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Isotope-based partitioning of streamflow in the oil sands region, northern Alberta: Towards a monitoring strategy for assessing flow sources and water quality controls

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ABSTRACT

Study region: This study is based on the rapidly developing Athabasca Oil Sands region, northeastern Alberta.
Study focus: Hydrograph separation using stable isotopes of water is applied to partition streamflow sources in the Athabasca River and its tributaries. Distinct isotopic labelling of snow, rain, groundwater and surface water are applied to estimate the contribution of these sources to streamflow from analysis of multi-year records of isotopes in streamflow.
New hydrological insights for the region: The results provide new insight into runoff generation mechanisms operating in six tributaries and at four stations along the Athabasca River. Groundwater, found to be an important flow source at all stations, is the dominant component of the hydrograph in three tributaries (Steepbank R., Muskeg R., Firebag R.), accounting for 39–50% of annual streamflow. Surface water, mainly drainage from peatlands, is also found to be widely important, and dominant in three tributaries (Clearwater R., Mackay R., Ells R.), accounting for 45–81% of annual streamflow. Fairly limited contributions from direct precipitation illustrate that most snow and rain events result in indirect displacement of pre-event water by fill and spill mechanisms. Systematic shifts in regional groundwater to surface-water ratios are expected to be an important control on spatial and temporal distribution of water quality parameters and useful for evaluating the susceptibility of rivers to climate and development impacts.

1. Introduction

Hydrograph separation based on streamflow data is one of the most widely used methods for quantifying surface water—groundwater interactions at the reach to catchment scales (Kalbus et al., 2006). Typically, geochemical or isotopic data have been used to trace changes in the proportion of event and pre-event water contributions during storms or snowmelt events. As noted in a recent review by Klaus and McDonnell (2013), these studies have forced a fundamental re-examination of the processes of water delivery to streams. In particular, they have revealed a high proportion of pre-event water in the storm hydrograph, even at peak flow, (Klaus and McDonnell, 2013). Depending on the distinctiveness of solute or isotope

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labelling and catchment properties it has been possible in some studies to resolve two or three separate components of the hydrograph, and to infer mechanisms of runoff generation such as groundwater ridging or variable source area contributions.

While a variety of tracer and non-tracer methods have been utilized for hydrograph separation (see Gonzales et al., 2009), stable isotopes of water have the advantage of being incorporated within the water molecule and being mass-conservative during mixing. Stable isotopes of water are especially useful due to natural labelling of flow sources that often arises from selection and fractionation processes that occur in the water cycle (Gat, 1996). Several examples include the distinctly depleted isotopic signatures normally associated with snow (and snowpack) compared to rainfall owing to temperature-dependent isotopic fractionation during condensation of atmospheric moisture (Gat, 1980), temporal isotopic variability in precipitation which serves to distinguish individual events from long-term averages typically reflected in meteoric groundwater (Gat, 1996), selective recharge, which may accentuate the difference between precipitation events and meteoric groundwater, and evaporative enrichment of wetland waters or lakes that have resided in surface storage (Gibson et al., 2015a). Evaporation from soil may also lead to distinctive isotopic labelling of shallow soil water, particularly in the arid zone (Gat, 1981).

Hydrograph separation using stable isotopes of water has been demonstrated mainly for hillslopes or small experimental catchments over event time scales (Tetzlaff et al., 2015) with less emphasis placed on application at larger scales or over seasonal time periods (see Uhlenbrook et al., 2002). This study explores use of isotope hydrograph separation as an integrated component of streamflow monitoring in meso- to macro-scale peatland-rich catchments to better understand the physical processes controlling runoff generation. The main questions that we wish to answer include: 'How do peatland catchments react to snowmelt and precipitation events?', 'What is the timing and proportion of various water sources to streamflow on a seasonal, annual and interannual basis?', 'What flow paths, storage effects, and runoff mechanisms are important?' and 'Are there important regional differences in streamflow response?' One of the primary applications we envision is better understanding and prediction of the temporal distribution of water quality and contaminants in peatland-dominated systems. It is also interesting to explore whether inter-annual time-series monitoring may be useful for assessing potential changes in streamflow drivers due to climate or development-related impacts.

Previous work on stream water chemistry including hydrograph separation studies have been conducted in the oil sands region by Schwartz (1980) and Schwartz and Milne-Home (1982a,b). Based on a three-year record of major ion tracers in five meso-scale catchments, they partitioned the hydrograph into direct precipitation, groundwater and muskeg water, and were successful in showing that muskeg (i.e. peatland) plays a significant role in determining the watershed chemistry, in attenuating runoff during spring melt, and in dilution of water chemistry during summer, particularly between runoff events. In addition, they determined that groundwater plays a dominant role during winter controlling water quantity and quality. Notably, these studies also demonstrated that meaningful partitioning could be achieved in the region over seasonal to inter-annual time periods. However, as these studies used geochemical rather than isotopic labelling for hydrograph separation they did not attempt to partition snowmelt from rainfall.

This paper offers basic confirmation of some of Schwartz's results for the Muskeg, Firebag and Steepbank Rivers, as well as some clarification on the role of different runoff components in each season and inter-annually for these and several additional basins (Mackay, Ells, Clearwater and several stations along the Athabasca River), based on datasets that extend for over a decade in some cases. We present a methodology for partitioning of snowmelt, rainfall, groundwater and surface water using stable isotopes of water and apply it to infer some of the major processes controlling runoff for mesoscale catchments as well as for the Athabasca River both upstream and downstream of the oil sands region. We identify the underlying sources of runoff and runoff generation mechanisms that produce spatial and temporal variations in streamflow in the wetland-muskeg runoff regime. Understanding runoff generation in the region is important as it is an essential control on water quality and aquatic habitat, yet may be changing due to ongoing development for oil sands or due to impact of climatic changes that are known to have affected permafrost thawing and other runoff generation processes in the region (Gibson et al., 2015a,b).

1.1. Study area

The study area lies within the Athabasca River basin, Alberta, Canada. The Athabasca River flows northeast over 1,231 km from its origins in the Rocky Mountains to the Peace-Athabasca Delta and Lake Athabasca, draining 156,000 km^2 of landscape varying from snow-capped and glaciated mountains to agricultural plains, boreal forest and wetlands. No dams are constructed along the river and consumptive divergences of water are small due to minimal agricultural use (Jasechko et al., 2012). The river is part of the Mackenzie River system, and its waters eventually flow to the Arctic Ocean. The lower reaches of the Athabasca River coincide with the Athabasca Oil Sands region (AOSR). Here, approximately 1% of the rivers annual flow is diverted for use as make-up water for oil sands mining and processing operations (Canada, Government of Canada, 2013).

The climate is highly seasonal with monthly mean temperatures that vary from $-19\,^{\circ}C$ in January to $17\,^{\circ}C$ in July, with a mean annual temperature near $0\,^{\circ}C$. Annual precipitation is 450 mm, with 60% falling as rain. Relief is subdued with the exception of large river incisions. Fine-grained soils, in combination with the climate, have resulted in formation of abundant wetlands across the region. Ombrogenous (precipitation-fed) bogs and geogenous (groundwater-fed) fens, which together occupy more than 50% of watershed areas in the AOSR (Gibson et al., 2015a), govern hydrology and infiltration at the surface (Vitt et al., 1994). Mineral soil uplands are also common in the lower, incised portions of river basins. Peatlands and mineral

Table 1
Summary of monitoring stations, period of record and site characteristics.

Station ID	Station name	Date range of isotope sampling	Area (km^2)	Discharge	
				Mean (m^3/s)	1σ (m^3/s)
07BE001	Athabasca R. at Athabasca	07/2002–05/2014	74,602	429	429
07DA001	Athabasca R. below McMurray	06/2002–05/2014	132,585	609	541
07DA0980[a]	Athabasca R. at Firebag R.	08/2007–05/2014	n.a.	n.a.	n.a.
07DD011	Athabasca R. near Old Fort	05/2003–05/2014	156,000	768	750
07DA008	Muskeg R.	06/2008–05/2014	1457	4.8	6.5
07DA006	Steepbank R.	04/2011–05/2014	1350	6.1	8.1
07DC001[b]	Firebag R.	04/2011–05/2014	5990	29.4	25.4
07DB001	Mackay R.	04/2012–05/2014	5570	16.9	28.3
07DA017	Ells R.	04/2011–05/2014	2450	7.1	12.1
07CD001	Clearwater R.	04/2011–05/2014	30800	115.6	91.2

[a] Water quality station only.
[b] Note that samples were collected slightly downstream at AB07DC0110.

soil uplands are underlain by glacio-fluvial and glacio-lacustrine sediments that can exceed 300 m depth in some areas overlying buried paleochannels (Andriashek and Atkinson, 2007). Permafrost in the region is sporadic, mainly occurring in bogs but actively degrading (Vitt et al., 1999).

River hydrology in the AOSR is strongly seasonal, with high flows associated with the snowmelt period in April–May–June, and low flows associated with ice-covered periods in November to March. The Athabasca River below Fort McMurray sustains flows ranging from 75 to 4700 m^3/s, with a mean discharge of 609 m^3/s (Canada, Environment Canada, 2015). Tributary peak flows in the AOSR are typically less than 50 m^3/s with low flows of less than 1 m^3/s (RAMP, 2015).

Recent studies by Jasechko et al. (2012), Gue et al. (2015), and Gibson et al. (2013) have described the geochemical and isotopic signatures of numerous springs and broader seepage along the lower reaches of the Athabasca River. These studies reveal the role of saline bedrock formation water in supplying a small proportion (up to 3%) of the flow to the lower Athabasca River. Tributaries, as noted by Schwartz and Milne-Home (1982b), are fed predominantly by shallower sources in glacial drift units. One exception they noted was for the Steepbank River which may have derived ~5% of its groundwater from deeper bedrock units.

1.2. Sample collection and analysis

The Athabasca River and several tributaries were sampled on a monthly basis as part of the Long-Term River Network monitoring program operated by Alberta Environmental Monitoring, Evaluation and Reporting Agency and its predecessors (Fig. 1). A list of sampling stations, dates and basic characteristics of the watersheds are shown in Table 1. Water samples were collected in 30 mL high-density polyethylene bottles (HDPE) following standard protocols for water quality sampling (Alberta Environment, 2002). HDPE bottles have been shown to be very effective at preventing isotopic fractionation for periods in excess of 1 year (Spangenberg, 2012). Snow data were obtained from a one-time regional survey of the snowpack across the oil sands region which included 67 isotopic analyses of integrated snowpack samples (Birks et al., 2014). Snowpack samples were fully melted in HDPE bags prior to being transferred to HDPE sample bottles. Data for rainfall were obtained in 2011–2012 from event sampling programs sponsored by the Cumulative Environmental Management Association in two watersheds situated within 70 km of Ft. McMurray. Surface water data were obtained from Gibson et al. (2015a) who reported values for 50 lakes in the region over a 9-year period.

