

Final Report for SMM-01-2021

Understanding Recent and Historic Isotope Signatures in the Milk River

Submitted to the International Watershed Initiatives (IWI) Program

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To whom it may concern,

Thank you for the opportunity to perform a preliminary analysis of the benefits of isotope water-mass balance estimation to better understand the hydrology of the Milk R basin, including the impact of zero-flow diversion scenario that occurred in 2020. It has been a pleasure to work on this study (SMM-01-2021).

Our study finds that overall, isotopes are beneficial to understanding the hydrology and water balance of the Milk R basin and were capable of identifying and isolating (1) the proportion of St. Mary's basin water diverted into the Milk R. basin, (2) surface water and groundwater sources, (3) the relative influence of evaporation and transpiration occurring within the basin, and (4) water yield, or runoff, estimates. Based on the evidence and findings summarized in this report, our recommendation is to **establish a long-term isotope monitoring network in the Milk/St. Mary's basins to support water balance and hydrologic estimation**. We estimate the cost of such a network to be ~\$2,000 per year of operation for a program that would meet the needs of water balance estimation and source separation identified by this report.

I would like to acknowledge the contributions of Ms. Tegan Holmes (PhD candidate), and Ms. Bailey Knapp (B.Sc. candidate) to this work. Should you have any questions or wish to follow up on these results, please do not hesitate to contact me (tricia.stadnyk@ucalgary.ca).

Sincerely,



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Scope & Objectives

The project is looking at stable hydrogen and oxygen isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) that are naturally occurring in water as a means of determining flow pathways, evaporation rates and sources of water in the Milk River. This work is exploratory in helping to determine, alongside hydrometric records for the Milk River, how much water may be evaporating in the reaches. It may also be instructive on understanding the sources of water (natural or diverted for the St. Mary system) within the Milk River itself. The methods being looked at may enhance our apportionment calculations and further our understanding of the complex prairie system.

Deliverables

The following key deliverables were identified in the project proposal and are here within reported on:

1. Assess the isotopic label of St. Mary's diversion water using historic and recently obtained samples and map the downstream evolution of isotopic compositions both with and without (2020 case-study) diversion flow.
2. Map isotopic end members for this system using a dual isotopic framework approach relying on the historic and new stable isotope data.
3. Summarize existing isotopic datasets from WSC, LTRN and USGS that can be leveraged for future studies.
4. Provide recommendations for the design of an isotopic monitoring program for this system to aide in understanding hydrologic sources and sinks along the Milk River.

Overview of Methods

The portion of the Milk/St. Mary's Basin considered in this study, including the relevant Water Survey of Canada (WSC) gauges used for flow and isotopic analyses, are provided on Figure 1. Subbasin delineations were used upstream of each gauge to delineate contributing areas for source water analyses. Gauge 11AA025 was the only gauge not impacted by the zero-diversion flows as it was the headwater basin for this region; all others were impacted by diverted (or zero-diversion) flows.

