Edmonton and Fort McMurray	−157 to −149	−21 to −20.3	Lemay (2002)
Clearwater Formation, South Athabasca Region	N/A	−22.0 to −18.4	Gibson et al. (2013)
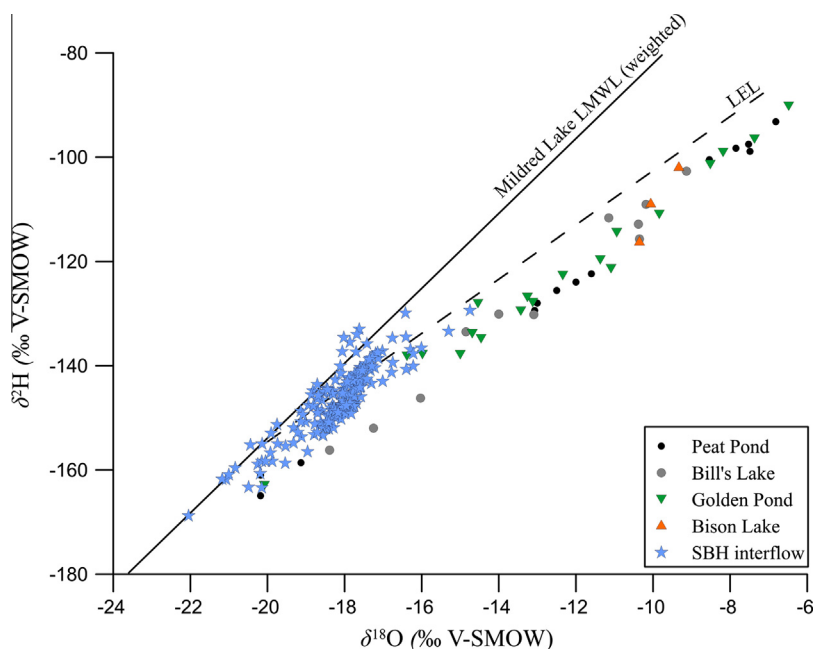
Fig. 5. Stable isotope signature of SBH ponds and interflow collection system.

Table 5
Stable isotope of water characteristics for mine site waters.

Sample	Number of samples	δ^2H (‰)				δ^{18}O (‰)			
		Average	Max	Min	Std Dev	Average	Max	Min	Std Dev
Rainfall[*]	58	−123.5	−75.7	−201.6	24.6	−15.4	−9.1	−26.2	3.4
Snow	48	−204.7	−172.8	−243.3	13.1	−26.4	−21.8	−31.5	1.8
Mildred Lake	19	−136.9	−125.3	−145.8	6.2	−16.6	−14.7	−18.9	1.4
Shale overburden (>3 m; Hilderman, 2011)	39	−158.9	−152.3	−163.3	2.4	−18.4	−16.7	−19.5	0.5
West in Pit (WIP)-tailings Profiles	115	−115.8	−108.0	−119.7	2.6	−12.5	−10.4	−13.6	0.5
Tailings Ponds (OSPW)[**]	145	−115.0	−99.7	−135.1	6.1	−13.1	−9.6	−16.1	1.2
Effluent Pond (OSPW)	13	−112.9	−100.5	−136.0	9.9	−15.1	−13.9	−16.6	0.9
North Mine Ditch (fresh surface water runoff)	9	−132.9	−112.5	−169.1	19.6	−15.9	−13.0	−21.4	2.8
SBH ponds	45	−123.1	−90.2	−163.0	19.8	−12.4	−6.5	−20.2	3.7
SBH interflow	187	−146.7	−129.4	−168.8	6.6	−18.2	−14.8	−22.0	1.0

[*] Averages are amount weighted averages.
[**] Excluding Effluent Pond and North Mine Ditch samples.

linear trajectories. This builds a foundation for applying stable isotopes of water for labelling and water balance studies at the Mildred Lake Mine and other mine sites in the oil sands region. Systematic patterns are further described in the following discussion.