All isotope results were analyzed by isotope ratio mass spectrometer, either at the University of Waterloo using a Micromass IsoPrime Dual Inlet/Gas Chromatograph (pre-2009) or at Alberta Innovates Technology Futures, Victoria using a Thermo Scientific Delta V Advantage Dual Inlet/HDevice system. In all cases analyses were made within 1 year of sample collection. Results are reported in δ notation in permil (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW) and normalized to the SMOW-SLAP scale where SLAP is Standard Light Arctic Precipitation (see Coplen, 1996). Analytical uncertainty is estimated to be better than ±0.1‰ for $\delta^{18}O$ and ±1‰ for δ^2H.

2. Theory

Mass balance equations are presented which describe the relative contributions of water sources to streamflow under a simple batch-mixing model with conservative tracers (Gibson et al., 2000). While an approach that accounts for spatial and temporal variability in end-members may be more realistic (e.g. Harris et al., 1995; Ogunkoya and Jenkins 1993), we currently lack detailed information to track systematic isotopic variations that may be occurring in the source waters. As a first approximation we apply the simple batch mixing model to separate instantaneous streamflow discharge into its source components or end-members.

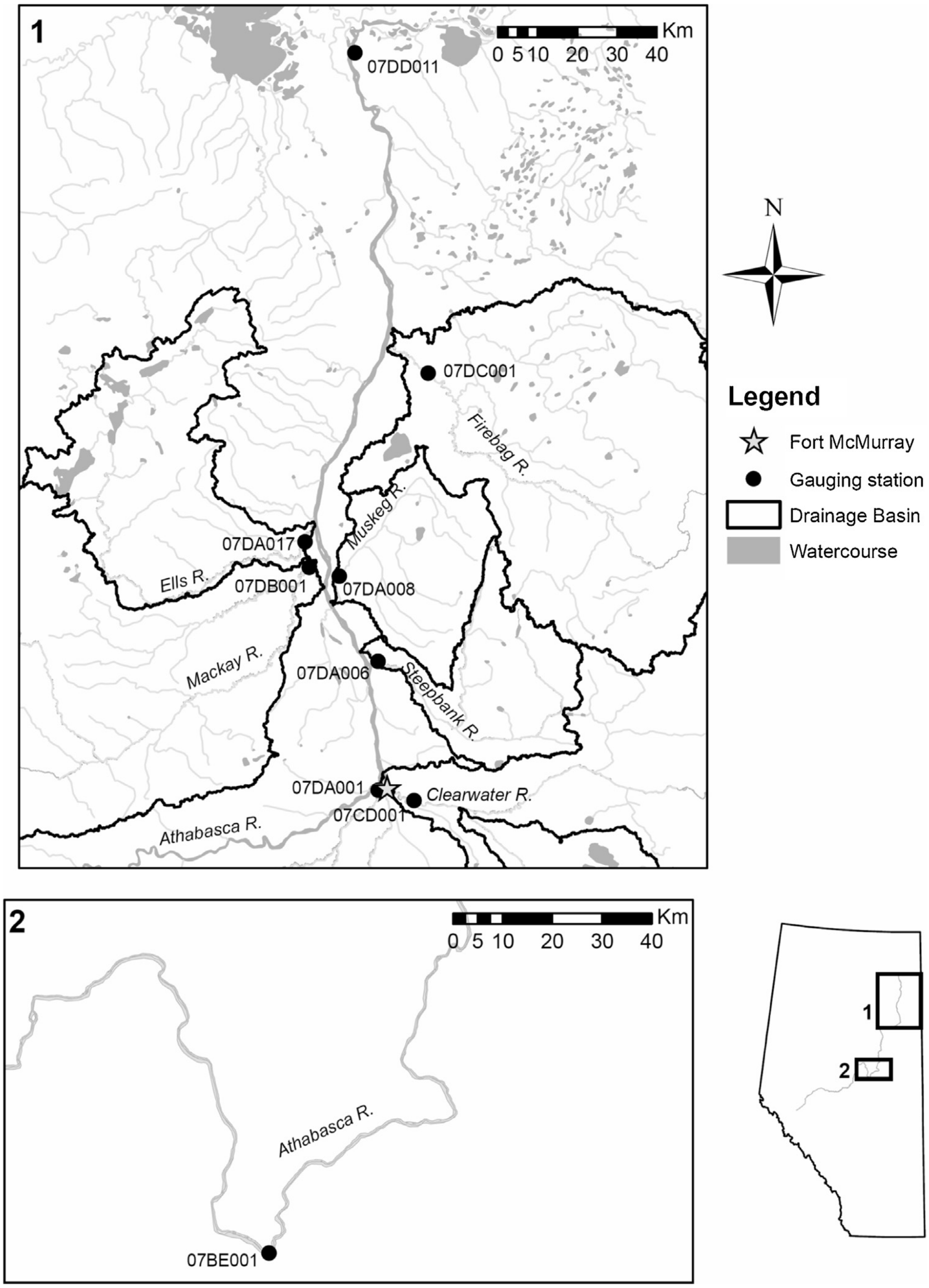

Fig. 1. Map showing gauging stations in the oil sands region where isotopic sampling was conducted. Watershed boundaries for tributaries are also shown.

For a three-component system, the instantaneous streamflow discharge Q is equal to the sum of the contributions from the streamflow sources (x_1, x_2, x_3):

$$x_1 + x_2 + x_3 = Q \quad (1)$$

If the isotopic composition of the water sources is also well-constrained then additional tracer balances can be constructed. In the case of δ^{18}O and δ^2H, which are mass conservative, the mass balance equations are:

$$x_1\delta_1^{18} + x_2\delta_2^{18} + x_3\delta_3^{18} = Q\delta_Q^{18} \quad (2)$$

$$x_1\delta_1^{2} + x_2\delta_2^{2} + x_3\delta_3^{2} = Q\delta_Q^{2} \quad (3)$$

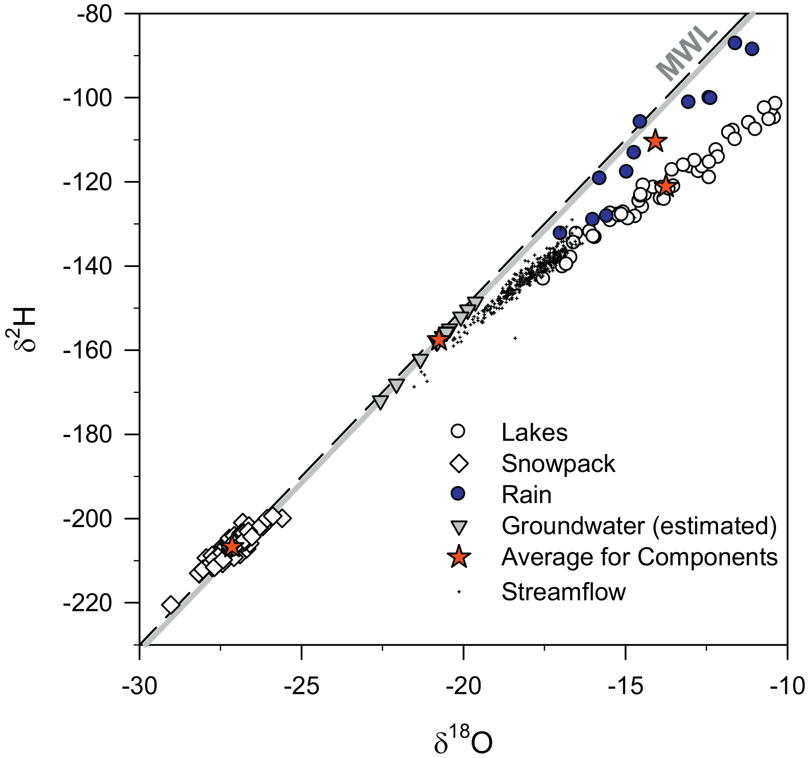

Fig. 2. δ^2H-$\delta^{18}O$ plot showing the isotopic composition of major streamflow sources as well as their average values measured in 2013. MWL is meteoric water line. Two are shown including the Global Meteoric Water Line of Craig (1961) (dashed line) and the Canadian Meteoric Water Line of Gibson et al., 2005 (grey line).

where δ_1^{18}, δ_2^{18}, δ_3^{18} and δ_1^2, δ_2^2, δ_3^2 are the δ^{18}O and δ^2H of water sources x_1, x_2, x_3, respectively.

Solving the system of Eqs. (1) through (3) for the fractional contributions of the components of total streamflow yields:

$$\frac{x_1}{Q} = \left[\frac{\left(\delta_Q^{18}-\delta_3^{18}\right)-\left(\delta_Q^{2}-\delta_3^{2}\right)\left(\delta_2^{18}-\delta_3^{18}\right)/\left(\delta_2^{2}-\delta_3^{2}\right)}{\left(\delta_1^{18}-\delta_3^{18}\right)-\left(\delta_1^{2}-\delta_3^{2}\right)\left(\delta_2^{18}-\delta_3^{18}\right)/\left(\delta_2^{2}-\delta_3^{2}\right)}\right] \tag{4a}$$

$$\frac{x_2}{Q} = \left[\frac{\left(\delta_Q^{18}-\delta_3^{18}\right)-\left(\delta_Q^{2}-\delta_3^{2}\right)\left(\delta_1^{18}-\delta_3^{18}\right)/\left(\delta_1^{2}-\delta_3^{2}\right)}{\left(\delta_2^{18}-\delta_3^{18}\right)-\left(\delta_2^{2}-\delta_3^{2}\right)\left(\delta_1^{18}-\delta_3^{18}\right)/\left(\delta_1^{2}-\delta_3^{2}\right)}\right] \tag{4b}$$

$$\frac{x_3}{Q} = \left[\frac{\left(\delta_Q^{18}-\delta_1^{18}\right)-\left(\delta_Q^{2}-\delta_1^{2}\right)\left(\delta_2^{18}-\delta_1^{18}\right)/\left(\delta_2^{2}-\delta_1^{2}\right)}{\left(\delta_3^{18}-\delta_1^{18}\right)-\left(\delta_3^{2}-\delta_1^{2}\right)\left(\delta_2^{18}-\delta_1^{18}\right)/\left(\delta_2^{2}-\delta_1^{2}\right)}\right] \tag{4c}$$

It should be noted that x_1/Q, x_2/Q and x_3/Q add up to unity as constrained by Eq. (1). An analytical solution to Eqs. (4a–c) also requires that x_1, x_2, x_3 are not collinear in δ^2H-$\delta^{18}O$space.