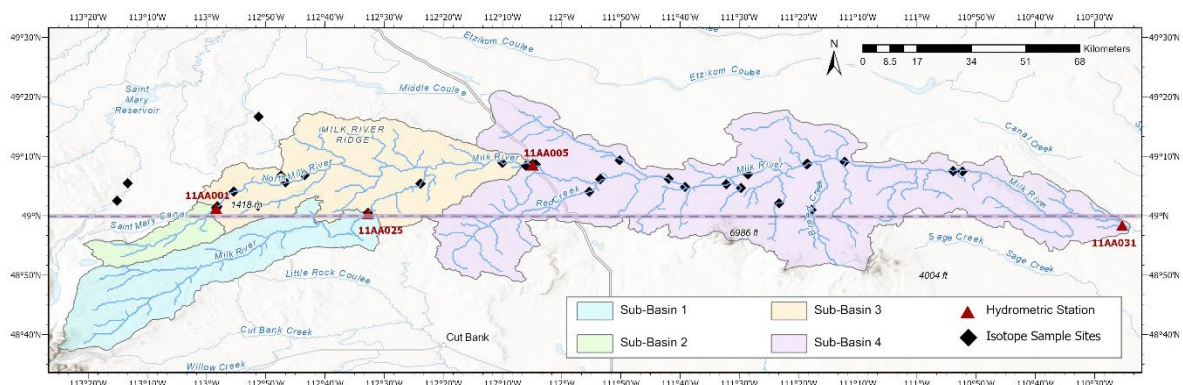


Figure 1. Overview of the Milk/St. Mary's sub-basin delineations, hydrometric gauges, and isotope sampling sites used in this study.

Meteorological variables for this study were obtained from the North American Regional Reanalysis (NARR) model to provide continuous input data across the study period (January 2016 to December 2020). Generally speaking, there were no significant differences in meteorological variables observed across the study time frame.

