Using stable isotopes to track hydrological processes at an oil sands mine, Alberta, Canada

Spencer J. Chad [a,b,*], S. Lee Barbour [a,b], Jeffrey J. McDonnell [b,c], John J. Gibson [d,e]

[a] Department of Civil and Geological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
[b] Global Institute for Water Security, School of Environment and Sustainability, University of Saskatchewan, Saskatoon, Canada
[c] School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK
[d] InnoTech Alberta, 3-4476 Markham Street, Victoria, BC V8Z 7×8, Canada
[e] University of Victoria, Geography, Victoria BC V8W 3R4 Canada

ARTICLE INFO

ABSTRACT

Study region: This study was conducted at an oil sands operation in the Athabasca Oil Sands Region (AOSR), northeastern Alberta, Canada. The mine comprises open pit excavation of bituminous sands at two sites (Mildred Lake, ML, and Aurora North, AN), with a single hot-water extraction circuit connecting extraction plants at each mine.

Study focus: Water samples were collected and analyzed regularly over an eight-year period to establish inventories of site-wide water isotope signatures including seasonal and interannual changes in the recycle water circuit, and to permit future application of an isotope balance model to constrain poorly quantified processes such as evaporation losses, dewatering of tailings, and tailings pond connectivity of the recycle water circuit.

New hydrological insights for the region: Sampling of precipitation inputs over an 8-year period was used to constrain a local meteoric water line for the area. Differences in evaporative isotopic enrichment of tailings ponds at ML and AN are attributed to use of Athabasca River makeup water at the former site *versus* basal dewatering sources at the latter, with similar atmospheric controls at both. A conceptual model is developed summarizing temporal variations in water balance and isotopic signatures within the recycle water circuit, including accurate simulation of the unique isotopic enrichment of cooling tower blowdown. This study provides foundational evidence for application of stable isotope mass balance to monitor and improve industrial water use efficiency and management.

1. Introduction

The global mining industry is under increasing pressure by public and governmental agencies to improve the sustainability of its operations (Tost et al., 2018). Foremost among sustainability issues is mine water demand and management due to high water consumption rates and the potential risk for contaminants to be transported off-site by water and air. The Mildred Lake and Aurora North mines, operated by Syncrude Canada Ltd. (Syncrude) are typical oil sands mining operations located north of Fort McMurray, Alberta, Canada. In 2019, 40.1 million m^3 or 13% of water used by Syncrude was withdrawn from the Athabasca River and the remaining 87% was comprised of recycled water from the process circuit. Overall, freshwater water use intensity was 2.33 m^3 per m^3 of bitumen

---

production excluding recycled waters (Syncrude, 2019 Sustainability Fact Sheet). Syncrude does not currently release process-affected water to the environment. Therefore, imported water that is not evaporated or chemically consumed in the upgrading process contributes to the existing on-site inventory of oil sands process-affected waters. As of 2017, the estimated volume of stored process water on site in engineered tailings management facilities (commonly referred to as tailings ponds) was 1.7 Gm^3, reflecting net accumulation since the start of operations over 50 years ago. Of this total, approximately 200 Mm^3 occurs as free water, whereas the remainder is interstitial tailings porewater (W. Zubot, Syncrude, pers. Comm. 2019).

Syncrude's recycled process water is drawn from the tailings ponds following settlement of the discharged tailings slurry (Zubot, 2010). The storage, supply, and recirculation of process water from tailings ponds through upgrading and bitumen extraction facilities is referred to as the recycle water circuit. The immensity of these stores and the critical stress on water for mine operations in this region highlight the importance of accurately tracking the water balance for on-site water such as the recycle water circuit.

The infrastructure of tailings management facilities and operational water demand at oil sands mines are constantly evolving relative to mining operations. As a result, water balance parameters are often difficult to directly measure and so must be routinely modelled or estimated. A recent review of water flow tracking at five oil sands mining operations found many differences in how operators track site wide water balances, with unique challenges evident for individual operations (COSIA Water EPA, 2019). This review recommended that site-wide water balances could be improved through quantification of meteoric water inputs and evaporative losses for all operations. Developing new and efficient tools for tracking the rates, pathways, and distribution of water moving through large scale mining operations is a major research challenge.

Here, we explore and evaluate the feasibility of using the stable isotopes of oxygen and hydrogen (^{18}O, ^{2}H) to track hydrological processes at an operating oil sands mine site, and in particular, to characterize major controls on isotopic composition and water balance of the recycled water circuit including addition of make-up waters and evaporative losses which have been shown to systematically modify isotopic signatures (see Baer et al., 2016).

Past studies involving ^{18}O and ^{2}H as tracers have been used primarily in gauged watersheds, and for a variety of applications including hydrograph separation (Buttle, 1994; Klaus and McDonnell, 2013), transit time modeling (Harman and Kim, 2014; Jasechko et al., 2016; Tetzlaff et al., 2018), vegetation water source partitioning (Evaristo et al., 2015), and water balance assessment (Ferguson et al., 2007; Gibson et al., 2020, 2021). The theory and methods associated with isotope tracer studies to investigate water balance of surficial water bodies are well established (Dincer, 1968; Zimmermann and Ehhalt, 1970; Zuber, 1983; Gonfiantini, 1986). Case studies in Canada have also demonstrated wider application of the technique in cold regions including ungauged lake and river watersheds; (Gibson et al, 2019, 2016a, 2016b, Gibson and Reid, 2014; Tondu et al., 2013; Turner et al., 2014; Turner, Wolfe, and Edwards, 2010). While much progress has been made in basic research within natural systems, the application of isotope tracing to mine water management has been less extensive.

A small number of studies have used stable isotopes for mine-related applications, including characterization of recharge rates or water movement through mine waste and tracing of off-site mine water migration (Allen and Voormeij, 2002; Gammons et al., 2010; Barbour et al., 2016; Dompierre and Barbour, 2016). Characterization of ^{18}O and ^{2}H signatures within the oil sands first began as part of a geochemical characterization pilot study performed by Gibson et al. (2011). This was the first oil sands study to hypothesize that process-affected water signatures were not necessarily controlled by pond water balance alone, as is the case at natural lakes. To date, there has been limited research conducted on why mine waters display their unique isotopic signatures and how these signatures have progressively evolved in response to mining operations. To our knowledge, this is the first study to publish a multi-year dataset of isotopic signatures for an operational recycle water circuit that captures interannual and seasonal variations.

This dataset builds spatially and temporally on investigations by Baer et al. (2016) conducted at Syncrude operations at Mildred Lake, and includes a new sampling program carried out concurrently at the nearby Aurora Mine Site. Baer et al. (2016) published the first local meteoric water line for the Alberta oil sands region and isotopic signatures for a variety of mine site waters. The study concluded that the contributions of cooling tower blowdown to the recycle water circuit and open water evaporation from tailings ponds were the primary controls on the unique isotopic signatures of oil sands process water.

Herein, we incorporate the findings of Baer et al. (2016) and describe results from a high frequency (*i.e.,* bi-weekly) isotope monitoring survey of site wide waters at both the Mildred Lake and Aurora North mine sites.

Characterization of the isotopic evolution of site wide waters was designed to further understanding of how naturally occurring waters (*e.g.,* meteoric waters and river import) mix with current process water inventories, to establish whether waters are systematically labelled across the mine site, and to assess whether these isotopic signals can be employed to investigate and quantify water balance of reservoirs within the recycle water circuit.

The specific research objectives for this study were as follows:

To characterize seasonal and interannual trends of ^{2}H and ^{18}O signatures within the source waters and process-affected water stores of the recycle water circuit; and.

To develop a conceptual model characterizing the relative effects of operational and hydrological processes contributing to the isotopic evolution of the recycle water circuit.

At the outset of this study, we expected that the temporal evolution of isotopic signatures observed from tailings ponds would mimic the seasonality of natural systems within the region (*i.e.*, lakes in a highly seasonal climate); and that mining processes such as the use of evaporative cooling towers or dewatering of enriched tailings porewater were expected to modify these seasonal patterns. Therefore, we anticipated that operational water demands would likely control the residence time of process water within individual tailings ponds and might dampen the build-up of evaporatively enriched waters.

1.1. Study site

Oil sands mining operations began in 1978 at the Mildred Lake (ML) mine, situated 40 km northwest of Fort McMurray, and in 2000 at the Aurora North (AN) Mine, located 35 km to the northeast of Mildred Lake. Operated by Syncrude Canada Ltd. (Syncrude), the mines are situated in the Athabasca Oil Sands Region (AOSR), an area characterized by low-relief, wetland-rich boreal forest and a cold highly seasonal climate with long winters and short summers. Monthly mean air temperature within the region ranges from $-19\,°C$ for January to $17\,°C$ for July, with a mean annual temperature near $1\,°C$. Daily temperatures vary by up to $60\,°C$ between winter lows and
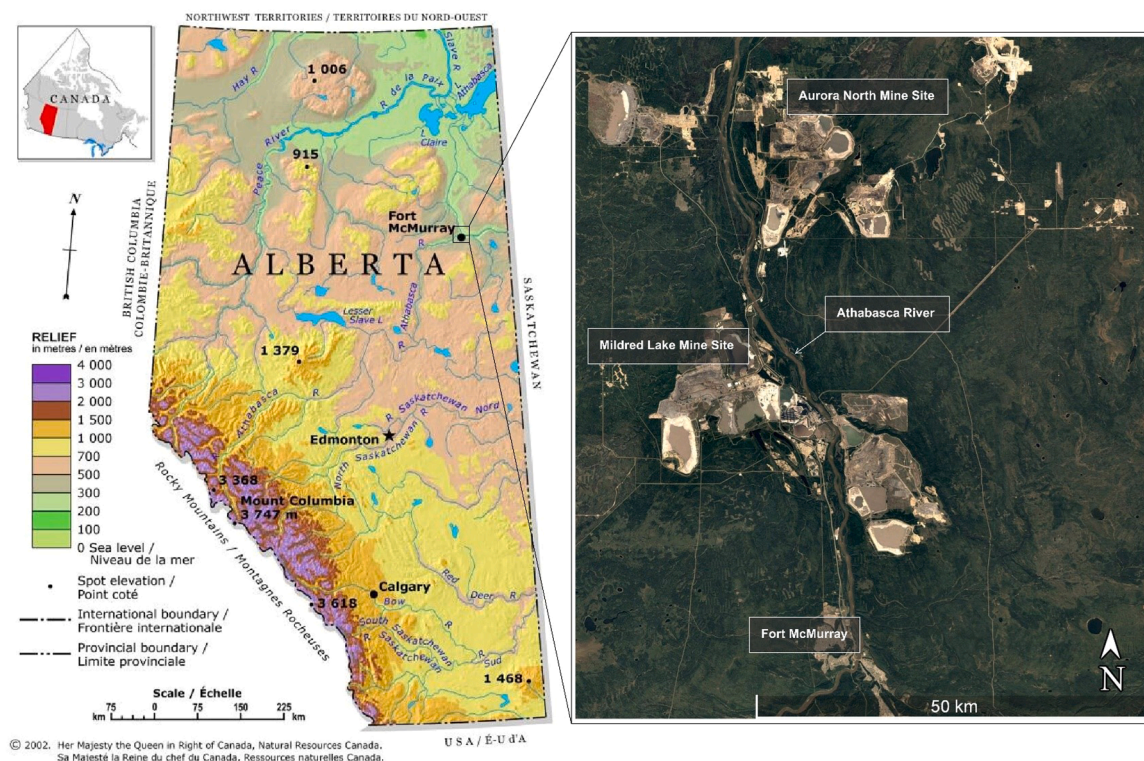

Fig. 1. Maps showing Syncrude's Mildred Lake Mine and Aurora North Mine including site wide surface waters at each site.
(original map reproduced from Google Earth, DigitalGlobe 2018).

summer highs. Annual average precipitation is approximately 450 mm, with one third occurring as snow (Huang et al., 2015). The average annual potential evapotranspiration is approximately 500 mm per year (Huang et al., 2015). Relative humidity follows a seasonal pattern ranging from daily values of 77% for winter months to 65% for high evaporation months of May to October (RAMP Regional Aquatic Monitoring Program, 2015).