3. Results

3.1. Isotope characteristics

Four primary streamflow water sources were identified for the oil sands region: snow, rain, surface water and groundwater. The isotopic composition of snow, rain and surface water were characterized based on water sampling programs in the vicinity of Fort McMurray (Fig. 2, Table 2). Snow was found to plot close to the meteoric water line (MWL) for Canada given by $\delta^2H = 8\delta^{18}O + 8.5$ (Gibson et al., 2005) and was significantly depleted in heavy isotopes relative to other streamflow sources. Similar patterns were noted previously for long-term snow sampling in the lower Liard Valley by St. Amour et al. (2005) and used effectively for snowmelt hydrograph separation in mesoscale basins. In contrast, summer rain was found to be enriched in heavy isotopes, plotting near but slightly below the MWL. Surface waters are distinguished by systematic evaporative enrichment, plotting along a local evaporation line (LEL) given by $\delta^2H = 5.20\delta^{18}O - 50.6$ (Gibson et al., 2015a). This is a 9-year dataset based on sampling in 50 lakes across the region. Water in peatlands (fens and bogs) subject to evapo-

Table 2
Summary of end-member isotopic compositions and their variability.

End-member	N	$\delta^{18}O$				δ^2H			
		Mean	Max.	Min.	1σ	Mean	Max	Min.	1σ
SN	67	−27.14	−25.60	−29.03	0.6	−206.7	−199.4	−220.5	3.5
RN	12	−4.07	−11.06	−16.98	1.9	−110.4	−87.3	−132.4	15.4
SW	50	−13.75	−10.35	−17.52	2.0	−121.1	−101.6	−143.2	10.7
GW	15	−20.75	−19.63	−22.56	0.8	−157.5	−148.5	−172.0	6.5

Note: SN—snow; RN—rain; SW—surface water; GW—groundwater.

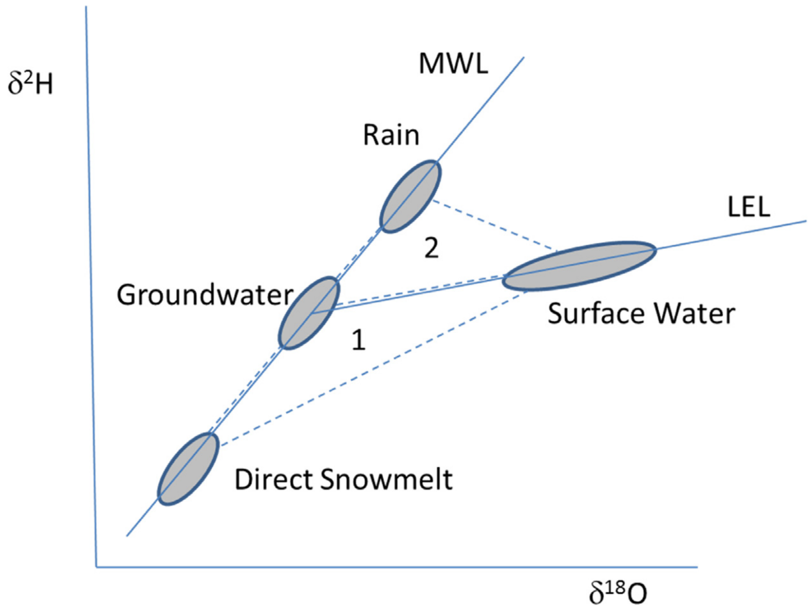

Fig. 3. Schematic showing the two 3-point mixing scenarios used in the hydrograph separation. Scenario 1 was applied during the winter and spring freshet periods whereas scenario 2 was applied during summer/fall.

ration has a similar evaporative signature plotting along the LEL, and as a result are counted as surface water contributions. Streamflow in tributaries and the Athabasca River generally has an isotopic composition that is intermediate between the major runoff sources (Fig. 2).

The isotopic composition of regional groundwater sources, which indirectly reflect the mixing of snow and rain, were estimated as the intercept of the winter baseflow recession and the meteoric water line in δ^2H-$\delta^{18}O$ space. Regression of winter streamflow isotopic records was made based on several years of record in five tributaries (Muskeg R. [2008–2014], Firebag R. [2011–2014], Steepbank R. [2011–2014], Ells R. [2011–2014], and Mackay R. [2011–2014]) using the meteoric water line for Canada, given by $\delta^2H = 8\delta^{18}O + 8.5$ (Gibson et al., 2005). The regression method was used instead of raw groundwater data to ensure that the values used were appropriately weighted to reflect conditions in the catchments under investigation. Maxima, minima and averages are found to be similar to the range previously reported for a wide survey of groundwaters collected from Quaternary, Cretaceous and Devonian units in the oil sands region (Gibson et al., 2013, 2015a; Andriashek and Parks, 2002), as well as from proprietary datasets owned by Alberta Innovates Technology Futures. A very similar average value is obtained as the intercept of the LEL and the MWL ($\delta^{18}O = -21.11$ ‰; $\delta^2H = -160.4$ ‰), which indicates the mean source of input (i.e. mean annual precipitation + groundwater) to lakes. Groundwater in our classification includes all subsurface flow contributing to streamflow and incorporates shallow interflow in peatlands as well as surficial and bedrock aquifers. It is presumed that shallow interflow in peatlands would have been classified differently, as muskeg waters, by Schwartz (1980) and Schwartz and Milne-Home (1982a,b) based on geochemical typing.

3.2. Model setup and outputs

As four distinct runoff components were identified and only two tracers were used (Table 2) some methodological simplifications were required. Fortunately, due to the limited duration of the snowmelt period, mixing in the system could be adequately approximated based on two time-dependent three-point mixing scenarios. During April and May, isotopic variations due to mixing between snowmelt, groundwater and surface water were modelled based on scenario 1 (Fig. 3); from June to October isotopic changes were simulated based on mixing between groundwater, surface water and summer

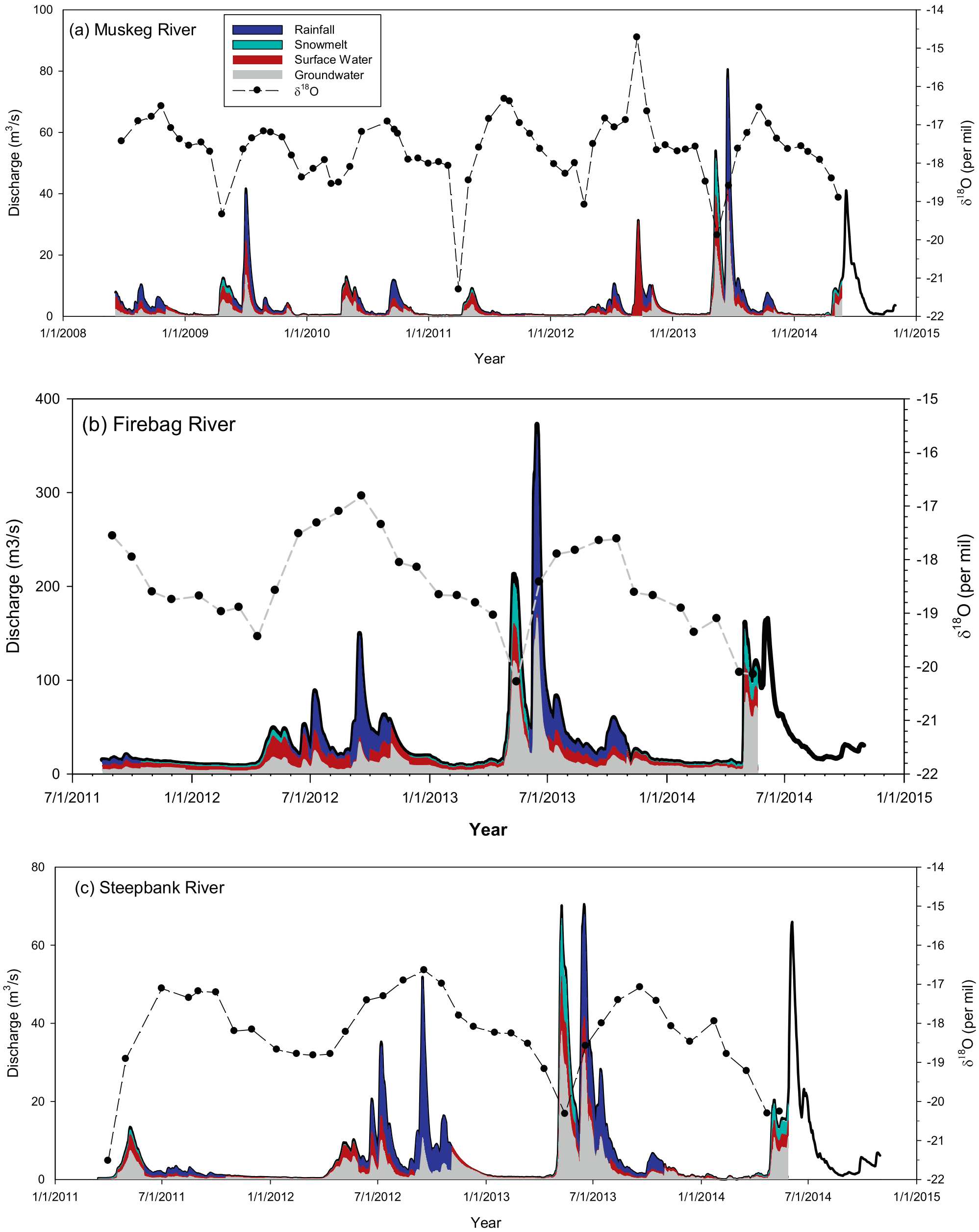

Fig. 4. Time-series partitioning summary for groundwater-dominated tributaries (a) Muskeg R, 2008–2014; (b) Firebag R. 2011–1014; (c) Steepbank R., 2011–2014.

rain according to scenario 2 (Fig. 3), and variations during winter months of November to March were modelled again using scenario 1 (Fig. 3). Note that this partitioning approach ignores the effect of rainfall during the snowmelt period, but was a necessary simplification to deal with mixing of four components with only two tracers. In effect, rain and snow mixtures during snowmelt were treated as groundwater—a reasonable assumption given that these waters will rarely interact outside the groundwater environment. June was consistently treated as a summer month in this analysis, applying scenario 2, although it is also possible to treat transition months as either snowmelt or summer months depending on when peak snowmelt occurs.