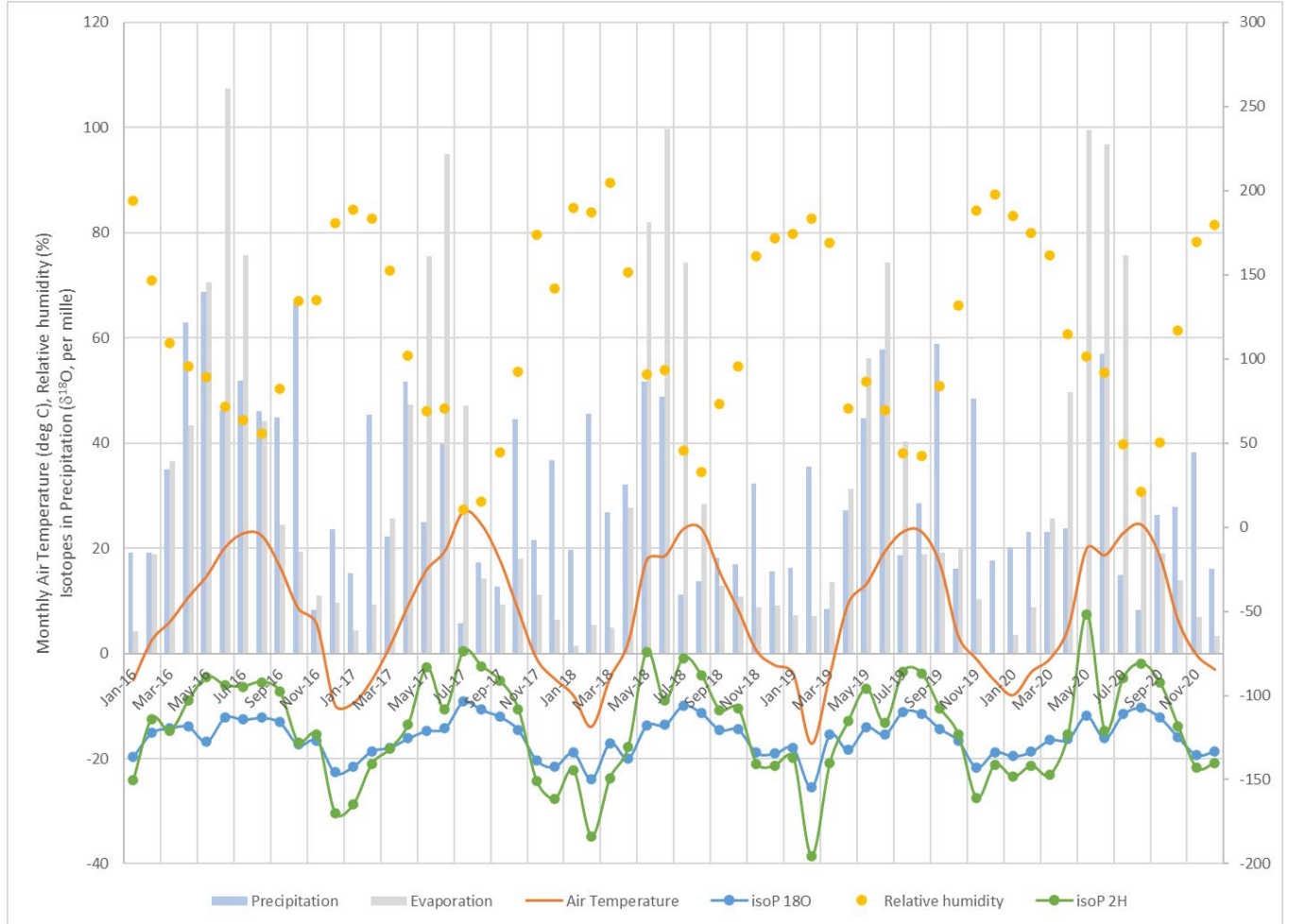


Figure 2. Summary of meteorological conditions obtained from NARR for the study period from January 2016 to December 2020, including modelled isotopes in precipitation signatures required for water balance modelling.

NARR data were also required for the isotope in precipitation (isoP) modelling (Delavau et al., 2015), which was a necessary input for the isotope-derived water balance computations. IsoP is based on observations from the long-term Canadian Network for Isotopes in precipitation (CNIP) and United States Network for Isotopes in Precipitation (USNIP), along with physiographic basin characteristics and meteorology derived from NARR. Time series (monthly) output from isoP is shown on Figure 2, and Figure 3 shows the variability in isotope in precipitation input across the Milk R basin. Note the more depleted rainfall composition at the headwaters (most western portion) of the basin that would impact the isotope in streamflow composition of the St. Mary's basin, and hence the canal water.