Daily bitumen production by Syncrude was 294,000 barrels per day in 2019 with a cumulative production exceeding 3 billion barrels since operations began. The mine sites occupy an area of 200 km^2 of which a variety of landforms are present including active mining pits, tailings sand structures, overburden dumps, above ground and in-pit tailings facilities, and freshwater reservoirs.

Historically, water for bitumen extraction and upgrading has been obtained through the import of Athabasca River makeup water, as well as use of recycle water primarily for tailings transport and extraction. Any fresh water that is not consumed during upgrading is added to the recycle water circuit *via* cooling tower blowdown.

This study focuses primarily on the recycle water circuit at ML; however, isotopic data collected from AN are presented alongside ML to demonstrate the unique isotopic fingerprints of process water with differing raw water sources. Both the ML and AN mines have their own mining and extraction facilities; however, the two mines are hydraulically connected. Process water from the recycle water circuit at ML is sent *via* a pipeline to AN and returned along with hydrotransported bitumen froth for upgrading. Water export from ML to AN decreased from 21.3 Mm^3 in 2012–8.4 Mm^3 in 2016 with the majority of water demand at the AN site now being provided by basal aquifer pumping (W. Zubot, D. Heisler, Syncrude, pers. Comm., 2019). The average return of process water from AN to ML is
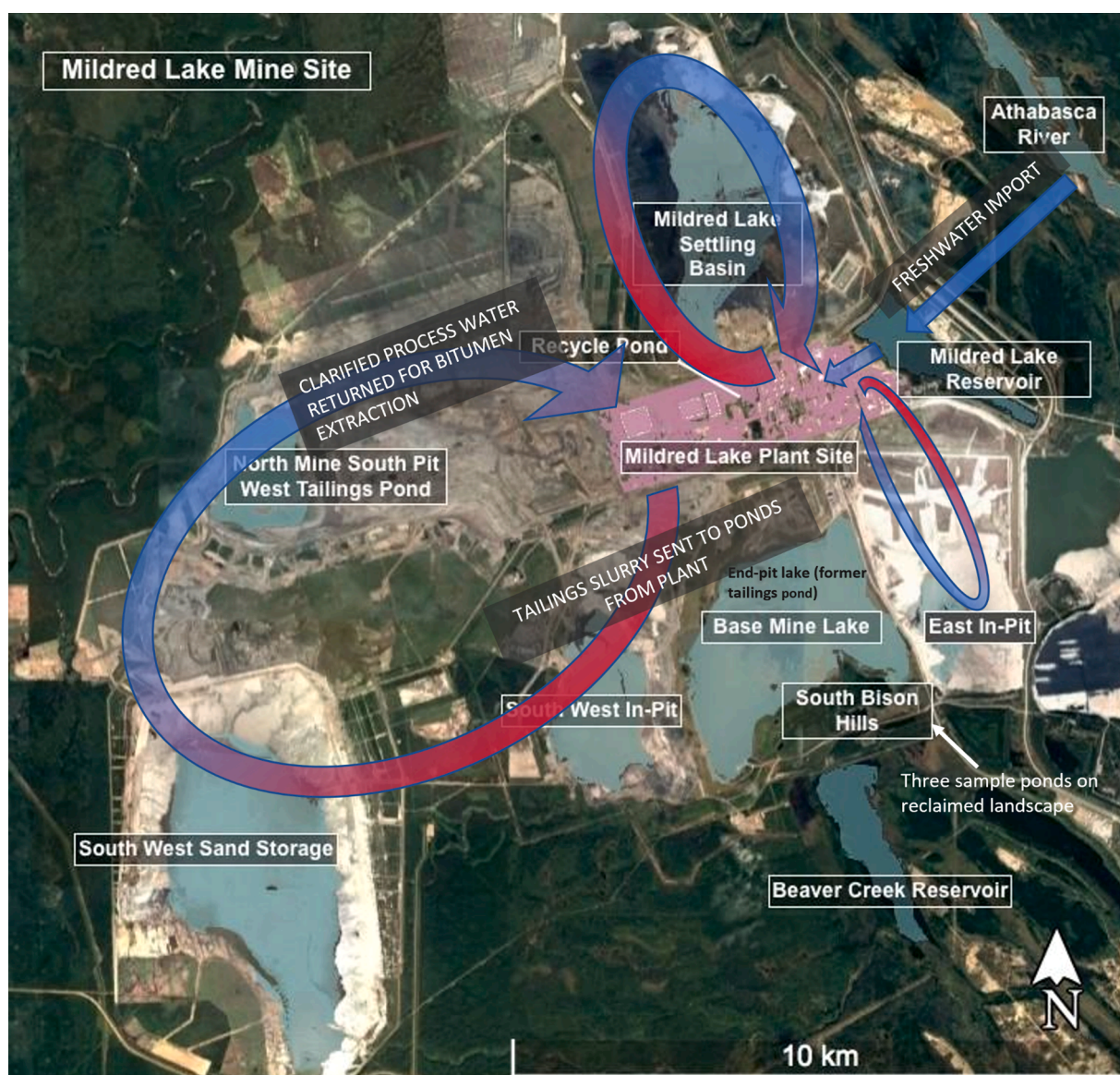

Fig. 2. Simplified depiction of raw water import and process water circulation making up the recycle water circuit at Mildred Lake mine.

approximately 3.7 Mm^3.

The five primary tailings ponds at ML mine site are East in-pit (EIP), Southwest in-pit (SWIP), Southwest sand storage (SWSS), North mine south pit west (NMSPW), and Mildred Lake settling basin (MLSB) (Fig. 1a). The four tailings ponds at AN mine are the Aurora settling basin (ASB), Aurora east pit northwest (AEPN-W), Aurora east pit northeast (AEPN-E), and Aurora east pit south (AEPS) (Fig. 1b).

Water and solids produced during the bitumen frothing process, which separates bitumen from the bitumen-rich ore, are transported and deposited into tailings ponds as a slurry referred to as fluid tailings. As the fluid tailings settle, pore water is released and becomes available as clarified process water for reuse in the extraction and hydrotransport of bitumen. This clarified water is directed to a centralized location at the ML plant referred to as the recycle pond (RP).

A simplified conceptual diagram of raw water import and process water circulation making up the recycle water circuit at ML mine is provided in Fig. 2.

2. Methods

2.1. Field sampling

Water samples were collected in 30 mL HDPE Nalgene bottles, tightly capped and with minimal headspace to minimize evaporation. Sampling was conducted primarily by Syncrude's Environmental Group or by site operators. Sampling locations were selected in consultation with Syncrude to accurately represent the recycle circuit water and contributing source waters. Samples obtained during 2012–2014 were collected as part of the initial characterization study performed by Baer et al. (2016). Primary sampling of the ML and AN circuits resumed in 2016 with key components sampled bi-weekly to capture seasonal changes.

This study presents analyses from 220 samples collected at the ML mine (including those collected by Baer et al., 2016) as follows: SWSS (n = 47); MLSB (n = 61); SWIP (n = 57), and RP (n = 55). Each tailings pond is sampled from the pump line supplying clarified water from the respective pond to the recycle pond. The tailings slurry line from the extraction plant was also sampled (n = 41).

Sampling at AN mine began in 2016 on a biweekly basis. These samples included 129 samples collected from three AN tailings ponds, as follows: AEPN-W (n = 41), AEPN-E (n = 43), and ASB (n = 45).

Rain samples (n = 263) were collected over a 9-year period (2009–2018). Samples were collected from rain collectors designed to minimize the atmospheric interactions and evaporative effects (see Baer, 2014). The rainfall collectors were located at 7 locations including 5 at the Mildred Lake site and 2 at the Aurora Mine site. Samples were collected after each major rainfall event and depths associated with each isotope-sampling event were monitored at on-site meteorological stations.

Snow samples (n = 147) were collected during annual snow depth surveys over the same period. Snow sampling for this study was performed along several transects and primarily collected from the top and bottom of the snowpack. Snow samples were sealed in Ziploc® freezer bags and allowed to melt at room temperature then transferred to water sample bottles.

A total of 46 samples were collected from four cooling towers used in the processing and upgrading of bitumen. Initial cooling tower blowdown samples were collected in the spring of 2016 from all cooling towers on site with a more extensive sampling campaign (biweekly) initiated in the fall of 2016. Only samples from the upgrading cooling tower could be obtained past the initial spring sampling of 2016.

Samples were also collected from the freshwater storage reservoir at ML known as Mildred Lake Reservoir (MLR; n = 22), as described by Baer at al., (2016), and Athabasca River samples (n = 522) were obtained from Gibson et al. (2016c) and subsequently from unpublished monthly data based on sampling conducted by Alberta Environment's Long-Term River Network (LTRN).

2.2. Laboratory analysis

Apart from the Athabasca River samples, which were analyzed by InnoTech Alberta (see Gibson et al., 2016c), all water samples were shipped to the University of Saskatchewan, Saskatoon, SK, and were analyzed in the Saskatchewan Isotope Laboratory using the methods described by Lis et al. (2008). An OA-ICOS water isotope analyzer (Picarro L-2130) is coupled to a CTC LC-PAL liquid autosampler for simultaneous $^2H/^1H$ and $^{18}O/^{16}O$ ratios measurements of H_2O. The autosampler injected 1.80 µL of H_2O into a vapourizer using a 5 µL SGE analytical syringe (SGE 001982). Water samples were heated to 110 °C with a Picarro Vapourization Module A0211 and the vapour was then analyzed by the water isotope analyzer. Data output was imported using LIMS for Light Stable Isotopes (U.S. Geological Survey, http://isotopes.usgs.gov).

All measured water samples were calibrated to internal laboratory standards (USGS 46, 47, and 48), normalized to VSMOW (0‰) and VSLAP (δ^2H-428‰ and $\delta^{18}O$ −55.5‰), and reported in per mil (‰) relative to VSMOW. Error values associated with this method are estimated to be ± 0.8‰ for δ^2H and ± 0.3‰ for $\delta^{18}O$.

2.3. Cooling tower blowdown fractionation model

Process units involved in the upgrading facility and other mining processes that require cooling are treated by open circulating evaporative cooling towers, whereby water is continuously circulated through heated process units and returned back to the cooling towers. Hot water is piped into the cooling tower unit and dispersed onto fill media providing maximum surface area for the water to collect. As the hot water interacts with ambient air passed through the cooling tower, a portion of the water evaporates, removing heat from the water. The cooled water is collected in a basin at the base of the cooling tower and subsequently recirculated through process

units or vessels requiring cooling. Saturated warm air is expelled through the top of the cooling tower units by fans. A conceptual diagram of an evaporative cooling tower is provided in Fig. 3. Further operational details of cooling towers at the site have been summarized by Zubot (2010).

The efficiency of the cooling towers is evaluated by the ratio of concentration of a dissolved species in the blowdown water (C_b) to the make-up water (C_{mu}) referred to as the cycles of concentration ($COC = C_b/C_{mu}$). For example, if the cycles of concentration is 10 or greater, performance is rated very high, and if COC is 2 or less, performance is rated as very poor (Zubot, 2010). The amount of water released as blowdown, and the commensurate volume of water lost to evaporation, can be calculated from the COC with the fraction (f) of water remaining after evaporation equal to 1/COC.