Bundles of eight mixing calculations were used for each scenario based on combinations of possible mixing triangles, choosing either maximum or minimum values for each end-member. Bundles were then averaged rather than using single average-value runs in order to capture potential uncertainty in the end-members. While isotope-based partitioning was conducted on monthly basis, and our analysis and summaries are based strictly upon the monthly results, for plotting purposes in Figs. 4–7 we also interpolated the partitioning results to match the daily record of discharge. A step-wise

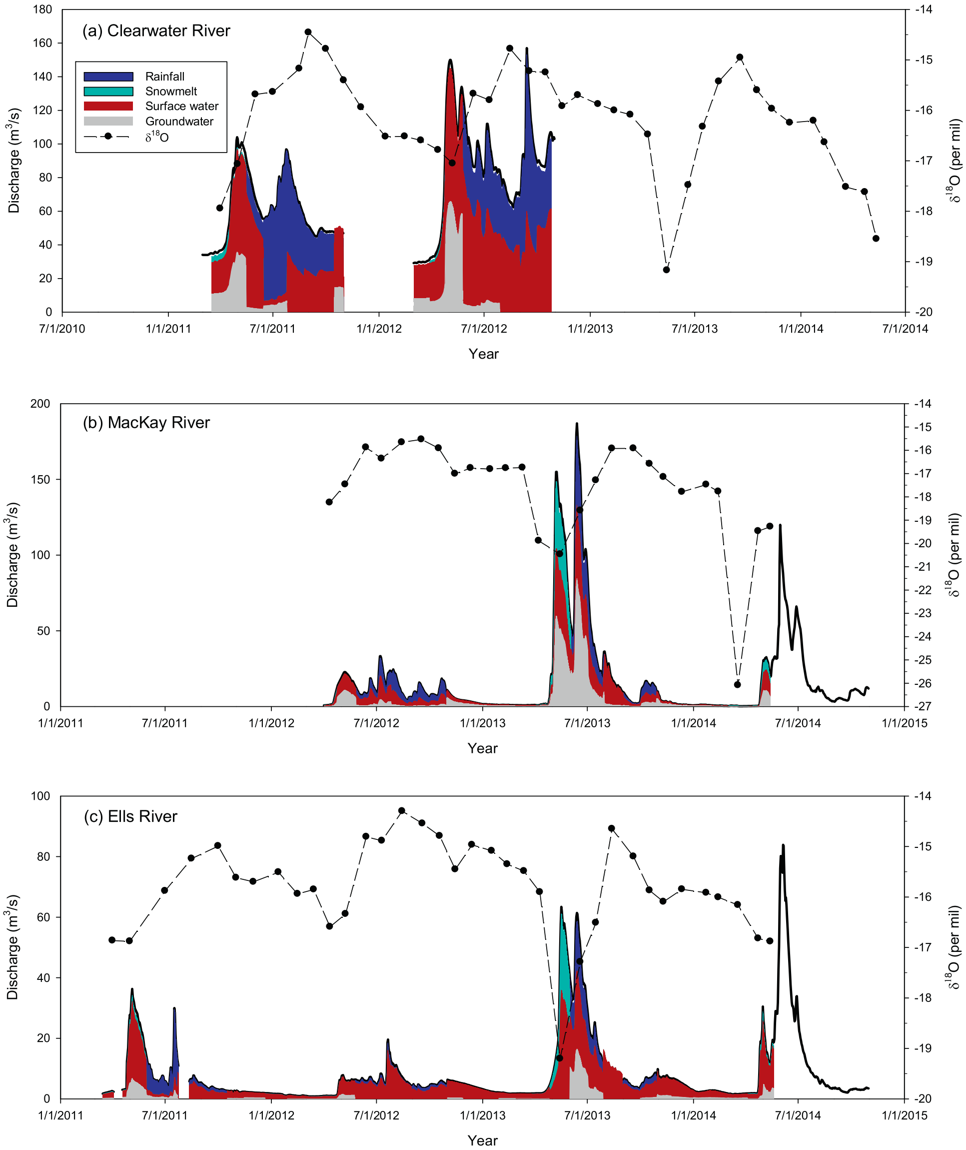

Fig. 5. Time-series partitioning summary for surface-water-dominated tributaries: (a) Clearwater R, 2011–2013; (b) Mackay R. 2011–1014; (c) Ells R., 2011–2014.

interpolation method was applied using fluxes of water rather than percentages of the various components. Similar results were also obtained in trials using a linear interpolation method although the step-wise approach was adopted here due to operational simplicity. We also present summaries for three distinct periods within the hydrological year, considered to run from November to October. These include: (i) the ice-on period (November–March), (ii) the spring freshet (April–May), characterized by snowmelt-driven processes, and (iii) summer/fall (June–October), characterized by more variable flows related to rainfall-driven processes.

Uncertainty for individual single-value mixing runs was first estimated based on the method of Phillips and Gregg (2001) which considers analytical uncertainty, sample size and standard deviation of end-members, as well as propagation of errors during mathematical derivations. Based on this approach uncertainty for individual (unbundled) runs was found to range from ±3% to ±87%, with average values close to ±27%. The large variability in uncertainty can be partially attributed to mathematical propagation of errors. For bundled scenarios used here we estimate uncertainty based on standard deviation between runs to be somewhat improved: ±9% for snowmelt proportions, ±12% for groundwater and ±22 for surface water during the freshet and winter periods (i.e. Scenario 1). Uncertainty for summer periods was higher: ±26% for rain, ±26% for groundwater and ±19% for surface water (i.e. Scenario 2). Greater uncertainty in summer/fall is primarily related to a more variable isotopic signature of rain than snow. Overall, while these uncertainties remain within a useful range for quantitative assessments, partitioning during the summer and fall needs to be interpreted more cautiously. The systematic regional

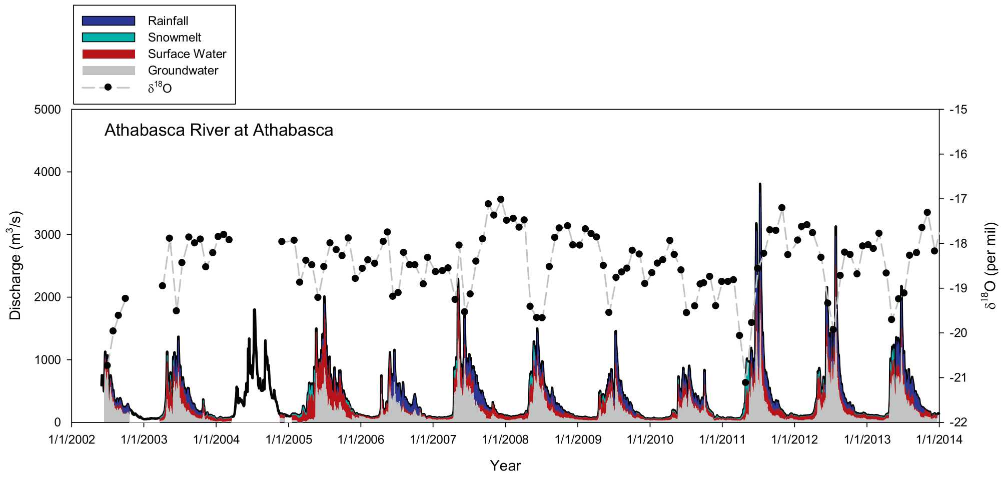

Fig. 6. Time-series partitioning summary for Athabasca R. at Athabasca, 2002–2014.

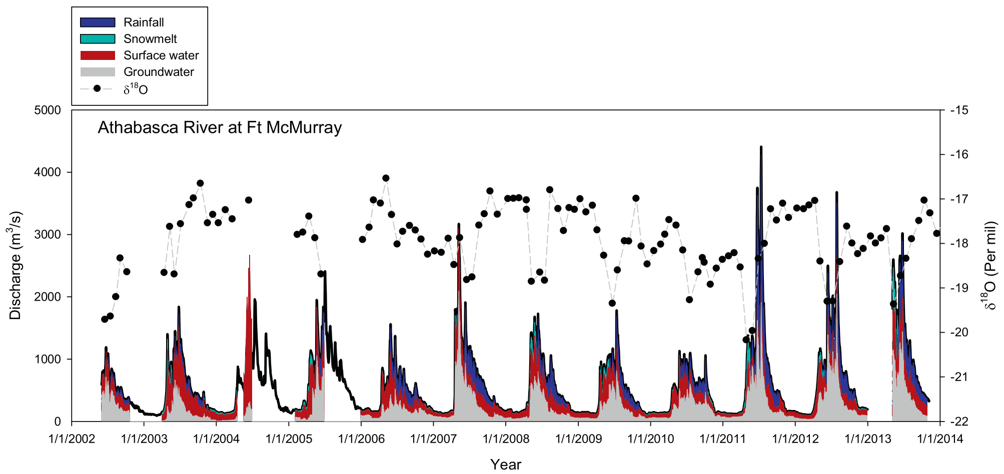

Fig. 7. Time-series partitioning summary for Athabasca R. below Ft. McMurray, 2002–2014.

evolution in groundwater/surface-water ratios presented later on is strong evidence that the proportions determined are generally conservative and meaningful.

3.3. Hydrograph characteristics

Streamflow regime, the general pattern of seasonal variation in streamflow, is influenced by water supply (e.g. snowmelt, rainfall, glacier melt), water losses (e.g. evaporation) and storage modification by lakes, wetlands, reservoirs and groundwater (Woo and Thorne, 2003). Small streams in the oil sands region are commonly classified as wetland or muskeg regime (see Church, 1974) where low relief and accumulation of peatlands creates a high water retention capacity and resistance to flow of water which promotes evaporation. Streamflow in these areas is typically reduced during the summer period compared to non-wetland regimes, and a pronounced nival (snowmelt-generated) freshet may occur in late spring when organic soils are still frozen and unable to absorb meltwater released by snow (Church 1974). Woo and Thorne (2003) described the streamflow regime in the Athabasca River below Fort McMurray as having an early hydrograph rise due to snowmelt in lowlands, followed by a summer peak, possibly sustained by glacier and high-elevation snowmelt. Severe ice jams may also form along the Athabasca River at Fort McMurray during breakup which can significantly influence channel storage and water levels (Andres and Doyle, 1984; She et al., 2009; Unterschultz et al., 2009).

Inter-annual variations in streamflow clearly reveal different styles of runoff for the watersheds examined here (see total discharge, Figs. 4–7), including sharp and broad peaks in some years. Several dominant peaks may occur in association with either snowmelt or summer/fall storms, with flashiness controlled also by freezing conditions, antecedent moisture and by connectivity of wetlands and water bodies. River flows are somewhat more sustained here than for more northerly permafrost regions which may cease to flow during winter months.

Table 3
Seasonal and annual source water partitioning summary for groundwater- and surface-water-dominated tributaries in the oil sands region, northern Alberta. Note that the Muskeg R. is classified as groundwater dominated based on ice-on flow conditions. Blank values indicate that the component was assumed to be zero for the specified time period. Small negative numbers for groundwater and snowmelt suggest that they are likely not present.