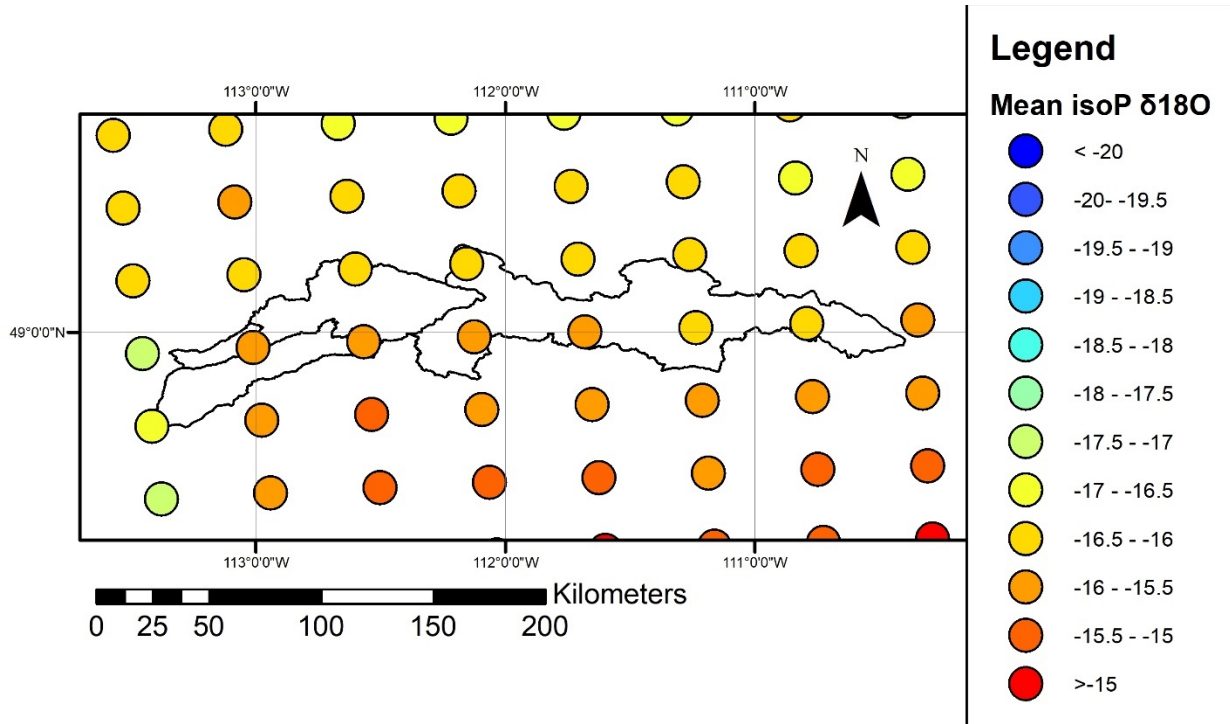


Figure 3. Spatial variability of the isotopes in precipitation input across the Milk River basin as predicted by iso P (2016-2020).

Stable Isotopes of Water

Stable isotopes of water (^2H and ^{18}O) are well known tracers of the hydrologic cycle because of their consistent and systematic variation resulting from evaporation. Evaporation favours lighter isotopes moving into the vapour phase (meaning surface water under-going evaporation will concentrate in heavy isotopes). This results in *enrichment* of surface waters (i.e., higher concentration of heavy isotopes), and *depletion* of vapour sources (i.e., absence of heavy isotopes).

A global standard exists, coordinated by the International Atomic Energy Agency (IAEA) that standardizes reporting of water isotopes around the world. Namely, changes in isotopic composition are measured as a ratio of the rare, heavy to the more common, light isotope species (R_{sample}), and related to a global standard ratio (R_{standard}) and reported in delta-notation:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

Values are reported in per mille (i.e., $\times 1000$, ‰) to account for the very small mass ratios being measured. In Canada, relative to the global standard, our *surface waters* tend to be more depleted in heavy isotope species (i.e., negative values) as a result of seasonality (i.e., a large proportion of our precipitation comes from snow), and colder average annual temperatures (i.e., less evaporation). Our vapour (i.e., origin of precipitation) also tends to be more depleted in heavy isotopes within the continental interior of North America as a result of the well-known continental affect (Gat et al., 2001).

Isotopic Labelling in Hydrology

Isotope frameworks, or $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plots, plot one stable isotope of water against the other and are useful in identifying differences in water source (i.e., precipitation as rain or snow, surface vs. groundwater, etc.), and the amount of evaporation that has occurred from input (rain or snow) to runoff (i.e., streamflow).

Regression lines are generated around flux-weighted sample points. For precipitation, points are either amount weighted (by amount of precipitation) or evaporation flux-weighted (to account for seasonal changes in the amount of evaporation). In this study, because we only looked at March to October samples when evaporation occurs, we amount-weighted our samples. The regression about local precipitation forms a local meteoric water line (LMWL), and the flux-weighted average of all global precipitation forms the global meteoric water line (GMWL). For this region, we report the GMWL and an estimated LMWL from isoP, using monthly data:

$$\text{GMWL: } \delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$$

$$\text{LMWL: } \delta^2\text{H} = 7.35 \times \delta^{18}\text{O} - 1.5$$

In North America, surface water tends to plot below the meteoric water line, indicating some amount of evaporation has occurred during the rainfall-runoff process. This is a result of our generally more arid climate (Benettin et al., 2018). The more evaporation that occurs, the greater the deviation, or offset, from the MWL to the sample will occur.

When surface water samples are plotted on the framework, flux-weighted regressions can be performed about them to generate either a local mixing line (i.e., streamflow values, LML), or local evaporation line (i.e., lakes and wetlands, LEL). The difference in slope between the MWL and LML or LEL is a direct measure of the amount of evaporation that has occurred from the meteoric input to the measured output or source. Groundwater samples, which tend to have less exposure to surface conditions and therefore less opportunity to undergo evaporation, tend to represent long-term average isotopic compositions of precipitation (meteoric water), plotting close to the MWL. On the other than, surface water in rivers will deviate more from the MWL, depending on how much evaporation occurs in a give year, or spatially along the flow path.