5. Discussion

Temporal isotopic variation observed in precipitation samples at the Mildred Lake site are similar to those observed for other locations in Canada (Gibson et al., 2005). Fig. 3a highlights the range of seasonal variability in the precipitation samples collected at the site since 2009 through to the end of 2014. Seasonal differences between snow and rainfall isotopic composition are the result of seasonality in climate in which cold weather events are generally more depleted than warm weather events (Clark and Fritz, 1997). An amount effect is also clearly noted (Fig. 3b). A majority of the highly enriched rainfall values observed in this study are associated with storm events with small volumes of rainfall (less than 20 mm) which occurred in late-June, July and August. The most depleted rains occurred in October when air temperature was close to 0 °C. Snow is found to be the most depleted precipitation source due to air temperatures below 0 °C. Because of the amount effect, the amount-weighting approach for averaging is more likely to produce isotopic values representative of hydrological inputs.

The LMWL was based upon a weighted regression using only rain samples (Table 3). Snowpack samples were excluded from this procedure due to difficulty in reconciling the relative weighting of snow coring with rain sampling. It is of note that both the weighted and unweighted LMWLs have a lower slope than the GMWL and both regression lines converge near the most enriched end of the snow sample values (Fig. 2). Although the difference between weighted and unweighted LMWL is small, the unweighted LMWL appears to consistently underestimate the δ^2H values for shallow groundwater, whereas the weighted LMWL intersects the cluster of shallow groundwater samples with a better overall fit. The weighted LMWL is therefore recommended as a more appropriate hydrological input function. We use the weighted LMWL in the following section to approximate the input or source water composition in various reservoirs by regression to their intersection point with the LMWL, a method discussed by Gat (1996) and Gibson et al. (2005).

For the small ponds at South Bison Hills we estimate the intersection with the LMWL to plot close to −24.6‰ for δ^{18}O and −187.4‰ for δ^2H, corresponding to about 78% snow and 22% rain, and is interpreted to be the weighted mixture of sources entering the pond. For the interflow drains we find average values of

−18.2‰ and −146.7‰ for δ^{18}O and δ^2H, respectively. This is close to the isotopic composition of mean precipitation (see Table 2). This signature is slightly enriched compared to the intersection point of the LMWL and local evaporation line (LEL) for natural lakes which is close to −20.1‰ for δ^{18}O and −155.4‰ for δ^2H, and may reflect less influence from snowmelt for reclaimed sites than for natural watersheds.

OSPW and tailings pore water are the most enriched waters found on the mine site. Despite these waters being mainly derived from precipitation and Mildred Lake water, the isotope signatures of these waters are significantly enriched in comparison to the source waters. For tailings ponds, the intersection point with the weighted LMWL is −16.6‰ in δ^{18}O and −130.1‰ in δ^2H. For the effluent pond, the intersection point is very similar: −16.6‰ in δ^{18}O and −129.8‰ in δ^2H. This similarity strongly suggests that both are fed from comparable source waters that are initially enriched along the LMWL compared to Mildred Lake water. We postulate that this is due to isotopic enrichment in cooling tower water (Ingraham et al., 1994) that is added to the tailings ponds and the recycle water circuit. This is the main difference between water balance conditions in the process circuit versus natural lakes.

The volume of freshwater input is approximately 2.5 m³ of water for every m³ of synthetic crude produced by Syncrude. Approximately 25% of the imported freshwater is lost to hydrogen production and for steam generation. A large, but not currently well defined, proportion of these losses are associated with the operation of the cooling towers. Although the losses associated with cooling tower operation are not well defined, they are estimated to be as much as 60% (Zubot, 2015, personal communication). The operational conditions for the cooling towers, which influences evaporative enrichment, include average temperatures of about 35 °C and relative humidity values that are close to 100%. We postulate that process-affected waters are subject to two isotopic enrichment stages during their life cycle: (i) a first stage of high humidity, near-equilibrium isotopic enrichment in cooling towers, followed by (ii) open-water evaporation losses in ponds exposed to the ambient atmosphere. We attribute the ~2‰ offset in δ^{18}O and 15‰ in δ^2H between Mildred Lake water and the tailings ponds (intercepts with the LMWL, see Fig. 4) to reflect the input of cooling tower blowdown. Addition of precipitation to the tailings ponds is expected to be buffering this enrichment somewhat. Subsequent isotopic enrichment of this input in tailings ponds along a slightly lower slope than natural lakes appears to occur due to the combination of an enriched input signature and similar limiting ambient atmospheric moisture conditions. Reduced offset along the tailings pond line may also reflect lower rates of evaporation from these ponds relative to natural lakes. It appears that enrichment in the West In Pit (WIP) MFT