River	Time period	Flow condition	% GW	% SW	% SN	% RN	GW/SW
Groundwater-dominated							
Steepbank R.	Apr–May	Freshet	51	27	17		1.89
	Jun–Oct	Summer/Fall	29	17		51	1.70
	Nov–Mar	Ice-on	69	26	−1		2.65
	Annual	Average	50	23	3	19	2.17
Muskeg R.	Apr–May	Freshet	35	42	18		0.83
	Jun–Oct	Summer/Fall	23	39		34	0.59
	Nov–Mar	Ice-on	54	40	−1		1.35
	Annual	Average	39	40	3	14	1.00
Firebag R.	Apr–May	Freshet	49	29	17		1.69
	Jun–Oct	Summer/Fall	32	27		37	1.19
	Nov-Mar	Ice-on	51	35	9		1.46
	Annual	Average	44	31	7	14	1.42
Surface-water dominated							
Mackay R.	Apr–May	Freshet	35	42	19		0.83
	Jun–Oct	Summer/Fall	14	46		36	0.30
	Nov–Mar	Ice-on	45	44	5		1.02
	Annual	Average	31	45	6	14	0.69
Ells R.	Apr–May	Freshet	8	77	10		0.10
	Jun-Oct	Summer/Fall	-2	78		19	Undef.
	Nov–Mar	Ice-on	9	86	−1		0.10
	Annual	Average	5	81	2	7	0.06
Clearwater R.	Apr–May	Freshet	38	52	4		0.73
	Jun–Oct	Summer/Fall	2	51		43	0.04
	Nov–Mar	Ice-on	29	69	−4.2		0.42
	Annual	Average	20	59	−1	14	0.34

Using stable isotopes we endeavor to take a closer look at the underlying causes of flow variations at specific sites in the following section.

3.4. Isotopic time-series

Isotopic time series for $\delta^{18}O$ are shown for selected stations on tributaries and the Athabasca River (Fig. 4–7). The characteristic isotopic pattern noted for most records/years is that of a rapid decline in isotopic composition during snowmelt with a gradual shift towards more enriched values in summer/fall which extends over-winter. Minor fluctuations are attributed to rain events in summer and fall. The most common variation noted is that of a weaker or delayed spring melt which results in a more subtle isotopic depletion, often accompanied by a broader peak in the hydrograph itself. Examples include 2006 and 2010 for stations along the Athabasca River and 2010 for the Muskeg River. Similar temporal variations were found for $\delta^{2}H$ (not shown) and we have already illustrated systematic variations in $\delta^{18}O$ and $\delta^{2}H$ relative to flow sources (see Fig. 2).

3.5. Partitioning of streamflow components

Partitioning results are shown for six tributaries (Muskeg R., Firebag R., Steepbank R., Clearwater R., Mackay R., Ells R.; Figs. 4 and 5) and two stations along the Athabasca River (Figs. 6 and 7), where the major source components (rain, snow, surface water and groundwater) are shown as colour-coded bands reflecting weighted contributions to the total discharge. Overall, more than 609 separate partitioning determinations were made for 10 stations included in the monitoring network, the vast majority (95%) yielding positive percentages for endmembers. The partitioning results reveal a significant groundwater contribution to total streamflow (Tables 3 and 4, Fig. 8), even during high flow episodes.

Both groundwater-dominated and surface-water dominated tributaries are identified. For groundwater-dominated systems (Steepbank R., Muskeg R., Firebag R.), groundwater averages 9–50% of total discharge, ranging between 23 and 32% during summer/fall when surface flow pathways are most active, 51–69% during winter, and 35–49% during freshet. Schwartz and Milne-Home (1982b) found similar groundwater-dominated conditions in the Muskeg and Firebag Rivers based on hydrograph separation using major ions. Schwartz also looked at smaller sub-basins of the Muskeg such as Hartley Creek and found even higher groundwater contributions, so these quantities are expected to be somewhat variable at smaller scales. Schwartz described the groundwater flow in these tributaries as dominated by flow through glacial drift (i.e. Quaternary deposits), with a small percentage derived from bedrock sources. Overall, he postulated that groundwater discharge to surface water systems in the upland portion of the basins was dominated by shallow flow systems, whereas it is derived increasingly from deeper flow systems which are intersected in the lower reaches of the basins as the stream channel becomes more incised. Surface water and direct precipitation are the other major sources of runoff in groundwater dominated systems.

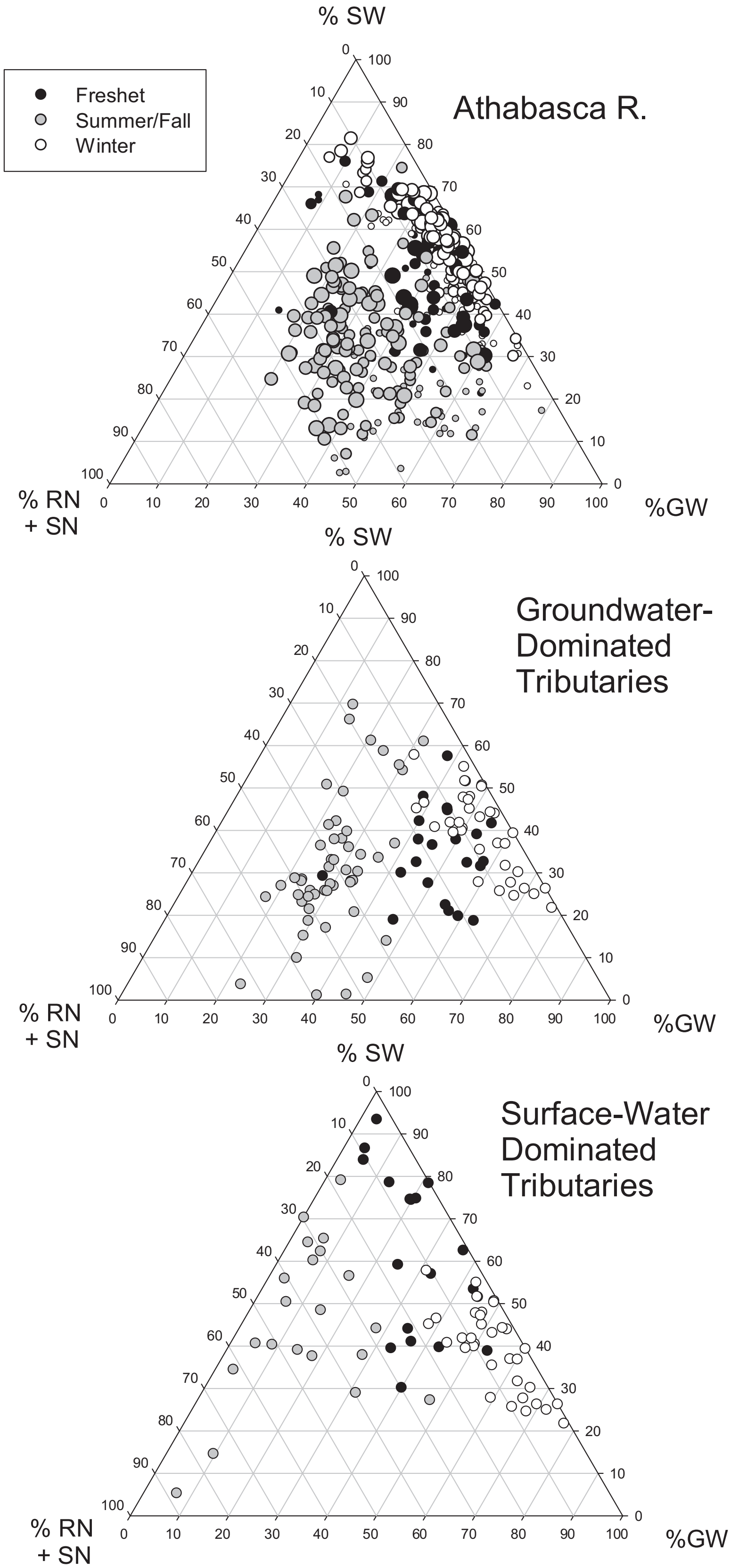

Fig. 8. Ternary plots showing partitioning results for (a) Athabasca River stations, (b) groundwater-dominated tributaries (Steepbank R., Muskeg R., Firebag R.), and (c) surface-water dominated tributaries (Clearwater R., Mackay R., Ells R.). Contributions are normalized to 100% for plotting purposes. Note in (a) that size of data points increases downstream.

Table 4
Seasonal and annual source water partitioning summary for Athabasca River stations in the oil sands region, northern Alberta.

Station	Time period	Flow condition	% GW	% SW	% SN	% RN	GW/SW
Athabasca	Apr–May	Freshet	39	43	13		0.91
	Jun–Oct	Summer/fall	47	22		27	2.14
	Nov–Mar	Ice-on	45	44	6		1.02
	Annual	Average	45	34	5	11	1.32
Fort McMurray	Apr–May	Freshet	37	49	8		0.76
	Jun–Oct	Summer/fall	39	31		26	1.26
	Nov–Mar	Ice-on	41	49	4		0.84
	Annual	Average	39	42	3	11	0.93
Firebag	Apr–May	Freshet	39	45	10		0.87
	Jun–Oct	Summer/fall	31	34		31	0.91
	Nov–Mar	Ice-on	35	57	2		0.61
	Annual	Average	35	47	3	11	0.75
Old Fort	Apr–May	Freshet	38	48	9		0.79
	Jun–Oct	Summer/fall	28	39		29	0.72
	Nov–Mar	Ice-on	36	55	2		0.65
	Annual	Average	33	48	2	12	0.68

Our analysis also extends to surface-water-dominated systems which include the Clearwater, Mackay and Ells Rivers. Surface water, mainly derived from peatlands and lakes, accounts for 45–81% of total discharge from these watersheds, ranging from 46 to 78% during summer/fall, 44–86% during ice-on period, and 42–77% during spring freshet. Groundwater is the second largest source in these watersheds accounting for 5–31% of streamflow. Surface-water dominated flows have also been noted in similar low-relief terrain such as peatland watersheds in the James Bay Lowlands (Orlova and Brianfireun, 2014).

Groundwater/surface-water ratios (GW/SW; Tables 3 and 4) are useful for distinguishing between stations/seasons that are groundwater-dominated and those that are surface-water dominated. The groundwater/surface-water ratios in the tributaries also appear to influence the ratios determined along the main stem of the Athabasca River. The Athabasca River transitions from groundwater-dominated conditions upstream of the oil sands region at Athabasca to balanced conditions near Fort McMurray and then becomes surface-water dominated in the downstream reaches near the confluence with the Firebag and at Old Fort (Table 4). Evolution of the groundwater/surface-water ratios across the region (Fig. 9) appears to show that flow from surface-water dominated tributaries becomes progressively more important downstream.