Isotope Hydrograph Separation (IHS)

Using long-term, known end member (water balance component) isotopic compositions, derived from isotope frameworks, a two-component hydrograph separation can be performed to separate contributions from (1) ‘new’ water, or meteoric inputs, and (2) ‘old’ water, or groundwater/baseflow. Mathematically, the sum of the two components is assumed to equal 1, or total streamflow, and therefore we can derive the following mass and isotope balances:

$$Q = R + P$$

$$\delta_Q Q = \delta_R R + \delta_P P$$

Where R is baseflow (m^3/s) and δ_R is the isotopic composition of long-term baseflow (i.e., typically obtained from late season ice-on streamflow samples); Q (m^3/s) is total streamflow and δ_Q the

isotopic composition of a streamflow sample at some point in time; and P is precipitation amount and δ_P the isotopic composition of long-term precipitation, or meteoric water. By substituting the first equation into the second, we can separate out a ratio of new water contributing to total streamflow (P/Q) using only isotope measurements (St Amour et al., 2005):

$$\frac{P}{Q} = \frac{\delta_Q - \delta_R}{\delta_P - \delta_R}$$

Old water contributions are assumed to be $R/Q = 1 - P/Q$.

Functionally, using isotope-water mass balances we can derive other hydrologic ratios that inform changes in water balance components such as transpiration (T) relative to total evapotranspiration (ET) loss, evaporation (E) relative to total basin inflow (P for headwater basins, I for nested downstream basins with upstream contributing streamflow), and water yield (WY) which is an estimate of total runoff for a basin area. These calculations are performed at the subbasin scale, with more details provided by (Gibson et al., 2021) using the Canadian isotope monitoring network (Gibson et al., 2020).

In this study, we applied the isotope-water mass balance equations at the subbasin scale for the following gauges regions:

Table 1. Gauges where isotope mass balance estimation was used for water balance component separation.

| Basin | WSC ID | Name | Area (km ²) |
|-------|---------|--|-------------------------|
| 1 | 11AA025 | Milk R at Western Crossing of International Boundary | 1054 |
| 2 | 11AA001 | North Milk R near International Boundary | 239 |
| 3 | 11AA005 | Milk R at Milk R | 1440 |
| 4 | 11AA031 | Milk R at Eastern Crossing of International Boundary | 3793 |

The following water balance component separations were attempted

$$WY = Q \times WA \times 1000 \left(\frac{mm}{yr} \right)$$

$$\frac{E}{I} = \frac{\delta_I - \delta_Q}{\delta_E - \delta_Q}$$

$$\frac{T}{ET} = \frac{[P - Q - xP]}{[P - Q]}$$

Where WA is watershed area in m²; I is basin inflow (m³/s) and δ_I is the isotopic composition of the inflow, as defined by streamflow samples; E is evaporation loss (m³/s) and δ_E is the isotopic composition of vapour under-going evaporation, as obtained from the Craig and Gordon model; and x is the E/I or E/P ratio.

Results and Findings

Isotopic labelling of source waters

The first deliverable identified for this study was to

Assess the isotopic label of St. Mary's diversion water using historic and recently obtained samples, and to

Map the downstream evolution of isotopic compositions both with and without (2020 case-study) diversion flow.

Compiling all isotope data obtained between 2016 and 2020, we provide the following isotope frameworks, plotting the two stable isotopes of water against each other ($\delta^{18}\text{O}$ - $\delta^2\text{H}$ space; Figure 2. From Figure 2a, we observed spatial differences in isotope signatures at various sampling points. Each dashed line represents the (discharge) flux-weighted regression of data points sampled at each location. The slopes of each line represent the relative amounts of evaporation occurring along the flowpath, with lower slopes indicating more evaporation loss, or a greater deviation from the GMWL (precipitation input). Figure 2b distinctly separates the Milk R samples by year of study.