profiles are more similar to natural lakes than to modern tailings ponds. Given that tailings pore water is expected to retain some memory of tailings pond water trapped at the time of deposition, we speculate that this may reflect historical conditions in the WIP pond.

The unique high-slope evaporation trend observed in the effluent pond, which is not normally observed in natural settings may be consistent with evaporation into a high humidity atmosphere consisting of boiler evaporate. Further information about the effluent pond is required to verify that this is a plausible scenario.

The data on the stable isotopic composition of the pore-water within shale overburden presented in this paper includes the data utilized previously by Huang et al. (2015b) for South Bison Hills (SBH). In that study, recharge rates into the SBH dump were estimated from the shifts in the isotopic profile within the upper 1–2 m of the shale dump from recent meteoric water (snow melt water) to that more characteristic of interstitial shale pore water. The samples reported here are for depths greater than 3 m below ground and consequently are assumed to represent interstitial waters present within the shale prior to excavation and dumping. Given the relatively shallow depths of the initial shale deposits at the mine site it is also possible that the interstitial shale waters may have been modified as the result of diffusive mixing between the shale and overlying glacial deposits as observed for deep till/shale sequences by Hendry and Wassenaar (1999) and Hendry et al. (2011). However; these authors report no evaporative enrichment of these interstitial shale pore waters from the LMWL so it is assumed that the slight enrichment observed for the overburden shale deposits may reflect evaporation during excavation and handling.

Overall, the characterization of site wide waters at the Mildred Lake Mine expands on existing knowledge of isotope variations that have been studied at natural sites in the oil sands region (e.g., Gibson et al., 2010, 2011, 2015, 2016) and elsewhere. New insight into variations in precipitation is helpful for future studies at both natural and disturbed sites. New perspectives on the evolution of make-up water and process-affected water in tailings ponds, and a proposed explanation for distinction between enrichment in tailings ponds and natural lakes is particularly valuable for improving ability to use the tracers for water balance investigations at SCL and similar operations in the region. Follow-up studies will include a quantitative isotope mass balance analysis of isotopic enrichment that occurs in cooling towers, the effluent pond and tailings ponds in comparison to natural lakes in the area, as a further step towards closing the site wide water balance at the Mildred Lake Mine.

6. Summary and conclusions

A newly defined LMWL is proposed for the Mildred Lake Mine site based on amount-weighted regression of two years of rainfall data collected on site. This LMWL is defined as: $\delta^2H = 7.20\delta^{18}O-10.3‰$. It is expected that this LMWL will be applicable to all of the oil sands mine sites in the region subject to refinement of the line with ongoing monitoring at both the Mildred Lake as well as the Aurora mine sites operated by Syncrude.

This study has shown that precipitation derived waters, particularly rain and snowmelt, and mine site waters associated with overburden dumps and tailings (water and fluid fine tailings) have distinct isotope compositions as defined by the relationship between δ^2H and $\delta^{18}O$ as plotted against the LMWL. The ability to distinguish between meteoric and various sources of mine site waters provides unique opportunities to track water migration and water releases from mine waste such as overburden and tailings.

The isotopic composition of the tailings water has a particularly unique isotopic composition as compared to the more natural sources of water on the site. This unique signature is consistent with the equilibrium fractionation ($\sim$100% humidity) of freshwater import from the Athabasca River as a result of cooling tower operation followed by mixing with precipitation and kinetic evaporative fractionation within the tailings ponds. Future work is underway to track the temporal evolution of these waters in more detail, including the volume of process water and precipitation, to more fully characterize water balances within the tailings ponds and recycle water circuit for these mines.

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