One of the most striking features of our partitioning analysis is that groundwater appears to be a significant contributor to high runoff, including both snowmelt and rain events. There has been considerable discussion and debate within the hydrological community on mechanisms that can promote groundwater-dominated runoff during peak flows. Sklash and Farvolden (1979) suggested that groundwater increases during storm events were due to groundwater ridging, i.e., precipitation causes conversion of the near-surface tension-saturated capillary fringe into phreatic water, particularly along footslopes and valley bottoms, leading to enhanced flow of groundwater to streams. Buttle (1994) also suggested that translatory flow or displacement of pre-event water by event water could be important. Translatory flows often originate from a limited portion of the drainage basin, as in the near channel areas or permanent wetlands where surface saturation is maintained. One mechanism that is widely known to operate in wetland- dominated areas is saturation overland flow or fill and spill (St. Amour et al., 2005; Spence and Woo, 2003), whereby frozen or unfrozen soils may become locally saturated due to snowmelt or rain events, and once depression storage capacity is exceeded, may result in flow overland or in macropores. In this case the runoff is translatory in that it will contain a mixture of event water and groundwater. Near-surface pipes or rills have also been shown to be important conduits for pre-event water movement from hillslopes to streams in similar wetland terrain (Gibson et al., 1993). These mechanisms, operating singly or in combination, are a reasonable hypothesis to explain the increases in groundwater discharge during both rain and snowmelt events in the tributaries.

Surface water contributions to total streamflow (as a percentage) were found to be greatest in winter for both surface- and groundwater-dominated systems. While winter groundwater discharge is expected, the drainage of peatland waters also apparently occurs throughout the winter at all stations. While not evident in all systems (exceptions being the Ells and Mackay Rivers), minimum contributions from surface water tend to occur in summer/fall during times of low antecedent moisture conditions. Surface-water-dominated systems such as the Ells and Mackay Rivers appear to buffer this effect, possibly due to the prevalence of lake drainage during dry periods.

Annual contributions from direct precipitation sources ranged between 0 and 7% for snowmelt and 7–19% for rainfall. It is likely that proportions of these sources may be underestimated at times if events occurred in the intervals between sampling. The relative contributions of groundwater, surface water and direct precipitation are shown in Fig. 8. Overall, the dominant pattern is for winter discharge to lie along the SW-GW axis (i.e. direct precipitation is minimal), and freshet and summer/fall periods tend progressively to have more direct precipitation contributions. Direct precipitation contributions typically reflect fast responding runoff generation mechanisms such as on-channel precipitation, near-channel runoff and overland flow, although the latter is likely to be minor without groundwater interaction in peat-dominated terrain. Fast responding sources also tended to decline slightly at the larger scale, accounting for less than 50% of streamflow for the vast majority of monthly runs at stations along the Athabasca R. as compared to up to 60% for tributaries. The high proportion of

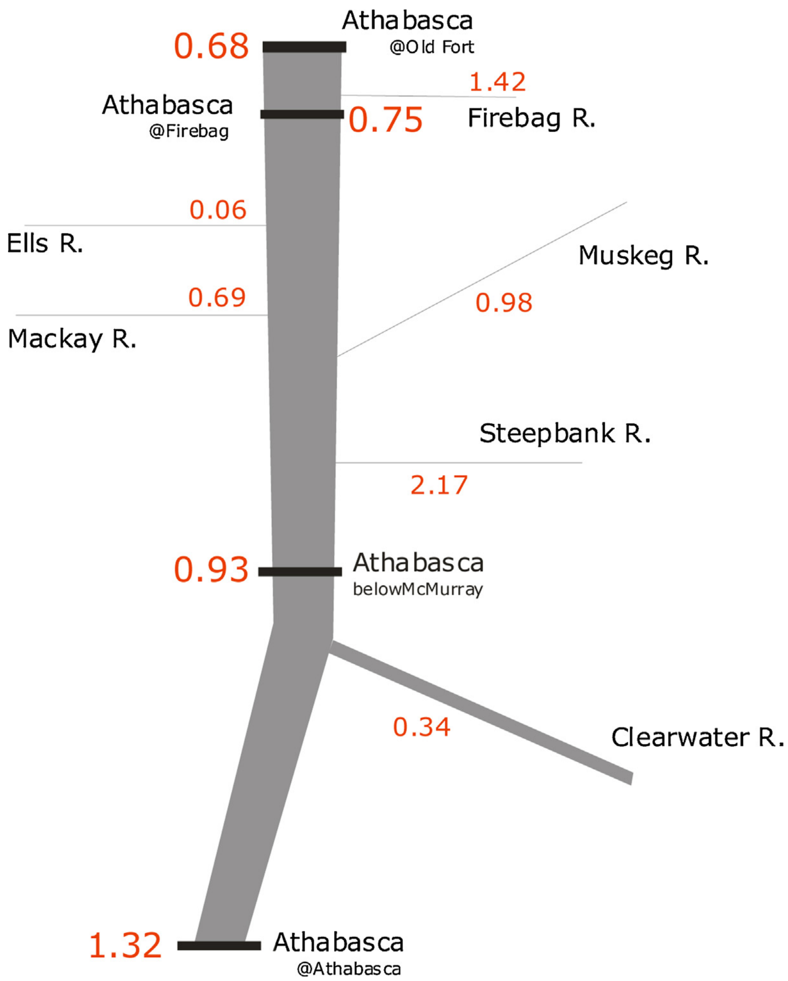

Fig. 9. Evolution of the isotope-based groundwater/surface-water ratio in the oil sands region. Note that the input of surface-water dominated tributaries (Clearwater R., Mackay R., Ells R.) causes an apparent decline in ratios along the main stem of the Athabasca River.

direct precipitation for many peak flows highlights the importance of near-channel areas for runoff generation both during freshet and in summer/fall. Contrasting responses are also noted for groundwater- and surface-water dominated systems. Surface-water dominated systems tend to have less groundwater influence during the summer/fall but increased influence during winter (Fig. 8).

3.6. Monthly patterns and inter-annual variability

This is the first study to our knowledge that has looked at multi-year source partitioning signals across a network of mesoscale tributaries and along a large river such as the Athabasca R. One interesting aspect of this work is to examine the stability of the partitioning results in multiple years. For the groundwater-dominated tributaries, a very stable inter-annual picture emerges (Fig. 10), with % groundwater peaking in late fall and gradually declining over-winter and into the freshet and summer periods. Absolute quantities of groundwater are shown to mimic the total hydrograph, peaking during the high flow months (May to July), and reflecting the role of events in the overall mechanism of groundwater discharge. For the Steepbank R., the only significant inter-annual variability was observed in January and April, although the specific cause is unknown. Negative correlations are noted between mean air temperature and % groundwater for the groundwater-dominated tributaries, suggesting that colder conditions and ice cover favor higher groundwater contributions. Note also the lower proportions of groundwater in the Ells R. (<20%), a surface-water dominated tributary (Fig. 10). One of the most interesting observations is made for the Athabasca River stations including the station below Fort McMurray (Fig. 10), where we find that percentage of groundwater peaks at the same time as absolute groundwater contribution, during the high flow period. This is contrary to the generally held view that groundwater proportions typically peak under ice in northern wetland-dominated river systems (see Gibson and Prowse, 2002). It is apparent from our partitioning analysis that groundwater plays an important role in runoff generation throughout the year.

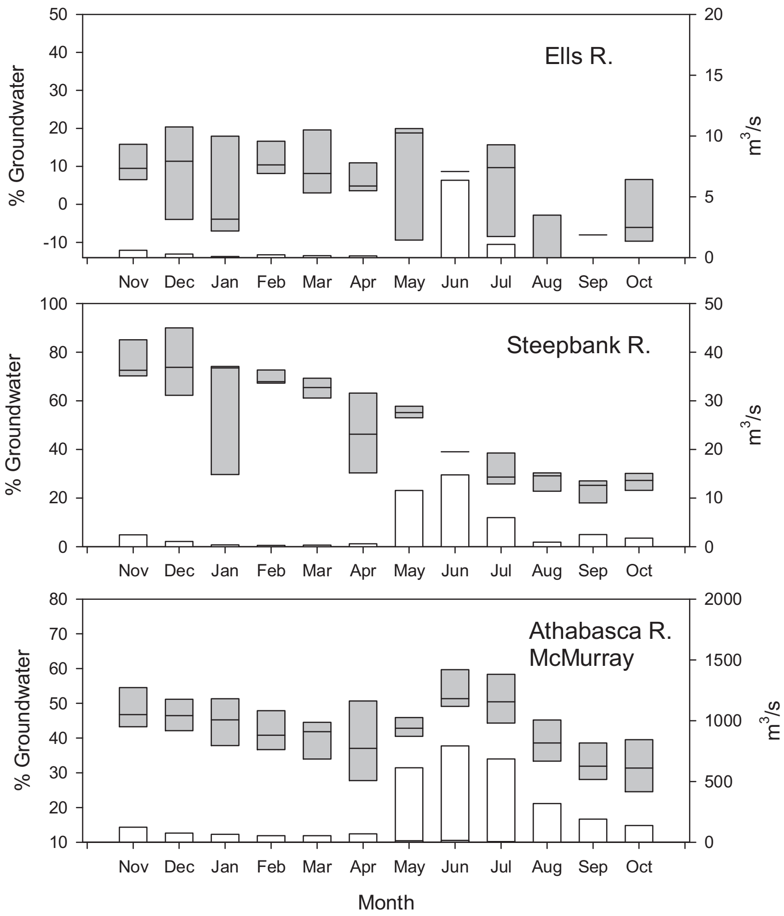

Fig. 10. Partitioning results for % groundwater and groundwater flow (m^3/s) showing inter-annual variability by month. Ells R. and Steepbank R. are examples of surface- and groundwater-dominated tributaries, respectively. Negative groundwater proportions shown for the Ells R. particularly in August/Sept. suggest that it is likely absent at this time.

Surface water, which is labelled in this study by the unique isotopic signature that water acquires when exposed to evaporation, is also shown to be an important flow regulator in all seasons. Percentage of surface water is fairly stable for tributaries over the course of the year with the exception of some summer months (particularly July) for surface-water dominated tributaries such as the Ells R. (Fig. 11). Slightly higher proportions are usually observed in winter, although the differences are subdued compared to groundwater. Absolute quantities of surface water are lowest in winter when hydrological pathways are frozen or disconnected, highest in spring when the ground is more saturated and depression storage is greater, with more variability during the summer/fall related to cycling of antecedent moisture conditions. While % surface water in the Ells, Mackay and Clearwater Rivers may account for close to 100% of discharge in some months, contributions in groundwater-dominated tributaries is often limited to less than 40%, as runoff typically contains a mixture of surface water, groundwater and event water. Limitations in the mixing model approach used are reflected in some months by proportions of surface-water estimated to be below 0% or exceeding 100%. While comparatively meaningful these results need to be interpreted cautiously.