The monitored COC can be used to estimate evaporation; however, the corresponding isotopic fractionation is also governed by temperature (T), humidity (h) = RH/100% where RH is relative humidity, and the ^{18}O and ^{2}H concentrations within the water vapour of the air (δ_{A18} and δ_{A2}) inside the cooling towers. Calculating fractionation due to evaporative losses would require knowledge of these parameters, which are not currently monitored for operational purposes. Estimates of these unknown parameters (T, h, δ_{A18}, δ_{A2}) can be made to compare the isotopic signatures of blowdown and relate it to the observed COC.

We found that when the ^{18}O and ^{2}H values of blowdown waters were plotted against the fraction of water remaining (f; where $f = 1/COC$) the enrichment proceeded in a linear relationship similar to that of closed-system Rayleigh distillation. Therefore, we attempted to constrain T and h by using a closed-system fractionation model following Criss (1999):

$$\delta_f = \frac{[\alpha_{tot} \cdot \delta_i + 1000 \cdot f(\alpha_{tot} - 1)]}{[\alpha_{tot}(1 - f) + f]} \tag{1}$$

where δ_i and δ_f are the initial and final isotopic composition of the reservoir over the model period, f is the residual water fraction (V_f/V_0), and α_{tot} is the total fractionation factor between liquid and vapour calculated by:

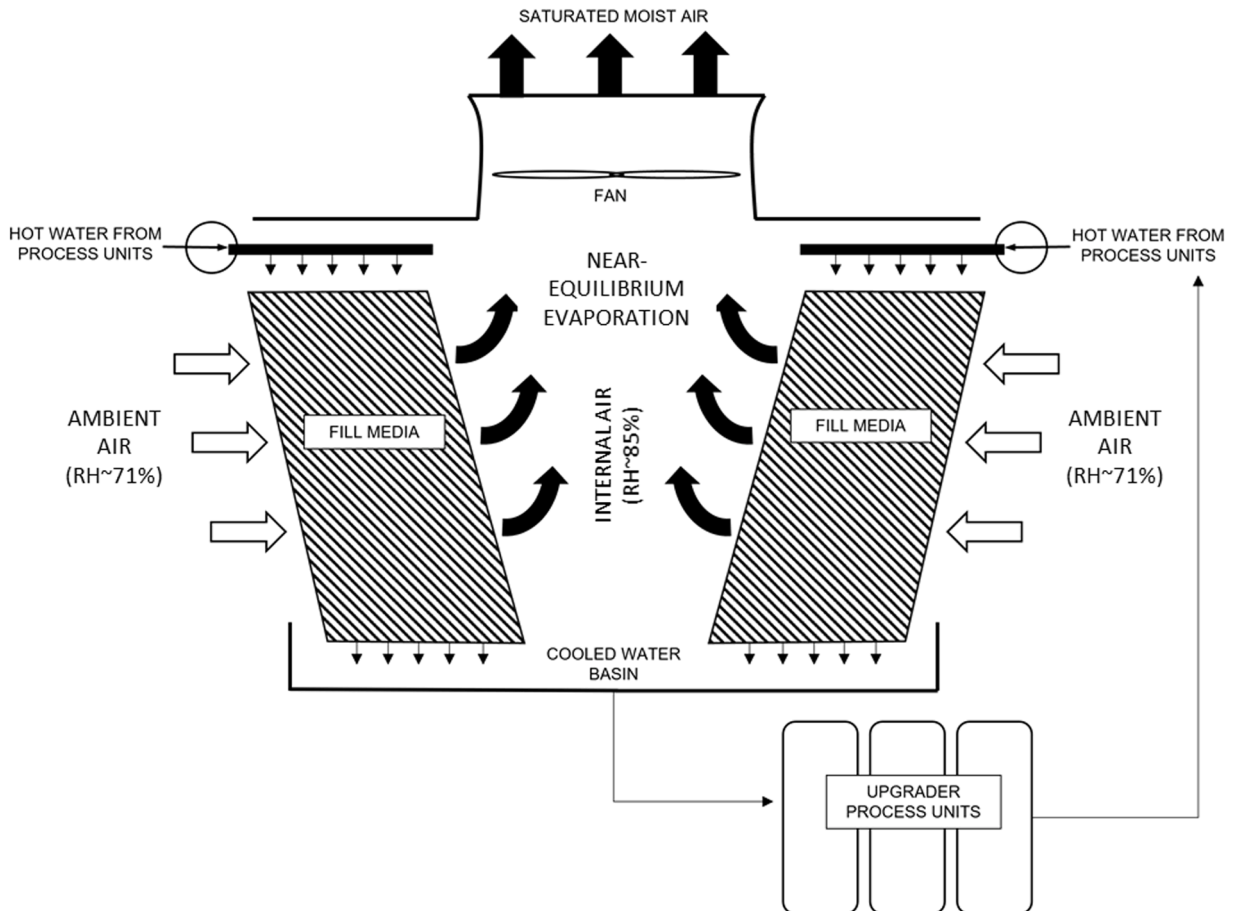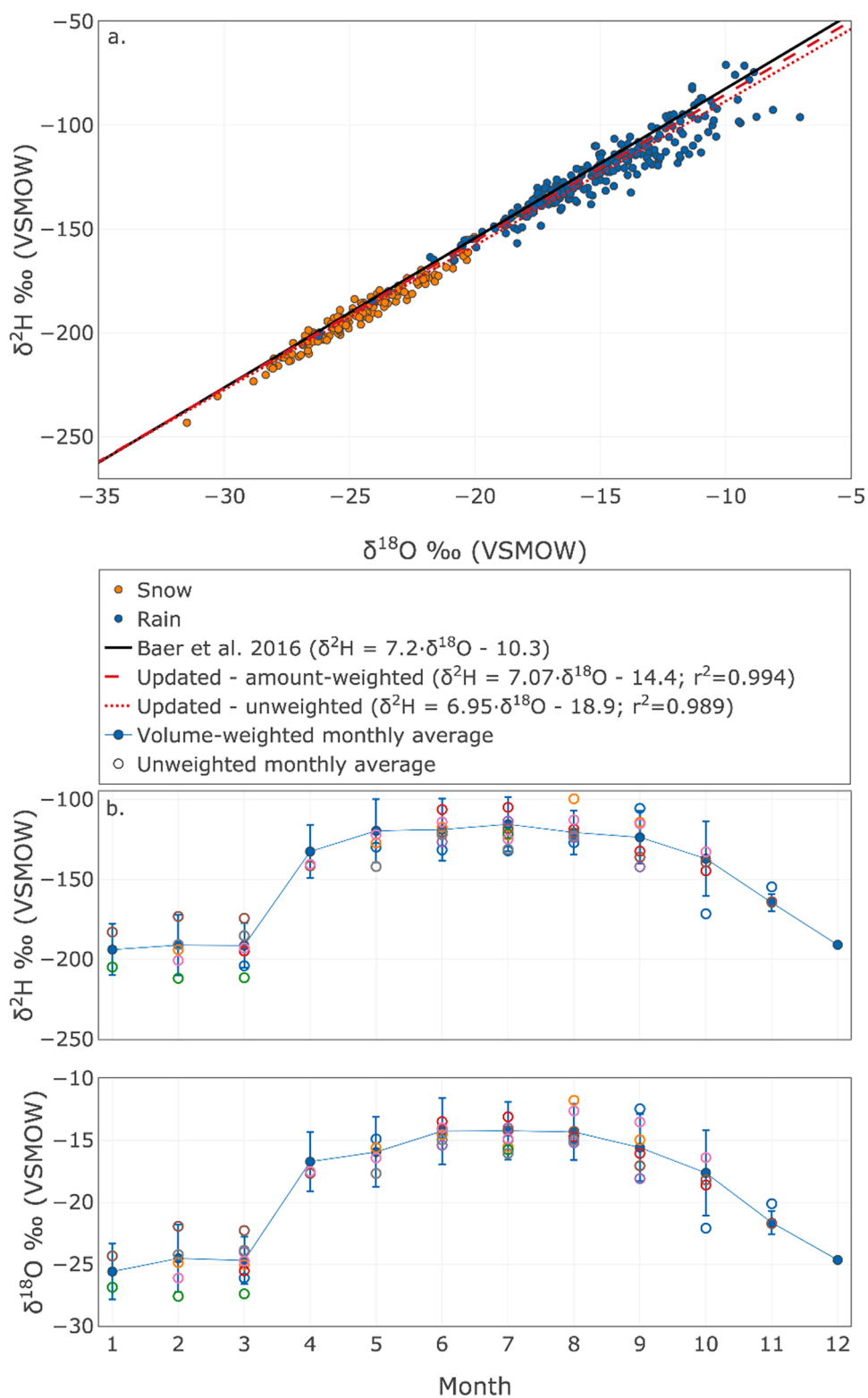$$\alpha_{tot} = \frac{(\varepsilon^* + \varepsilon_K)}{1000} + 1 \tag{2}$$

Fig. 3. Conceptual diagram of evaporative cooling tower operations.

(caption on next page)

Fig. 4. a.) Stable isotopic signatures of site wide meteoric water samples with published LMWL (Baer et al., 2016) and updated LMWL (amount weighted and unweighted). b.) Monthly volume-weighted isotopic signatures of ^{18}O and ^{2}H in precipitation samples collected from 2009 to 2018. Numbers 1–12 represent the calendar month, error bars indicate the monthly standard deviations, and coloured open circles are the unweighted monthly means from each year of collection. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

where ε^* and ε_K are the equilibrium and kinetic enrichment in per mil (‰) calculated based on relationships with temperature and humidity (*h*) as outlined in Horita et al. (2008).

The enrichment of the cooling tower blowdown was also modelled using a fraction-dependent model that requires δ_A values and incorporated a linear resistance model for estimating the isotopic composition of the evaporate (Craig and Gordon, 1965) Cooling towers were modelled as evaporation-only reservoirs (*i.e.*, dV/dt = -E) for which δ_f was estimated, according to Gonfiantini (1986), as:

$$\delta_f = \left(\delta_i - \frac{A}{B} \right) f^B + \frac{A}{B} \qquad (3)$$

where

$$A = \frac{h\delta_A + \varepsilon_K + \frac{\varepsilon^*}{\alpha}}{1 - h + \varepsilon_K} \qquad (4)$$

and

$$B = \frac{h - \varepsilon_K - \frac{\varepsilon^*}{\alpha}}{1 - h + \varepsilon_K} \qquad (5)$$

where α is the equilibrium enrichment factor which is empirically predicted based on *T*, as outlined in Horita et al. (2008). Similar isotope balance approaches have been applied to predict isotopic enrichment in drying evaporation pan experiments and shallow evaporative lakes (see Gibson et al., 1999, 2002).

3. Results

3.1. Temporal isotopic signatures of precipitation and makeup water

3.1.1. Precipitation sampling

Annual rainfall recorded from 2009 to 2017 ranged from 151 mm in 2011 to 387 mm in 2016 with an annual mean of 310 mm. The isotopic composition of rain and snow samples collected across the site are shown in a dual isotope crossplot in Fig. 4a. A total of 263 rainfall samples collected during 2009–2018 ranged between − 26.23 and − 7.03‰ in δ^{18}O and − 201.62 and − 71.3‰ in δ^{2}H, with a weighted average of − 14.77‰ and − 120.06‰ for δ^{18}O and δ^{2}H, respectively (see Table A.1).