Figure 3 maps the differences in isotopic composition between the St. Mary's and Milk R sources by combining all data within each river basin and performing a flux-weighted regression about the sample points. Sampling years are identified by the symbol used.

To further examine the impact of the diversion on Milk R downstream isotope signatures, we separate above the diversion, at the diversion and below the diversion time series of isotope signatures ($\delta^{18}\text{O}$ only shown) to look at spatial and temporal patterns (Figure 4).

From the isotope framework analyses, we find the following:

- The North Milk R and St. Mary's R isotopic compositions are similar, and closely follow meteoric water inputs (i.e., GMWL)
- Downstream basins and tributaries exhibit differing amounts of evaporative influence and isotopic enrichment (i.e., lower slopes, deviating further from the GMWL)
- The downstream portion of the Milk R is heavily influenced by tributary inputs that undergo more evaporation along longer flow paths
- In 2020, the Milk R was significantly more isotopically enriched (i.e., lowest slope among all the years), indicating it experienced higher amounts of evaporation

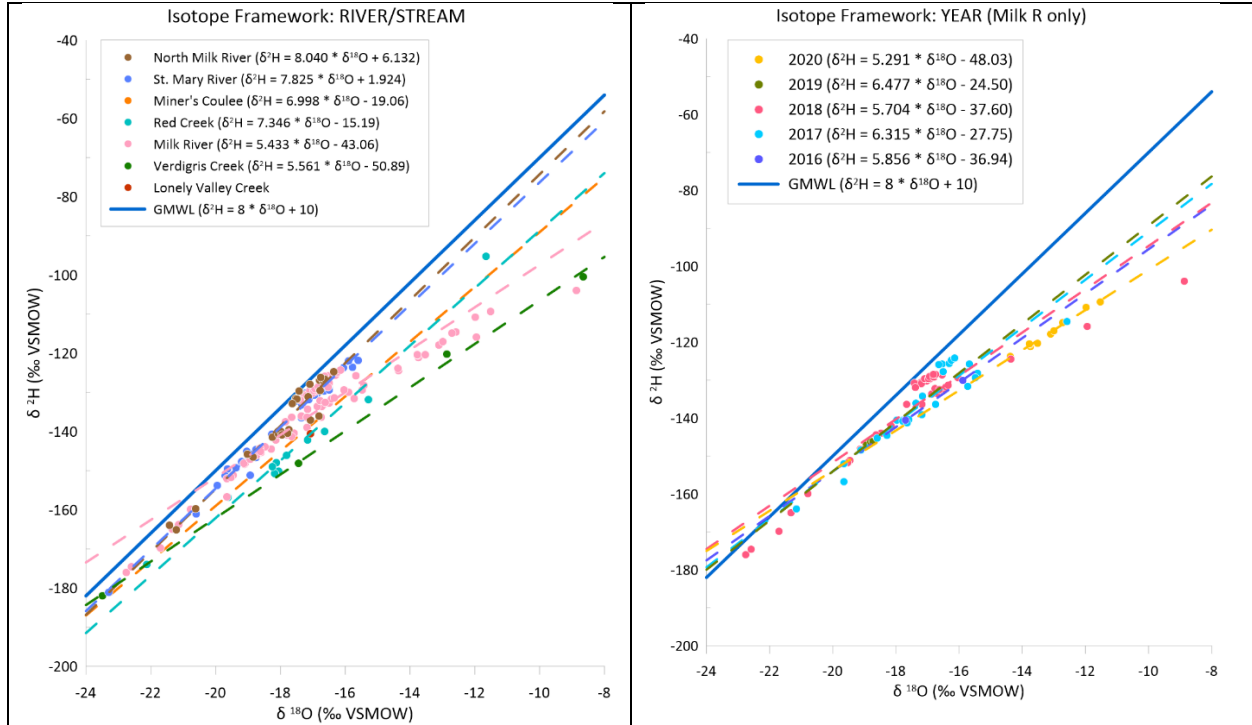


Figure 4. Isotope frameworks for (a) all data collected from all rivers and streams, and (b) the Milk R samples separated by year of collection.