4. Discussion

The application of stable isotope tracers to detect runoff components, combined with an understanding of the hydrologic setting of the landscape in the oil sands region enables a conceptual model of runoff generation mechanisms to be outlined (Fig. 12). The major processes identified include on-channel precipitation and near-channel overland flow, which are thought to be important sources of direct snowmelt and rainfall runoff. In unsaturated off-channel areas infiltration capacity is often too high for these processes to occur. In wetlands, mixed water sources are delivered to the stream via fill and spill, which involves event water raising the groundwater table until depression storage is satisfied and then flow occurs. Macropore flow involves flow of mixed water predominantly through organic soils and interflow/return flows are shallow groundwaters that flow between mineral soil and peat, contributing either to fill and spill or macropore flow. The fill and spill process

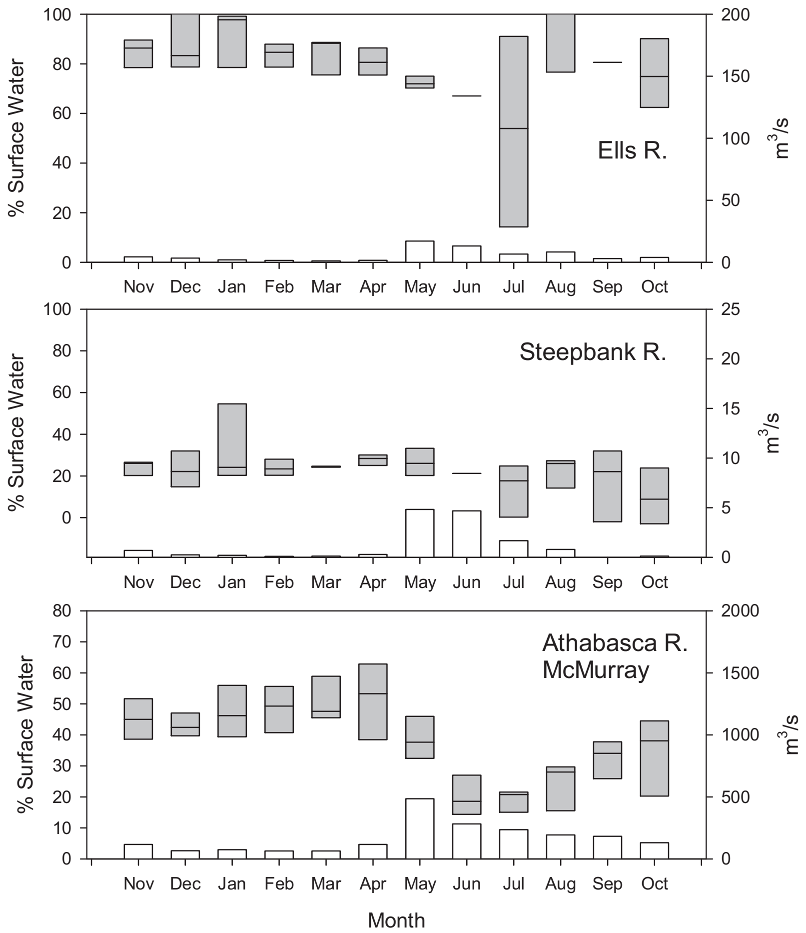

Fig. 11. Partitioning results for % surface water and surface water flow (m^3/s) showing inter-annual variability by month. Ells R. and Steepbank R. are examples of surface- and groundwater-dominated tributaries, respectively. While comparatively meaningful proportions below 0% and above 100% suggest limitations with our quantitative mixing model.

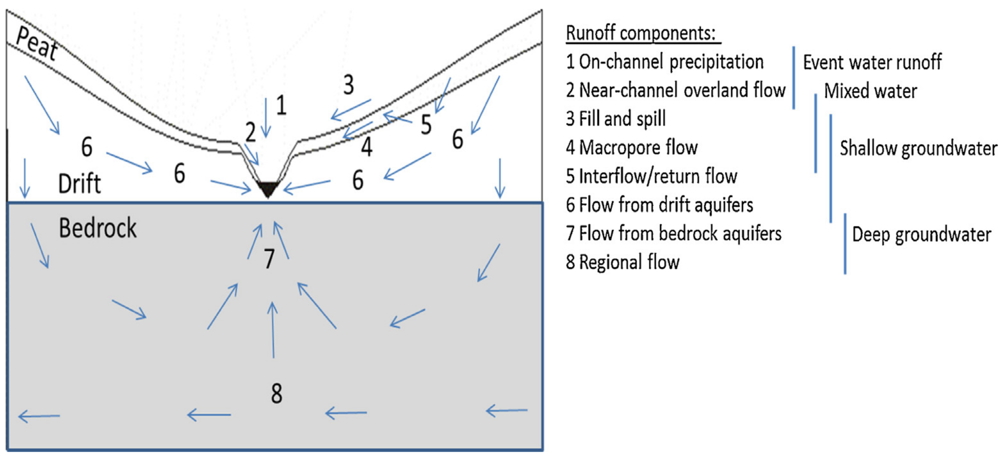

Fig. 12. Conceptual model of runoff generation in wetland-dominated tributaries in the oil sands region. Important flow mechanisms are identified. Note that on-channel precipitation and near-channel overland flow produce event-dominated runoff, shallow runoff components (2–5) typically produce mixtures of surface water and groundwater whereas deep runoff components (6–8) are exclusively groundwater-fed.

also applies to larger bodies of surface water including lakes and ponds that are often connected by permanent outlets to the tributaries. Flow from these sources is isotopically labelled as surface water due to exposure to evaporative isotopic enrichment. Groundwater sources also include shallow flow in drift aquifers and deeper sources, including bedrock aquifers or regional groundwater.

In general, the residence time of water increases from runoff component (1) through to (8) (see Fig. 12). Deeper groundwater sources also tend to be more important lower down in the drainage network as the channels become more incised, in places within bedrock. If groundwater ridging is occurring in the watersheds, then it must lead to interaction with organic soils, otherwise we would not see increases in both groundwater and surface water contributions during the freshet or during rain events. Translatory flows appear to dominate runoff. Microtopography (hollows and hummocks) in organic terrain is important in the fill and spill process because it promotes subsurface interactions (Frei et al., 2010) and translatory flows. The fate of event water, if it does not fall in near-channel areas, is to become mixed with groundwater if recharged, or surface water if it lands on saturated wetlands and is exposed to evaporation.

This study refines and extends the interpretations of Schwartz and Milne-Home (1982a,b), particularly for the Muskeg and Firebag tributaries. Schwartz estimated the groundwater contribution to the Muskeg R. during 1976–1978 to range between 30 and 50% during summer, reducing to 14–18% during freshet, and increasing to 70–80% during winter. Our analysis, albeit for a different and extended time period, suggests an average groundwater contribution of 34% during freshet, 23% during summer, and 54% during winter. Schwartz and Milne-Home (1982b) found the Firebag River to contain between 10 and 20% groundwater during summer, reducing to as low as 2% during freshet, to as high as 65% (but averaging ~30%) in winter. We find 32% groundwater during summer, 46% during freshet and 51% during winter. Schwartz declined to partition the Steepbank R. flows as it derived significant groundwater from bedrock, an end-member that he did not evaluate geochemically. For the Steepbank River, our analysis suggests that groundwater (including both drift and bedrock sources) averages 27% during summer, 69% during winter, and 49% during the freshet.

The main difference between our assessment and that of Schwartz and Milne-Home (1982b) is the greater role we determine groundwater fluxes to play during the spring freshet, which is clearly illustrated in Fig. 10. This may reflect bias in technique, as our partitioning approach includes shallow peatland groundwater (which is not evaporatively modified) in the groundwater classification, whereas Schwartz and Milne-Home would have classified this as muskeg water. Our study also used the three-component snowmelt-mixing scenario (Scenario 1; Fig. 3.) during April and May neglected the role of rainfall, and may therefore have led to a slight overestimation of groundwater contribution by a few percent during this time. We find a definitive decrease in the proportion of groundwater during freshet as compared to winter and summer/fall. However, moderate reduction in proportions of groundwater combined with a significant increase in stream discharge implies significant increases in groundwater fluxes during the freshet. Meanwhile assumptions made in the analysis by Schwartz, including that precipitation contained no dissolved ions, seems to be oversimplified. Another difference between our assessment and that of Schwartz and Milne-Home (1982b) is that we find similar source partitioning during winter in the Muskeg and Firebag Rivers, whereas they find a weaker groundwater response in the Firebag River. One explanation might be that flow paths for groundwater are deeper in the Muskeg River which would tend to influence chemistry more than isotopic composition of streamflow. Isotope-based partitioning also includes shallow subsurface water as groundwater, regardless of the pathway that it enters the stream. It is conceivable that in some cases this water may have geochemical properties that are more similar to peatland waters. Our approach appears to capture the enhanced role of groundwater during freshet in groundwater-dominated tributaries as compared to surface-water dominated tributaries, as illustrated in Fig. 10, which demonstrates encouraging sensitivity of the method.

Overall, our method reveals a wide range in the groundwater contribution across the region. We can order the rivers in terms of groundwater dominance as follows:

for tributaries: Steepbank > Firebag > Muskeg > Mackay > Clearwater > Ells

for the Athabasca River: Athabasca > McMurray > Firebag > Old Fort

Given that isotopic records on the Athabasca River at Ft. McMurray sometimes reach minimum values as late as June or July, and this occurs well after local snowmelt has concluded, we posit that summer flows along the lower reaches of the Athabasca River may be supported by snow or glacial melt in the mountains, as suggested by Woo and Thorne (2003). Contribution of high elevation runoff to streamflow in June/July would result in more negative isotope values for these months and an overestimation of groundwater contribution in the summer period. Overall, glacial contributions are expected to be a minor source of flow, estimated at 0.8% of discharge during 2000–2007 (Marshall et al., 2011).

Rasouli et al. (2013) showed that flow in the Athabasca River at Ft. McMurray has declined by roughly 30% between 1960 and 2010, which has had a large impact on Lake Athabasca water levels. Woo and Thorne (2003) also reported that the variability of discharge in the Athabasca River at Ft. McMurray increased in the latter half of the 20th century. We postulate that the high proportion of groundwater in the total discharge likely plays a significant role in buffering variability and long-term trends in the total discharge in the Athabasca River. Surface-water dominated tributaries that have more limited groundwater inputs may be especially susceptible to climate or development impacts. As such, we suggest that one focus of future research might be to look into long-term trends in the individual streamflow components to better understand the drivers of current change. This would likely complement recent studies of changes in runoff generation by Peters et al. (2013). Another one of the fundamental implications of this research is that the method may be suitable for examining the underlying causes of water quality changes, as these may be more tightly controlled by the origin of the streamflow and runoff generation mechanisms than the total discharge. For example, the distribution of some organic species (such as dissolved organic carbon) may be closely tied to surface water sources if they originate from peat, and some (such as naphthenic acids) may be more closely tied to variations in groundwater contribution if they originate from contact with bitumen or anthropogenic sources. Monitoring of individual runoff components may also aid in characterizing development related impacts such as removal of peatland, forests or groundwater abstraction that may differentially impact the runoff generation pathways across the oil sands region.