Snow samples (n = 147) were collected in February/March from 2009–2018 (see Table A.2). The Snow water equivalent (SWE) during these surveys ranged from 22 mm (2009) to 80 mm (2017). Only a bulk representation of the isotopic composition of snow was possible given the collection methodology. The non-weighted mean isotopic composition of all snow samples, considered representative of input during spring melt, were found to be − 24.67‰ and − 191.04‰ for δ^{18}O and δ^{2}H, respectively (Fig. 4b).

Monthly precipitation values depict seasonality in isotopic composition at the closely located study sites (Fig. 4b). Estimates of mean annual amount-weighted precipitation was calculated using the rainfall amounts and corresponding isotopic composition of rain events (for warm months) and average snow composition and the measured SWE (for cold months). The mean annual amount-weighted precipitation is estimated to be − 18.04‰ for δ^{18}O and − 143.54‰ for δ^{2}H.

3.1.2. Local meteoric water lines

Local Meteoric Water Lines (LMWLs), updated to include the 2014–2019 data (Fig. 4a), are calculated as follows:

$$\delta^2 H = 7.07 \cdot \delta^{18}O - 14.4 [‰] \quad \text{(amount − weighted; r − squared = 0.994)} \qquad (6)$$

and

$$\delta^2 H = 6.95 \cdot \delta^{18}O - 18.9 [‰] \quad \text{(unweighted; r − squared = 0.989)} \qquad (7)$$

as compared to $\delta^2 H = 7.20 \cdot \delta^{18}O - 10.3 [‰]$) reported by Baer et al. (2016) for ML. While the slope and intercept are slightly decreased compared to the previous LMWL calculated by Baer, these lines are essentially indistinguishable from the perspective of defining hydrologic inputs. As snow was sampled opportunistically during winter, and because bulk SWE and average snowpack isotope values were used to amount weight for each month in winter rather than adhering strictly to monthly sampling, the resulting LWML should be viewed as a first approximation. However, generally, it appears to confirm differences between isotopic values for precipitation in the AOSR as compared to Edmonton ($\delta^2 H = 7.70 \cdot \delta^{18}O - 0.02 [‰]$) or Ft. Smith ($\delta^2 H = 6.8 \cdot \delta^{18}O - 20.9 [‰]$ see Baer et al. (2016).

3.1.3. Athabasca river source water

The temporal evolution in Athabasca River samples (n = 524, 2002–2020; Table A.3) both upstream and downstream of Fort McMurray are shown in Fig. 5a. Based on an 18-year record, average isotope values were found to be − 17.87‰ and − 142.42‰, for $\delta^{18}O$ and δ^2H respectively.

The Athabasca River dataset was grouped by month to highlight seasonal patterns that could influence the isotopic composition of the imported waters for extraction, with the monthly mean and standard deviations shown in Fig. 5b. There was little variability found in the isotopic signature of Athabasca River samples on a monthly basis with the monthly mean of $\delta^{18}O$ shifting by only ~1.00‰ and δ^2H by ~8.00‰ between the most enriched months (Mar/Sept/Oct) and most depleted months (June/July). The coefficient of variation (CV) for all river samples assessed was − 4.30% and − 3.35% for ^{18}O and ^2H respectively.

3.2. Temporal isotopic signatures of mine site waters

3.2.1. Mildred lake reservoir (MLR)

MLR is used to hold the raw water imported on-site from Athabasca River and differs from Athabasca River due to storage effects which dampen seasonal and interannual variations. Surface water samples (n = 22) were collected from MLR over the period of 2012–2017 with the majority of samples collected in 2013 and 2014 (see Table A.4). Fig. 5a shows the temporal distribution of $\delta^{18}O$ and δ^2H from the sampling period. The mean of all samples spanning the five-year study was − 16.72‰ and − 137.49‰ for ^{18}O and ^2H respectively, which was more enriched than the average isotopic composition of the Athabasca River. The isotopic signatures of the reservoir in spring 2013 and 2015 are very similar between each year and appear to be largely influenced by the spring freshet characterized by depleted snowmelt isotopic values. Isotopic signatures of the reservoir observed during late summer/early fall in 2013 and 2014 differ noticeably between the years. Signatures from 2014 displayed more enriched values for both $\delta^{18}O$ and δ^2H,
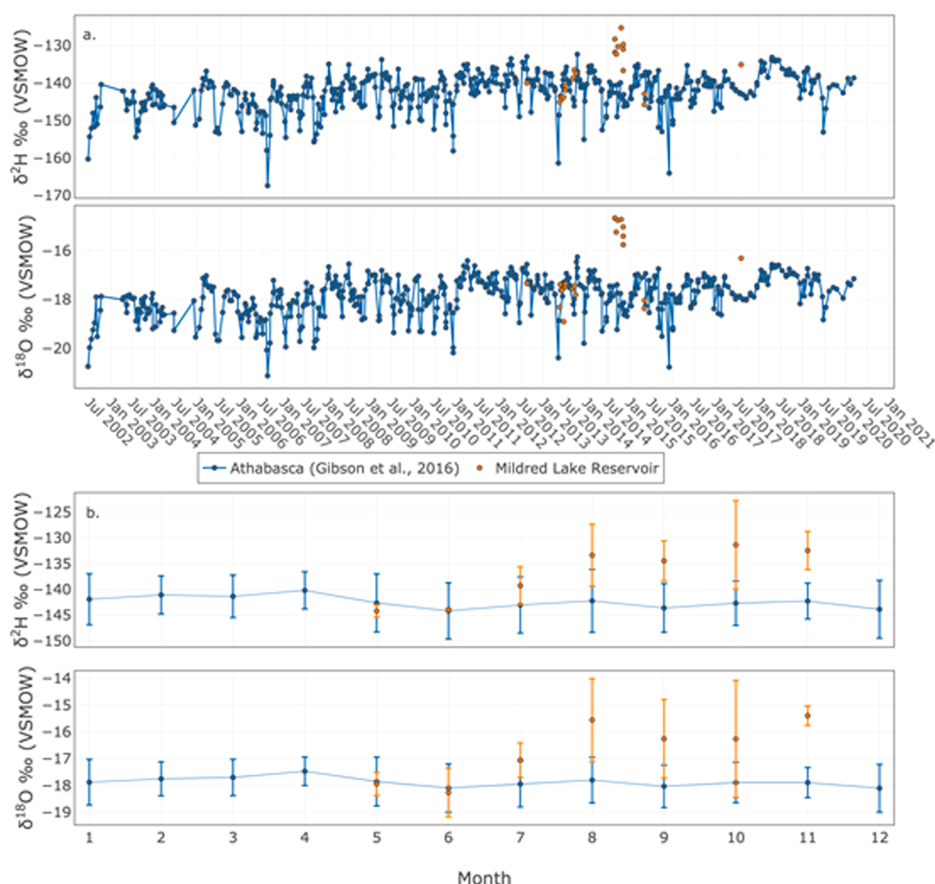

Fig. 5. a.) Time-series summary of $\delta^{18}O$ and δ^2H from 524 water samples collected from the Athabasca River upstream and downstream of Fort McMurray, AB over the years 2002–2020, and 22 water samples collected from the Mildred Lake Reservoir during the ice-free period over years 2012–2017. b.) Monthly means of ^{18}O and ^2H from Athabasca River and Mildred Lake Reservoir water, error bars represent the standard deviation for each month.
Provided by Gibson et al. (2016c) and unpublished data)

suggesting the influence of changes in mine water demand on the isotopic signature, rather than solely on changes in seasonal water balance components. Monthly variations and standard deviations are shown for MLR in Fig. 5b. Standard deviations were low for the spring and early summer months (May-July), but became much higher in late summer and fall (Aug-Oct) with isotopic ranges greater than 4‰ and 15‰ for ^{18}O and ^{2}H respectively. The CVs of all MLR samples were found to be − 8.44% and − 4.52% respectively.

3.2.2. Cooling tower blowdown

A total of 46 blowdown samples were collected from the cooling tower blowdown streams (CAP: n = 2; UE-1: n = 2; Utility: n = 2; Upgrading: n = 40) over the period of 2016–2018 (see Table A.5). Of the 46 samples collected, the most depleted isotopic signatures were − 16.18‰ and − 132.5‰ for ^{18}O and ^{2}H, respectively. These signatures occurred on 8 Nov 2017 and were collected from the upgrading tower. The most enriched values of − 10.03‰ and − 95.5‰ for ^{18}O and ^{2}H, respectively, were collected from the CAP tower on 7 March 2016. Mean values for blowdown were − 13.37‰ and − 116.25‰ for ^{18}O and ^{2}H, respectively. Raw water discharge was also measured in April 2016 to characterize the input water before fractionation effects. This water had an isotopic signature of − 18.32‰ and − 144.4‰ for ^{18}O and ^{2}H, respectively, which was similar to relatively stable Athabasca River signatures.

Both ^{18}O and ^{2}H of cooling tower blowdown becomes more enriched as cycles of concentration increases (Fig. 6). All the samples collected in this study fell along a similar enrichment trendline with a slope of 5.52 (referred to as an evaporation line). Offset along the evaporation line indicates a higher degree of evaporation loss, as confirmed by higher cycles of concentration (COC) values. COC during sampling was typically 1.5–2.0. When sorted by month of collection, the samples collected in the cooler months (Oct-May) plotted between the local evaporation line for tailings ponds and the LMWL whereas the warmer months (June-Sept) plotted below the local evaporation line. This may be partly due to seasonal shifts in operating conditions (T and possibly h) in the cooling towers but must also reflect the influence of seasonal variations in the isotopic composition of ambient atmospheric moisture.

3.2.3. Recycle water circuit

A 6-year record from ML mine (2012–2018; n = 220; see Table A.6) and a 2-year record from AN mine (2016–2018; n = 129; see Table A.7) are presented in Fig. 7a. Up until 2015 all three existing tailings ponds located at ML mine (SWSS, SWIP, RP) and MLSB tracked closely to each other indicating similar sources and water balance conditions. However, from the end of 2016 onward, the SWSS became significantly more enriched than MLSB, indicating reduced connectivity of the SWSS to the remaining recycle water
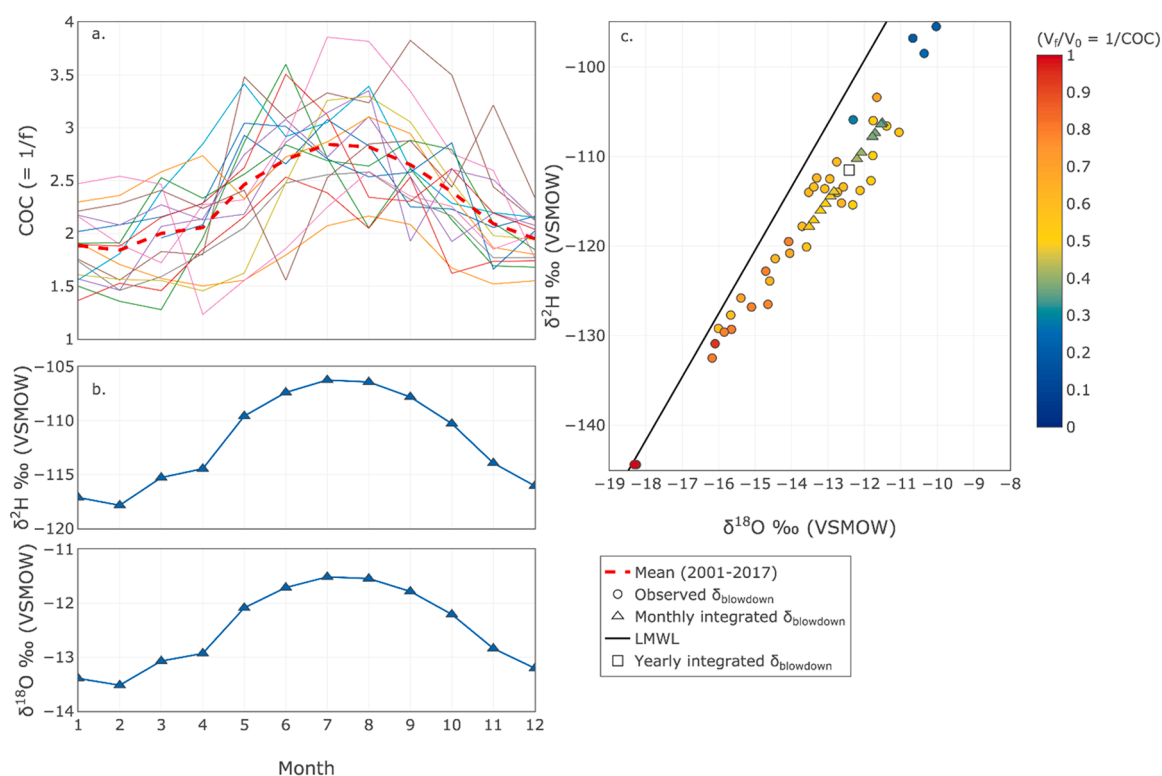

Fig. 6. a.) Mean monthly cycles of concentration values plotted alongside the historical monthly blowdown values from 2002 to 2017 (coloured lines); b.) Volume-weighted monthly-integrated blowdown signatures based on the closed-system model in conjunction with historical operations data of cooling towers. Model parameters are T = 35 °C, RH = 85%, and initial isotopic composition equal to the average annual Athabasca River signature; c.) Dual isotope plot of both monthly and annual blowdown signatures alongside observed blowdown signatures for reference. It should be noted that the observed signatures are primarily collected from only one tower, whereas the integrated signatures are representative of a collective signature from all towers.

circuit, leading to a cumulative evaporative enrichment as a result of reduced throughput and increased residence time. The enrichment of SWSS is more evident when plotted in dual-isotope space (Fig. 7c).

Overall, the MLSB samples plotted closer to the LMWL than the other ponds, while the RP samples displayed signatures consistent with a mixture of all tailings ponds. Predicted mean values and annual ranges for the recycle circuit, based on mixture of MLSB, SWSS and RP signatures are provided in Table 1.

Tailings ponds at AN mine are found to plot below those of the ML mine (Fig. 7). AN initially relied on clarified water supplied by ML for bitumen extraction, although water demand decreased from 21.3 Mm^3 in 2012–8.4 Mm^3 in 2016 as basal aquifer pumping became the primary source water at the AN site. AN returns an average of 3.7 Mm^3 of water in the form of bitumen froth to ML annually. ^{18}O values are similar to those at ML and display the same magnitude of seasonal enrichment (Fig. 7b). However, ^{2}H values are consistently lower than those at ML by approximately 10–15‰, likely due to the effect of basal McMurray Formation aquifer sources with depleted isotopic signatures at AN. Based on 58 samples collected from the basal aquifer, mean δ^{18}O and δ^{2}H were found to be − 19.92‰ and − 158.76‰, respectively, with standard deviations of 0.76 and 4.20. This contrasts with Athabasca River water averaging close to − 17.87‰ for δ^{18}O and − 142.42‰ for δ^{2}H, which was the dominant source at ML. The enrichment slopes from each mine site, calculated by regression analysis of ^{18}O and ^{2}H in dual isotope space, are slightly lower for ML (4.20) as compared to the AN (4.54), which appears to suggest similar open-water evaporative conditions, but expectedly based on theoretical considerations, also may produce slight convergence of evaporation trajectories at both sites towards similar limiting isotopic enrichment values as predicted from Eqs. 4 and 5, by A/B. The latter assertion assumes similar ambient atmospheric moisture controls at both sites.

3.2.4. Tailings slurry

Tailings slurry samples (n = 41) were collected between the years 2013–2018 ranging from − 14.82‰ to − 11.75‰ and-124.10‰ to − 106.90‰ for ^{18}O and ^{2}H respectively, with mean values of − 13.58‰ and − 117.89‰, respectively (see Table A.8). When plotted temporally, the ^{18}O and ^{2}H values of the tailings slurry track closely with the RP values over time although the latter are relatively enriched below the LMWL due to evaporative isotopic enrichment.

3.2.5. Constraints on cooling tower fractionation

One of the goals of this study was to quantify the isotopic signatures of input waters to the recycle water circuit for future isotope tracer studies. Firstly, we utilized a closed-system fractionation model (Eq. 1) to estimate the isotopic signature of cooling tower blowdown using operational data provided by Syncrude. The primary controls affecting fractionation according to Eq. 1 are the cycles of water recirculation (expressed as cycles of concentration, *COC*) as well as internal *T* and *h* within the cooling tower units. *COC* values
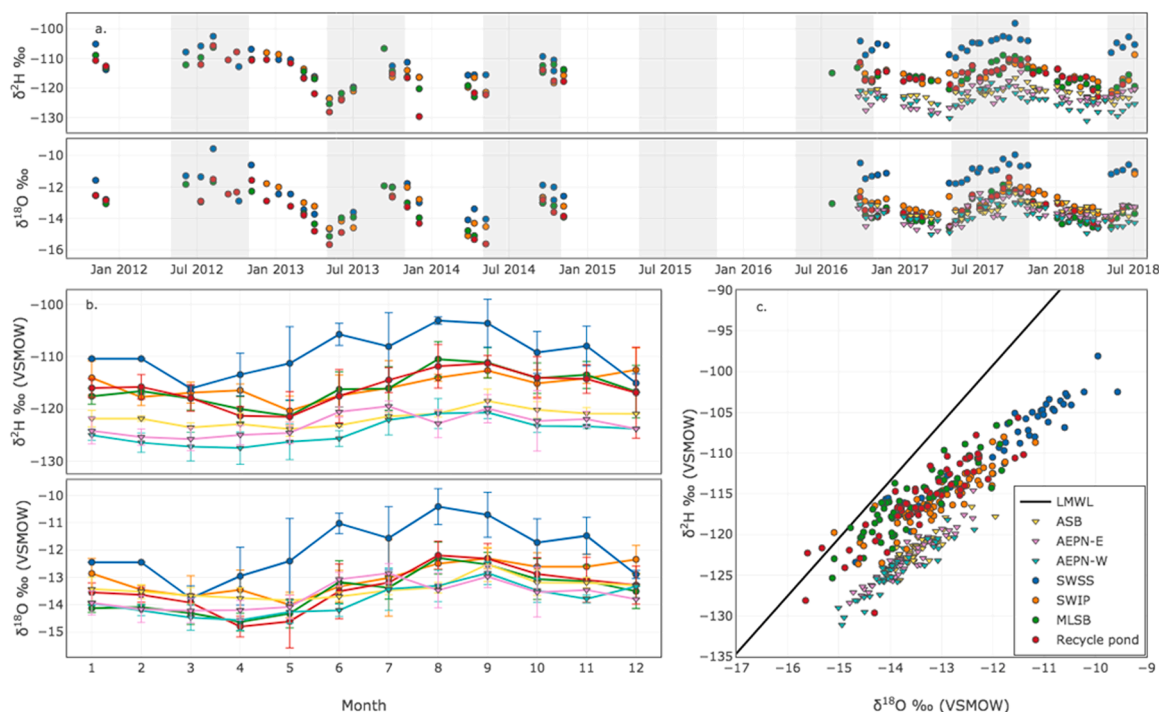

Fig. 7. a.) Time series summary of ^{18}O and ^{2}H values of process water samples collected from tailings ponds at Mildred Lake Mine (n = 220) from a 6-year period (2012–2018) and Aurora North Mine (n = 129) from a 2-year period (2016–2018). Southwest sand storage: SWSS; Mildred Lake settling basin: MLSB; Southwest in-pit: SWIP, Aurora settling basin: ASB, Aurora end pit northeast: AEPN-E, and Aurora end pit northwest: AEPN-W. b.) Monthly means of each tailings pond with standard deviations. c.) Process water samples plotted in dual isotope space along the LMWL.

Table 1

Annual statistical analysis of Mildred Lake settling basin (MLSB), Southwest in-pit (SWIP), and recycle pond (RP) grouped together to represent the recycle water circuit.

				$\delta^{18}O$ [‰]					δ^2H [‰]			
Year	n	Mean	STD	CV	Min	Max	n	Mean	STD	CV	Min	Max
2011	4	-12.74	0.26	-2.04	-13.06	-12.53	4	-111.32	1.92	-1.72	-113.13	-108.90
2012	11	-12.19	0.55	-4.51	-12.95	-11.51	11	-109.39	2.18	-1.99	-112.13	-105.65
2013	26	-13.59	1.05	-7.73	-15.65	-11.93	26	-118.19	5.59	-4.73	-129.62	-106.61
2014	18	-13.88	0.99	-7.13	-15.61	-12.64	18	-117.10	3.51	-3.00	-122.97	-112.00
2016	16	-13.22	0.51	-3.86	-13.96	-12.27	16	-115.08	1.95	-1.69	-118.00	-111.30
2017	64	-13.07	0.76	-5.81	-14.58	-11.40	64	-114.78	2.82	-2.46	-121.00	-108.90
2018	34	-13.68	0.66	-4.82	-14.59	-11.17	34	-117.94	2.87	-2.43	-122.90	-108.70

for each cooling tower were provided by Syncrude, but unfortunately *T* and *h* were not measured.

To constrain temperature and humidity, and to provide a better indication of potential influence of these internal conditions on the resulting isotopic enrichment, a sensitivity analysis was conducted varying temperature from 5° to 65 °C, and varying *h* between 0.75 and 0.95. As shown in Figs. S1 and S2, simulations suggested a best fit to the observed evaporation line slope for $h \approx 0.85$ and T ≈ 35 °C. As the annual mean outside air temperature on-site varied between − 35 °C and 25 °C, averaging 3 °C, we estimate that the cooling towers operated at temperatures that were 30–40 degrees higher than the external ambient atmosphere, which notably influences the effective equilibrium fractionations.

Potential sensitivity of the cooling tower enrichment process to ambient atmospheric moisture was also tested by simulating evaporation under a range of δ_A values, based on Eqs. 3–5 using best fit values for *h* and *T* determined by the previous sensitivity tests (Figs. S1 and S2). As shown in Fig. S3, the lower boundary for the δ_A values ($\delta^{18}O = -24.94$‰, $\delta^2H = -194.72$‰) was calculated using the total weighted mean value of precipitation from the period May to Oct and the assumption that atmospheric moisture is in equilibrium with precipitation (following Gibson et al., 2016b). A variety of lower boundary values were then tested in 10% intervals for sensitivity analysis.

Simulations using more enriched values of δ_A were found to predict evaporation slopes adequately; however, the degree of enrichment associated with measured volumetric reduction was greatly overpredicted (Fig S3). In fact, better results were obtained for more depleted values of δ_A, which we attribute to the atmosphere in cooling towers being derived predominantly from evaporate itself, with only minor influence of ambient δ_A introduced from the outside atmosphere. In this case, cooling towers can be viewed in a similar way to large lakes or oceans with very high evaporation recycling ratios (see Jasechko et al., 2014; Gibson et al., 2016b). This highlights our initial hypothesis that the cooling towers operated more similar to a closed-system and are controlled primarily by temperature and humidity shifts rather than δ_A.