5. Summary

- Monthly isotopic records of streamflow are presented for the Athabasca River and its tributaries in the Athabasca Oil Sands region, northeastern Alberta, with records dating back to 2002 for some stations.
- An isotopic database of source waters including snow, rain, groundwater and surface water was used to estimate the proportion of each component in streamflow during freshet, summer/fall and winter periods.
- Groundwater- and surface-water-dominated systems are identified. Groundwater-dominated tributaries include the Steepbank, Muskeg, and Firebag Rivers, where groundwater accounted for 39 to 50% of annual streamflow, and surface-water-dominated systems, mainly sustained by drainage from lakes and peatlands, which include the Clearwater, Mackay, and Ells Rivers.
- Evolution of groundwater to surface-water ratios across the region reveals an overall increase in surface water sources downstream.
- Streamflow sources are expected to be important underlying controls on water quality, and may influence climate and development impacts on streamflow and other processes in area rivers.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ejrh.2015.12.062.

References

Alberta Environment, 2002. Water Quality Sampling Methods. Water Monitoring Group, Compliance Branch, Regional Services, Alberta Environment.
Andriashek, L.D., Atkinson, N., 2007. Buried channels and glacial-drift aquifers in the Fort McMurray region, northeastern Alberta. Alberta Energy Utilities Board/Alberta Geological Survey Report ESR. 2007–01 (March 2007), 160pp.
Andriashek, L.D., Parks, K., 2002. Baseline investigations into the groundwater resources of the Athabasca oil sands (in situ) area, Northeast Alberta. Alberta Energy and Utilities board, Alberta Geological Survey EUB/AGS Special Report 98, 480pp.
Andres, D.D., Doyle, P.F., 1984. Analysis of breakup and ice jams on the Athabasca River at Fort McMurray, Alberta. Can. J. Civil Eng. 11, 444–458.
Birks, J., Y., Yi, S., Cho, E. Taylor, J., Gibson, 2014. Characterizing the organic composition of snow and surface water across the Athabasca Region: Phase 2. OSRIN Report No. TR-64. 47pp.
Buttle, J.M., 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Prog. Phys. Geogr. 18, 16–41.
Canada, Environment Canada, 2015. Water survey of Canada archived hydrometric data, Athabasca River below Ft. McMurray, http://www.ec.gc.ca/rhc-wsc. (accessed 17.09.15.).
Canada, Government of Canada, 2013. Oil sands water management—fact sheet. https://www.nrcan.gc.ca/sites/www.nrcan.gc.ca/files/energy/pdf/eneene/pubpub/pdf/11-%20OS-factsheet_Water%20Management-eng-February-2013.pdf; (accessed 29.09.15.).
Church, M., 1974. Hydrology and permafrost with reference to northern North America. In: Proceedings, Workshop Seminar on Permafrost Hydrology. Canadian National Committee, International Hydrological Decade, Ottawa, pp. 7–20.
Coplen, T.B., 1996. New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. Geochim. Cosmochim. Acta 60, 3359–3360.
Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703.
Frei, S., Lischeid, G., Fleckenstein, J.H., 2010. Effects of micro-topography on surface-subsurface exchange and runoff generation in a virtual riparian wetland—a modelling study. Adv. Water Resour. 33, 1388–1401.
Gat, J.R., 1980. The isotopes of hydrogen and oxygen in precipitation. In: Fritz, P., Fontes, J.C.H. (Eds.), Handbook of Environmental Isotope Geochemistry, 1. Elsevier, Amsterdam/Oxford/New York, pp. 21–47.
Gat, J.R., 1981. Groundwater. In: Gat, J.R., Gonfiantini, R. (Eds.), Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle, 10. International Atomic Energy Agency, Vienna, pp. 223–240.
Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrological cycle. Annu. Rev. Earth Planet. Sci. 24, 225–262.
Gibson, J.J., Prowse, T.D., 2002. Stable isotopes in river ice: identification of primary over-winter streamflow signals and their hydrological significance. Hydrol. Processes 16, 873–890.
Gibson, J.J., Edwards, T.W.D., Prowse, T.D., 1993. Runoff generation in a high boreal wetland in northern Canada. Nordic Hydrol. 24, 213–224.
Gibson, J.J., Fitzgerald, D., Aravena, R., Price, J.S., Maloney, D., 2000. Streamflow generation in a hypermaritime bog-forest upland. Hydrol. Processes 14, 2711–2730.
Gibson, J.J., Edwards, T.W.D., Birks, S.J., Amour, St. N.A., Buhay, W., McEachern, P., Wolfe, B.B., Peters, D.L., 2005. Progress in isotope tracer hydrology in Canada. Hydrol. Processes 19, 303–327.
Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca River in the northern Athabasca oil sands region. Can. J. Earth Sci. 50, 1244–1257, dx.doi.org/10.1139/cjes-2013-0027.

Gibson, J.J., Birks, S.J., Yi, Y., Vitt, D., 2015a. Runoff to boreal lakes linked to land cover, watershed morphology and permafrost melt: a 9-year isotope mass balance assessment. Hydrol. Processes http://dx.doi.org/10.1002/hyp.10502.
Gibson, J.J., Birks, S.J., Yi, Y., 2015b. Higher tritium concentrations measured in permafrost thaw lakes, northern Alberta. Hydrol. Processes (accepted 24.06.15.).
Gonzales, A.L., Nonner, J., Heijkers, J., Uhlenbrook, S., 2009. Comparison of different base flow separation methods in a lowland catchment. Hydrol. Earth Syst. Sci. 13, 2055–2068.
Gue, A.E., Mayer, B., Grasby, S.E., 2015. Origin and geochemistry of saline spring water in the Athabasca oil sands region, Alberta, Canada. Appl. Geochem. 61, 132–145.
Harris, D.M., McDonnell, J.J., Rodhe, A., 1995. Hydrograph separation using continuous open system isotope mixing. Water Resour. Res. 31, 157–171.
Jasechko, S., Gibson, J.J., Birks, S.J., Yi, Y., 2012. Quantifying saline groundwater seepage in the Athabasca oil sands region. Appl. Geochem. 27, 2068–2076.
Kalbus, E., Reinstorf, F., Schirmer, M., 2006. Measuring methods for groundwater-surface water interactions: a review. Hydrol. Earth Syst. Sci. 10, 873–887.
Klaus, J., McDonnell, J.J., 2013. Hydrograph separation using stable isotopes: review and evaluation. J. Hydrol. 505, 47–64.
Marshall, S.J., White, E.C., Demuth, M.N., Bolch, T., Wheate, R., Menounos, B., Beedle, M., Shear, J.M., 2011. Glacier water resources on the eastern slopes of the Canadian Rocky Mountains. Can. Water Resour. J. 36, 109–134.
Ogunkoya, O.O., Jenkins, A., 1993. Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model. J. Hydrol. 142, 71–88.
Orlova, J., Brianfireun, B.A., 2014. Surface water and groundwater contributions to streamflow in the James Bay Lowland, Canada. Arctic Antarctic Alpine Res. 46, 236–250.
Peters, D.L., Atkinson, D., Monk, W.A., Tenenbaum, D.E., Baird, D.J., 2013. A multi-scale hydroclimatic analysis of runoff generation in the Athabasca River, western Canada. Hydrol. Processes 27, 1915–1934.
Phillips, D.L., Gregg, J.W., 2001. Uncertainty in source partitioning using stable isotopes. Oecologia 127, 171–179.
RAMP, 2015. Regional Aquatics Monitoring Program, http://www.ramp-alberta.org/data/ClimateHydrology/hydrology/Hydrograph.aspx, (accessed 17.09.15.).
Rasouli, K., Hernandez-Henriquez, M.A., Dery, S.J., 2013. Streamflow input to Lake Athabasca, Canada. Hydrol. Earth Syst. Sci. 17, 1681–1691.
Schwartz, F.W., 1980. Hydrogeological investigation of Muskeg River basin, Alberta. Alberta Oil Sands Environmental Research Program, Report 48, 97pp.
Schwartz, F.W., Milne-Home, W.A., 1982a. Watersheds in muskeg terrain: 1. The chemistry of water systems. J. Hydrol. 57, 267–290.
Schwartz, F.W., Milne-Home, W.A., 1982b. Watersheds in muskeg terrain: 1. Evaluations based on water chemistry. J. Hydrol. 57, 291–305.
She, Y., Andrishak, R., Hicks, F., Morse, B., Stander, E., Krath, C., Keller, D., Abarca, N., Nolin, S., Tanekou, F., Mahabir, C., 2007. Athabasca River Ice Jam formation and release events, 2006 and 2007. J. Cold Regions Sci. Technol. 55, 249–261, Special Issue on River Ice.
Sklash, M.G., Farvolden, R.N., 1979. The role of groundwater in storm runoff. J. Hydrol. 43, 45–65.
Spangenberg, J.E., 2012. Caution on the storage of waters and aqueous solutions in plastic containers for hydrogen and oxygen stable isotope analysis. Rapid Commun. Mass Spectrom. 26, 2627–2636.
Spence, C., Woo, M.K., 2003. Hydrology of subarctic Canadian Shield: soil filled valleys. J. Hydrol. 279, 151–166.
Amour, St. N.A., Gibson, J.J., Edwards, T.W.D., Prowse, T.D., Pietroniro, A., 2005. Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River Basin, Northwest Territories, Canada. Hydrol. Processes 19, 3357–3381.
Tetzlaff, D., Buttle, J., Carey, S.K., McGuire, K., Laudon, H., Soulsby, C., 2015. Tracer-based assessment of flow paths, storage and runoff generation in northern catchments: a review. Hydrol. Processes 29, 3475–3490.
Unterschultz, K., van der Sanden, J., Hicks, F.E., 2009. Potential of RADARSAT-1 for the Monitoring of River Ice: results of a case study on the Athabasca River at Fort McMurray, Canada. J. Cold Regions Sci. Technol. 55, 238–248, Special Issue on River Ice.
Uhlenbrook, S., Frey, M., Leibundgut, C., Maloszewski, P., 2002. Hydrograph separation in a mesoscale mountainous basin at event and seasonal timescales. Water Resour. Res. 38 (6), 1096, http://dx.doi.org/10.1029/2001WR000938.
Vitt, D.H., Halsey, L.A., Zoltai, S.C., 1994. The bog landforms of continental western Canada in relation to climate and permafrost patterns. Arctic Alpine Res. 26, 1–13.
Vitt, D.H., Halsey, L.A., Zoltai, S.C., 1999. The changing landscape of Canada's western boreal forest: the current dynamics of permafrost. Can. J. For. Res. 30, 283–287.
Woo, M.K., Thorne, R., 2003. Streamflow in the Mackenzie Basin, Canada. Arctic 56, 328–340.