While some *h* gradient is suggested by the fitted enrichment trends, the results are consistent with an atmosphere inside the cooling towers with a relative humidity of about 85%. The effect of temperature gradients on the fractionation would be limited by the fact that δ_A is inside the cooling towers and the main source of atmospheric humidity is the cooling tower source water itself rather than the free atmosphere. While further work will be required to test our approach, similar near-equilibrium fractionation has been shown by Ingraham et al. (1994) for a cooling tower used at a power generation facility.

The volume-weighted monthly and annual blowdown signatures were calculated for each tower using the reported cycles of concentration values and blowdown values (2002–2017, Table A.9 and A.10) assuming a closed-system model, using raw water values sampled from the discharge line for inputs (~ average isotopic signature for Athabasca River), and best-fit values for *T* and *h* based on the sensitivity analysis. The monthly range for $\delta^{18}O$ (δ^2H) was − 13.52‰ to − 11.51‰ (−117.84‰ to −106.24‰) with a monthly mean blowdown volume of 490,000 m³. The integrated annual signature was calculated as − 12.53‰ and − 112.16‰ for ^{18}O and ^2H respectively, with an average annual blowdown volume of 5.9 Mm³.

4. Discussion

4.1. Tracing meteoric waters through the recycle water circuit

Isotopic signatures of the sampled meteoric waters displayed consistent seasonal patterns. Highly enriched precipitation values were observed during mid-summer convective events and shifted along the LMWL. Precipitation in cooler periods (*e.g.*, late season rain and snowfall) had more depleted signatures in comparison to warmer months. The isotopic composition of snow had the lowest isotope values of all sampled precipitation, also shifting along or close to the LMWL. The most enriched monthly means occurred in June-August and shifted to progressively more negative values over the months of September to November as temperatures cooled (Table A.1). These seasonal trends can be seen in the distribution of individual precipitation samples plotted in dual isotope space and categorized by month of collection (Fig. 4b). Meteoric waters entered and mixed with stored process water through direct contact in tailings ponds and as direct surface runoff during spring melt events. Our observations indicate that the influence of individual precipitation events on the recycle water circuit is minor, given the volume and isotopic signatures of individual tailings ponds. Notwithstanding, the influence of the spring freshet was discernable each year by systematic depletion of the tailings ponds signatures.

Cumulative evaporation, sublimation, and mid-winter melting can contribute to enrichment of the snowpack over the winter and

spring as melting progresses (Moser and Stichler, 1975; Clark and Fritz, 1997; Taylor et al., 2002). Nevertheless, little evidence was found for systematic enrichment based on our snowpack measurements. As a result, we assumed that the average weighted value of snow samples collected was representative of snowmelt input to surficial waters on site. This is consistent with Lee et al. (2010) who found that mean isotopic values of new snow, snowpack, and meltwater were not significantly different based on observations of temporal variation of the isotopic composition of the evolving snowpack and melt. Therefore, it is considered appropriate to employ the average isotopic composition of the snowpack from the dataset for any future isotopic mass balance work quantifying the influence of snow and snowmelt to the recycle water circuit.

The intersection of the evaporation line with the LMWL has sometimes been used to estimate the representative isotopic signature of source waters to surface ponds (Gat, 1996; Gibson et al., 2005). Employing this approach for the case of the ML reclaimed areas, we find primary source waters to be strongly skewed towards snowmelt runoff. From a similar assessment of the LMWL intercepts of three shallow ponds on reclaimed sites at the ML site collected between May and November, 2003–2018, we find the estimated source values for the ponds to be − 23.2‰ and − 178.5‰ for ^{18}O and ^{2}H respectively, very similar to the average measured values for the snowpack (δ^{18}O = −24.67‰ and δ^{2}H = −191.04‰). Overall, given the close agreement between intercepts and snowpack measurements, we can conclude that snowpack was a dominant source anchoring the evaporation line trajectories for reclaimed areas, while the influence of rainfall appeared to be relatively minor. Contrary to this observation, evaporation lines developed for the recycle water circuit intersected the LMWL at a more enriched point beyond the cluster of snowpack values, despite displaying seasonal depletion during the spring freshet when plotted temporally. This observation indicates the greater influence of mining processes affecting isotopic mixing and fractionation within the recycle water circuit over the input of isotopically depleted snow and snowmelt.

Our comprehensive isotope dataset of meteoric waters also reveals a high degree of variability of isotopic composition for individual precipitation events, although these perturbations are not necessarily observable in the various mine circuits at the time of the events due to the residence-time weighting effect of source waters in the system. Low residence times are expected in the tailings ponds due to high throughflow rates induced by high onsite water demand. While Syncrude does not track pumping rates to and from individual tailings ponds, we estimate the (free water) volume of MLSB in 2016 to be 3.4 Mm^3 (Syncrude Canada Ltd, 2017), whereas 200 Mm^3 yr^{-1} circulates through this pond in a year. This suggests a residence time on the order of six days. Industry monitoring of water demand and exchange between tailings ponds, including at a minimum seasonal volume of tailings ponds, would greatly improve any attempts at isotope mass balance modelling to assess water balance parameters of the recycle water circuit. Consequently, for isotope mass balance modelling of the mine circuits, we recommend use of longer time intervals to buffer potentially short-term perturbations in water supply demands, which are currently not well quantified. For this purpose, seasonal, or annual calculations using volume-weighted averages of the isotopic signature of meteoric waters are recommended.

4.2. Tracing river import to the recycle water circuit

Stable isotopic variations in the Athabasca River, the source of mine makeup water, have been monitored monthly over the past two decades under the AEP/OSM Long-Term River Network (LTRN) program. Isotopic signatures in the river, both upstream and downstream of ML, have been shown to respond seasonally to variations in timing and proportions of input from snowmelt, groundwater, surface water, and rainfall events, as well as routing of water from both local and upstream tributaries and headwaters (Gibson et al., 2016c). Interannual variations are also observed, particularly in response to variations in snowpack extent, timing of spring melt, and summer storms. Typical seasonal isotopic variations are found to be in the range of 2–3‰ for δ^{18}O and 10–15‰ for δ^{2}H, and generally become more depleted during spring melt and then rebound and enrich again during summer and fall. Winter variations are typified by subtle but progressive isotopic depletions which reflect recession to baseflow as groundwater becomes the dominant source of water under ice. Compared to isotopic variations noted for the Athabasca River, on-site water reservoirs were found generally to undergo earlier spring melt depletion trends in May/June rather than in June/July which was typical for Athabasca River.

MLR, which is used to store raw water imported on site from Athabasca River is operated at an average depth of 5 m (D. Heisler, Syncrude, pers. Comm. 2018). The reservoir receives meteoric water inputs both as direct precipitation and *via* surface runoff and snowmelt events. MLR freezes over during the winter, with ice generally persisting from mid-November to April/May; however, it continues to receive water from Athabasca River and supplies water to the mine site throughout the ice-on period.

4.3. Tracing cooling tower blowdown

The largest use of freshwater import from Athabasca River is for bitumen upgrading (Matte, 2005; Zubot, 2010). The majority of this water is heated and ultimately passes through the cooling towers prior to being added to the recycle circuit. The isotopic composition of cooling tower blowdown is largely controlled by the number of cycles (and resulting evaporative enrichment) water has experienced. However, if the isotopic composition of the input water varies seasonally this signal could be reflected in the blowdown composition.

The mean annual relative humidity at ML is close to 71%, with higher values in winter and lower values in summer. Initially, humidity within the cooling towers was thought to be high and close to saturation (*i.e.,* near ∼100%). Our sensitivity analyses and modelling efforts have demonstrated that the cooling tower blowdown signatures are likely sensitive to internal conditions in the cooling towers (*i.e.,* humidity and temperature), which affects evaporative fractionation of ^{18}O and ^{2}H, but we have also postulated a weak dependence on ambient atmospheric moisture δ_A and local climate conditions based in part on theoretical considerations but also based on observed isotopic enrichment levels in the blowdown (Fig. S3). These findings appear to be consistent with basic operation of the cooling towers, as noted by mine site personnel, which involve circulating outside air through the towers to prevent saturation

within the chambers, a procedure necessary to maintain required evaporation rates for optimal performance. As a result, it appears that ambient climate conditions may influence the overall extent of enrichment whereas internal humidity and temperature are more influential in determining the isotopic fractionations and the slope of the enrichment trend in dual isotope space. Overall, the cooling towers might best be viewed as partially closed systems. We suggest that these reservoirs could be accurately modelled using an isotope mass balance model that accounts for feedback of evaporate to its atmosphere. In this case, a high degree of feedback (70–80% evaporate) provides a suitable fit to the observed evaporative trend noted in cooling tower blowdown.

We suggest that monitoring of blowdown signatures from all four towers, and use of integrated averages, both monthly and annually, could compliment measured cycles of concentration information to better understand operational conditions at the site, as well as to trace the influence of cooling tower blowdown on the water balance of the mine circuits.

4.4. Isotope mass balance considerations

The most common approach taken in isotopic mass balance studies for natural systems is to assume the system is in isotopic and hydrologic steady state annually or to simulate systematic changes based on a series of monthly or short-term time steps (Gibson, 2002; Gibson & Reid 2014; Gibson et al., 2016a). Although much of the same water is recycled year over year, with the exception of water lost to evaporation, we show that there are consistent levels of depletion in spring and enrichment in fall for both ^{18}O and ^{2}H each year based on our six years of sampling. Application of a steady state model using average annual values for various components of the mine water circuits could therefore be useful for providing a first-approximation of long-term operational variables such as evaporation losses, total process water storage, and pore-water release during tailings self-weighted consolidation. If seasonal variations are of interest, a monthly time series model could be similarly applied to characterize progressive changes in evaporation and water balance over the course of each season, although with considerably greater effort.

At the ML site, water samples were collected from the three largest and most active tailings ponds (SWSS, MLSB, and SWIP), as well as RP. Clarified process water is drawn from all tailings ponds concurrently and stored in a centralized location, the recycle pond, to provide "recycled" water to meet operational demands. Therefore, we suggest that samples collected from RP should be representative of the overall isotopic signature of the recycle water circuit, which could simplify monitoring and application of an isotope mass balance approach. Interestingly, monitoring of recycle water could potentially provide a temporal record of proportions of the three main inputs to the recycle water circuit, which are meteoric water, cooling tower blowdown, and pore water released following tailings settlement. In addition to monitoring of mean water balance of tailings reservoirs, including evaporation and expressed porewater, we note that it could be used to track water balance interactions between the two mine sites, as ML relies primarily on Athabasca River water whereas AN relies also on basal McMurray aquifer sources, and these waters are uniquely labelled. Shifts in isotopic composition due to changes in balance of source waters, evaporation from open water, and evaporative enrichment inherited from cooling tower
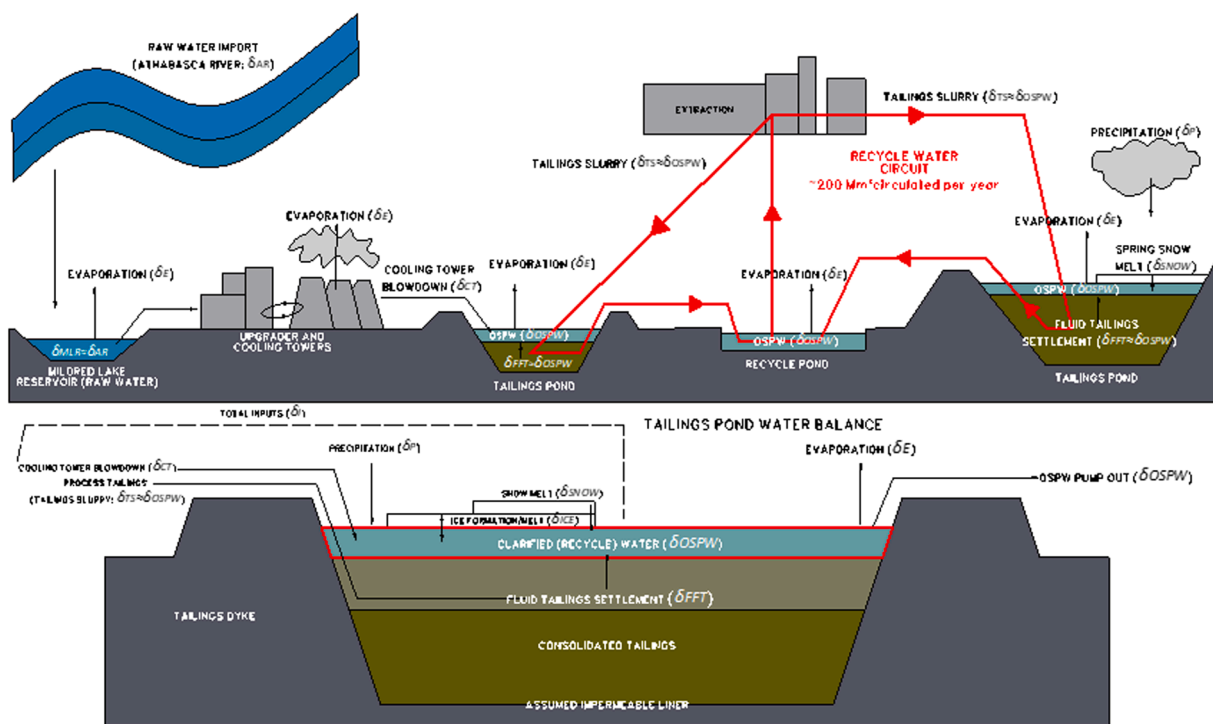

Fig. 8. Diagram illustrating raw water import to an oil sands mine, recycling of process water, and a standard water balance of a tailings pond. Isotopic signatures of sampled components (δ values) are shown.

blowdown may in fact lead to long-term changes that do not mimic natural lakes or watersheds in the region, and would be informative for characterizing these differences.

4.5. Conceptual model development

A conceptual model was developed to summarize our current understanding of how water is imported and circulated through Syncrude's Mildred Lake Mine, a typical oil sands operation, from an isotope perspective (Fig. 8). A monthly simulation of isotopic changes in the various mine circuit waters are shown in Fig. 9.

As shown, raw water is sourced from Athabasca River, which has only minor seasonal variations when compared to other mine site waters. This water is stored in MLR and is then pumped at varying rates to meet operational water demands. Our samples indicate that when water demands are high (*i.e.,* high pumping rates from MLR), the isotopic signature of the reservoir is reflective of the imported river water due to low residence times. However, if pumping rates are low during high evaporative months (*i.e.,* late summer) there may be observable enrichment resulting from evaporative enrichment.

Evaporation within the cooling towers is the dominant cause of enrichment in imported freshwater prior to input to the recycle water circuit. The isotopic signature of the cooling tower blowdown varies depending on the recirculation time of water within the circuit (quantified as cycles of concentration), the internal conditions within the cooling towers (*i.e.,* temperature and humidity) and to a lesser extent ambient atmospheric moisture. Cooling tower blowdown then mixes with the current stores of clarified process water or "recycle" water contained within the tailings ponds of the recycle water circuit. Mixing calculations show minimal response annually in the overall isotopic signature of the recycle water circuit from the addition of enriched cooling tower blowdown – likely due to the massive reservoir of process water when compared to the much smaller blowdown volume being added. Despite this observation, it is expected that the cumulative addition of cooling tower blowdown over multiple decades of operations may be a primary driver of unique isotopic signatures in recycled process-affected water.

Analysis of isotopic signatures of the clarified process water collected within this study demonstrates that the isotopic signature within the various storage facilities of the recycle water circuit fluctuates seasonally but seems to return to similar values year after year. The isotopic composition of the recycle water circuit appears to replicate typical seasonal patterns associated with natural lakes in cold regions. Depleted process water signatures were observed following the spring melt of depleted snow accumulated on both ponds, and across the site. A systematic enrichment of process water was observed over the duration of the open water period attributed to evaporative fractionation resulting in isotopic enrichment within the recycle water circuit (Fig. 9). The recycle water circuit remains active throughout the winter despite freeze-up of the tailings pond surfaces. Process water samples collected throughout the ice-on period demonstrated progressive isotopic depletion. This pattern is believed to be due to higher throughput in
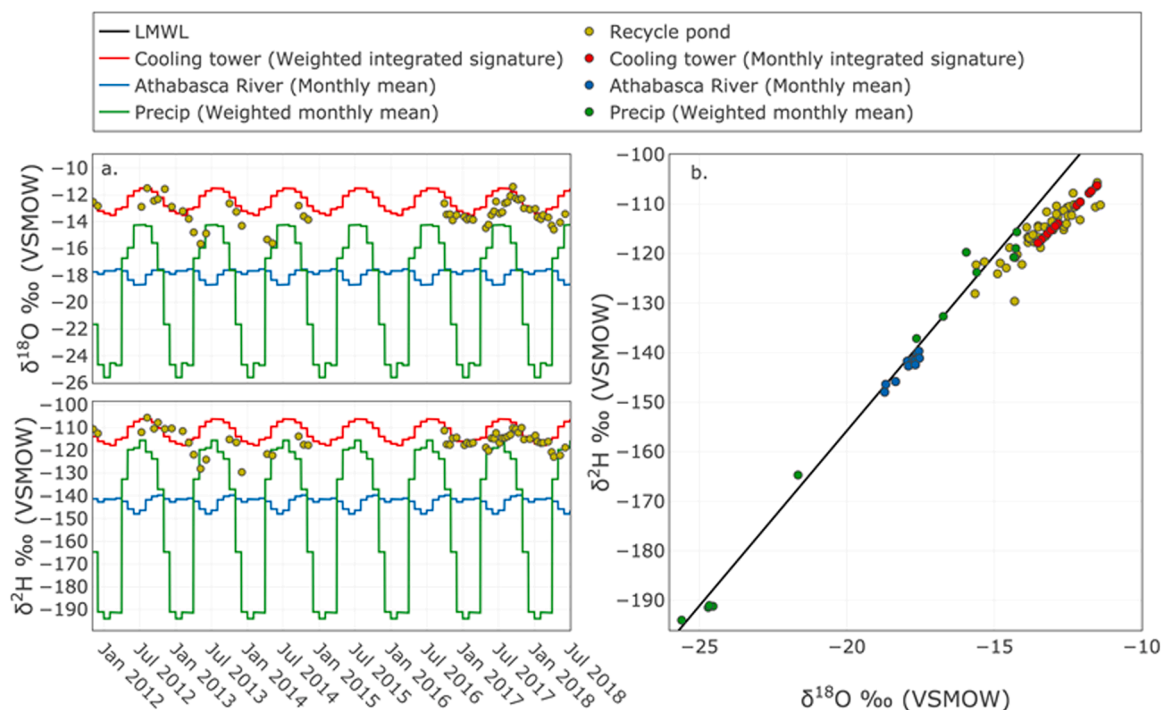

Fig. 9. a.) Temporal variability of ^{18}O and ^{2}H from recycle pond samples plotted with the integrated monthly cooling tower signature, monthly weighted average of precipitation, and monthly average of Athabasca River water; b.) Dual isotope plot displaying the variations of each component relative to the LMWL.

the circuit and lack of substantial evaporation, but may also be enhanced by formation of ice, as ice-water fractionation tends to temporarily sequester heavier isotopic species within the ice cover (see Gibson and Prowse, 1999).

The tailings ponds act as both storage facilities for process water and settling basins for fluid tailings created during the extraction of bitumen from ore. Process water originally used for extraction is returned to the tailings ponds as a tailings slurry, where settling and consolidation of the fluid tailings releases the pore water. While young pore water is found to be similar to contemporary process water, these relatively immobile waters may be stored for decades within fine tailings deposits, and can be viewed as a deep reservoir of 'archival' water associated with its year of deposition. Dompierre and Barbour (2016) measured the isotopic depth profile of fluid tailings placed within a 45 m deep mined out pit and showed that the average signature of the tailings, deposited at Syncrude from 1994 to 2012, was $-12.4‰$ for $\delta^{18}O$ and $-112.2‰$ for $\delta^{2}H$. These values are more enriched than the isotopic signature of today's recycle water circuit, as represented by the overall average of the recycle pond samples ($-13.37‰$ and $-115.86‰$ for $\delta^{18}O$ and $\delta^{2}H$, respectively). This is presumed to be the result of higher recycling ratios at present than historically when the tailings were deposited, which is a testament to progressive improvements in operational efficiency. From an isotope mass balance perspective, tailings settlement and pore water release potentially distinguish response of tailings ponds and natural lakes, and this effect needs to be considered in any quantitative isotope mass balance assessment. One potential opportunity that emerges from this observation is that pore water from known-age tailings deposits may serve as a temporal archive that can be used to reconstruct the historical isotopic signatures and related water balance history of a tailings pond or mine water circuit.

5. Concluding remarks

The recycle water circuit is crucial to bitumen extraction and tailings management for oil sands mining operations. Isotope tracers provide the opportunity to quantify site wide water balance parameters, such as meteoric water inputs, evaporative losses, and potentially infiltration or dewatering, which are difficult or costly to directly monitor. Better understanding of these parameters would aid in improving efficiency of site wide water use and management.

Within this work we characterized both the temporal evolution of the isotopic signatures of source waters to an oil sands mine and the process waters that make up the recycle water circuit based on a bi-weekly water isotope-monitoring program. This builds upon prior studies conducted at Syncrude's oil sands mines in the AOSR.

We developed a conceptual model outlining the isotopic evolution of imported water as it transitions from a freshwater signature to one reflective of oil sands mining processes. This model highlights the roles of mixing, evaporation, cooling tower blowdown, and water demand, which have contributed to the unique and evolving isotopic signatures of process water, as they develop distinct characteristics compared to natural surface waters in the region.

This study has shown that the recycle water circuit exhibits seasonal isotopic patterns characteristic of cold region reservoirs, specifically a rapid depletion following the spring freshet, which is then followed by systematic enrichment during the open water period. Interannually, the recycle water circuit appears to be close to isotopic steady state, with isotopic signatures collected from the late summer and fall (*i.e.,* following prime evaporative months) consistently falling between $-11‰$ to $-12‰$ and $-105‰$ to $-110‰$ for ^{18}O and ^{2}H respectively. Expressed pore water released from the settlement of fluid tailings appears to be contributing to a systematic depletion of the clarified process water stores within the recycle water circuit during the ice-on period.

Isotopic signatures and temporal trends were found to be similar within the three tailings ponds sampled throughout the recycle water circuit, as well as the recycle pond, which acts as a storage reservoir for clarified process water to the extraction plant. We postulate that interconnectivity between each reservoir in the recycle water circuit, and high pumping rates resulting in low residence times of clarified process water in each pond, have contributed to an isotopically well-mixed system. This finding allows for the isotopic signatures collected from the recycle pond - the collection point for all clarified process water pumped from ponds to act as a proxy for the entire recycle water circuit. Overall, the systematic nature of the variations measured at the mine sites will enable isotope-based quantification of the major water balance parameters operating within the process water circuit. Quantification of the water balance is indeed the next step in our workplan at the site.

We also anticipate that future investigations will target water balance of the first demonstration end-pit lake, a common element included within closure strategies being evaluated by government and industrial operators across the mineable oil sands region. End pit lakes are excavated, water-capped reservoirs that essentially allow for submergence or sequestration of tailings intended to store fluid fine tailings with the potential to limit weathering and promote evaporation, thereby limiting contaminant mobility.

CRediT authorship contribution statement

Spencer J. Chad: Conceptualization, Methodology, Data curation, Validation, Formal analysis, Investigation, Visualization, Writing – original draft. **Lee Barbour:** Conceptualization, Methodology, Writing – original draft, Supervision, Funding acquisition. **Jeffrey J. McDonnell:** Writing – original draft, Supervision. **John J. Gibson:** Writing – review & editing, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ejrh.2022.101032.

References

Allen, D.M., Voormeij, D.A., 2002. Oxygen-18 and deuterium fingerprinting of tailings seepage at the Sullivan Mine. Mine Water Environ. 21 (4), 168–182.

Baer, T., University of Saskatchewan, College of Graduate Studies Research. (2014). An Evaluation of the Use of Natural Stable Isotopes of Water to Track Water Movement through Oil Sands Mine Closure Landforms.

Baer, T., Barbour, S.L., Gibson, J.J., 2016. The stable isotopes of site wide waters at an oil sands mine in northern Alberta, Canada. J. Hydrol. 541, 1155–1164.

Barbour, S.L., Hendry, M.J., Carey, S.K., 2016. High-resolution profiling of the stable isotopes of water in unsaturated coal waste rock. J. Hydrol. 534, 616–629.

Buttle, J.M., 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Prog. Phys. Geogr. 18 (1), 16–41.

Clark, I., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. CRC Press/Lewis, Boca Raton, FL.

COSIA Water EPA , 2019. 2018 Water Research Report. Canada's Oil Sands Innovation Alliance. ⟨https://www.cosia.ca/sites/default/files/attachments/COSIA% 20Annual%20Report%202018_WATER_FINAL%20Nov%2021_0.pdf⟩.

Craig, H., Gordon, L.I., 1965. Deuterium and oxygen 18 variations in the ocean and marine atmosphere. In: Tongiorgi, E. (Ed.), Stable Isotopes in Oceanographic Studies and Paleotemperatures. Laboratorio di Geologia Nucleare, Pisa, pp. 9–130.

Criss, R., 1999. Principles of Stable Isotope Distribution. Oxford University Press, Oxford, NY.

Dincer, T., 1968. The use of oxygen 18 and deuterium concentrations in the water balance of lakes. Water Resour. Res. 4 (6), 1289–1306.

Dompierre, K.A., Barbour, S.L., 2016. Characterization of physical mass transport through oil sands fluid fine tailings in an end pit lake: a multi-tracer study. J. Contam. Hydrol. 189, 12–26.

Evaristo, J., Jasechko, S., McDonnell, J.J., 2015. Global separation of plant transpiration from groundwater and streamflow. Nature 525 (7567), 91–94.

Ferguson, P.R., Weinrauch, N., Wassenaar, L.I., Mayer, B., Veizer, J., 2007. Isotope constraints on water, carbon, and heat fluxes from the northern Great Plains region of North America. Glob. Biogeochem. Cycles 21, 2–n/a.

Gammons, C.H., Duaime, T.E., Parker, S.R., Poulson, S.R., Kennelly, P., 2010. Geochemistry and stable isotope investigation of acid mine drainage associated with abandoned coal mines in central Montana, USA. Chem. Geol. 269 (1–2), 100–112.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. Annu. Rev. Earth Planet. Sci. 24 (1), 225–262.

Gibson, J., 2002. Short-term evaporation and water budget comparisons in shallow Arctic lakes using non-steady isotope mass balance. J. Hydrol. 264 (1), 242–261.

Gibson, J.J., Prowse, T., 1999. Isotopic characteristics of ice cover in a large northern river basin. Hydrol. Process. 13, 2537–2548.

Gibson, J.J., Edwards, T.W.D., Birks St, S.J., Amour, N.A., Buhay, W.M., McEachern, P., Peters, D.L., 2005. Progress in isotope tracer hydrology in Canada. Hydrol. Process. 19 (1), 303–327.

Gibson, J.J., Birks, S.J., Moncur, M., Yi, Y., Tattrie, K., Jasechko, S., Richardson, K., Eby, P., 2011. Isotopic and geochemical tracers for fingerprinting process-affected waters in the oil sands industry: a pilot study. Oil Sands Research and Information Network, OSRIN Report No. TR-12, University of Alberta, Edmonton, April 2011, 109 pp.

Gibson, J.J., Reid, R., 2014. Water balance along a chain of tundra lakes: A 20-year isotopic perspective. J. Hydrol. 519, 2148–2164.

Gibson, J.J., Birks, S.J., Yi, Y., Moncur, M.C., McEachern, P.M., 2016a. Stable isotope mass balance of fifty lakes in central Alberta: assessing the role of water balance parameters in determining trophic status and lake level. J. Hydrol. Reg. Stud. 6, 13–25.

Gibson, J.J., Birks, S.J., Yi, Y., 2016b. Stable isotope mass balance of lakes: a contemporary perspective. Quat. Sci. Rev. 131, 316–328.

Gibson, J.J., Yi, Y., Birks, S.J., 2016c. Isotope-based partitioning of streamflow in the oil sands region, northern Alberta: towards a monitoring strategy for assessing flow sources and water quality controls. J. Hydrol. Reg. Stud. 5, 131–148.

Gibson, J.J., Birks, S.J., Moncur, M.C., 2019. Mapping water yield distribution across the southern Athabasca Oil Sands area: baseline surveys applying isotope mass balance of lakes. J. Hydrol. Reg. Stud. 21, 1–13.

Gibson, J.J., Holmes, T., Stadnyk, T., Birks, S.J., Eby, P., Pietroniro, A., 2020. ^{18}O and ^{2}H in streamflow across Canada. J. Hydrol. Reg. Stud. 32, 100754.

Gibson, J.J., Holmes, T., Stadnyk, T., Birks, S.J., Eby, P., Pietroniro, A., 2021. Isotopic constraints on water balance and evapotranspiration partitioning across Canada in gauged watersheds. J. Hydrol. Reg. Stud. 37, 100878.

Gonfiantini, R., 1986. Environmental isotopes in lake studies. Handb. Environ. Isot. Geochem. 2, 113–168.

Google. (2018). [Google Earth Pro image of Syncrude mine sites]. Retrieved 2018 from Google Earth DigitalGlobe 2018.

Harman, C.J., Kim, M., 2014. An efficient tracer test for time-variable transit time distributions in periodic hydrodynamic systems. Geophys. Res. Lett. 41 (5), 1567–1575.

Horita, J., Rozanski, K., Cohen, S., 2008. Isotope effects in the evaporation of water: a status report of the Craig–Gordon model. Isot. Environ. Health Stud. 44 (1), 23–49.

Huang, M., Hilderman, J.N., Barbour, L., 2015. Transport of stable isotopes of water and sulphate within reclaimed oil sands saline–sodic mine overburden. J. Hydrol. 529, 1550–1561.

Ingraham, N.L., Johnson, R.J., Broadbent, R., 1994. Facility-altered stable isotopic ratios of power generation cooling wastewater: opportunity for tracing leakages. Environ. Sci. Technol. 28 (11), 1983–1986.

Jasechko, S., 2016. Partitioning young and old groundwater with geochemical tracers. Chem. Geol. 427, 35–42.

Jasechko, S., Gibson, J.J., Edwards, T.W.D., 2014. Stable isotope mass balance of the North American Great Lakes. J. Gt. Lakes Res. 40, 336–346.

Klaus, J., McDonnell, J.J., 2013. Hydrograph separation using stable isotopes: review and evaluation. J. Hydrol. 505, 47–64.

Lee, J., Feng, X., Faiia, A., Posmentier, E., Osterhuber, R., Kirchner, J., 2010. Isotopic evolution of snowmelt: a new model incorporating mobile and immobile water. Water Resour. Res. 46, 11.

Lis, G., Wassenaar, L.I., Hendry, M.J., 2008. High-precision laser spectroscopy D/H and 18O/16O measurements of microliter natural water samples. Analytical chemistry 80 (1), 287–293.

Matte, C., 2005. Water Conservation. Recycling and Reuse. NACE Int, Houston.

Moser, H., Stichler, W. , 1975 , Deuterium and oxygen-18 contents as index of the properties of snow blankets. In: Snow Mechanics (Proc. Grindelwald Symp., April 1974), 122–135. IAHS Publ. No. 114.

RAMP (Regional Aquatic Monitoring Program), 2015 , Steepbank Climate Station (C#-RAMP), 3 November 2010- 31 October 2014 ⟨http://www.ramp-alberta.org/ data/ClimateHydrology/climate/DailyClimate.aspx⟩.

Syncrude Canada Ltd , 2017 , 2016 Tailings Report Syncrude Mildred Lake. submitted for publication to Alberta Energy Regulator. submitted for publication by Syncrude Canada Ltd., Fort McMurray Alberta. April 27, 2017.

Syncrude. Sustainability Fact Sheets. Syncrude Canada Ltd. https://www.syncrude.ca/wp-content/uploads/2021/01/2019-Sustainability-Fact-Sheets-Combined_compressedV3.pdf.

Taylor, S., Feng, X., Williams, M., McNamara, J., 2002. How isotopic fractionation of snowmelt affects hydrograph separation. Hydrol. Process. 16 (18), 3683–3690.

Tetzlaff, D., Piovano, T., Ala-Aho, P., Smith, A., Carey, S., Marsh, P., Soulsby, C., 2018. Using stable isotopes to estimate travel times in a data-sparse Arctic catchment: Challenges and possible solutions. Hydrol. Process. 32 (12), 1936–1952.

Tondu, J.M.E., Turner, K.W., Wolfe, B.B., Hall, R.I., Edwards, T.W.D., McDonald, I., 2013. Using water isotope tracers to develop the hydrological component of a long-term aquatic ecosystem monitoring program for a northern lake-rich landscape. Arct., Antarct. Alp. Res. 45 (4), 594–614.

Tost, M., Hitch, Chandurkar, Moser, Feiel, 2018. The state of environmental sustainability considerations in mining. J. Clean. Prod. 182, 969–977.

Turner, K.W., Wolfe, B.B., Edwards, T.W., 2010. Characterizing the role of hydrological processes on lake water balances in the Old Crow Flats, Yukon Territory, Canada, using water isotope tracers. J. Hydrol. 386 (1–4), 103–117.

Turner, K.W., Wolfe, B.B., Edwards, T.W., Lantz, T.C., Hall, R.I., Larocque, G., 2014. Controls on water balance of shallow thermokarst lakes and their relations with catchment characteristics: a multi-year, landscape-scale assessment based on water isotope tracers and remote sensing in Old Crow Flats, Yukon (Canada). Glob. Change Biol. 20 (5), 1585–1603.

Zimmermann, U., Ehhalt, D.H., 1970. Stable isotopes in study of water balance of Lake Neusiedl. Austria Isot. Hydrol. 129–138.

Zuber, A., 1983. On the environmental isotope method for determining the water balance components of some lakes. J. Hydrol. 61 (4), 409–427.

Zubot, W. , 2010 , Removal of Naphthenic Acids from Oil Sands Process Water Using Petroleum Coke (Master's thesis, University of Alberta, Calgary, AB).