By separating and comparing the Milk and St. Mary's R basin samples directly, we observe that the St. Mary's R basin closely resembles meteoric water inputs (i.e., the GMWL) while the Milk R shows a strong evaporatively enriched signal (i.e., lower slope and deviation from the GMWL). This indicates the two source water regions are isotopically distinct over the long-term and can be traced using water isotopes.

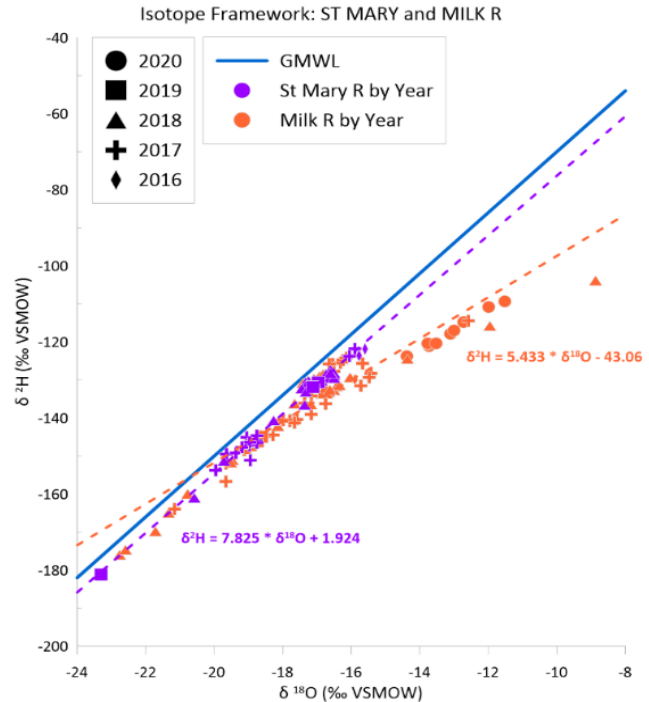
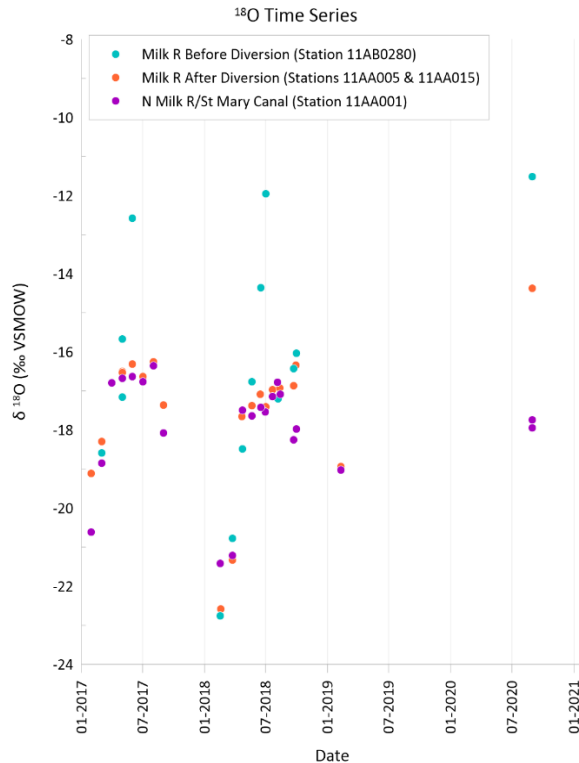


Figure 5. Separation, or mapping, of the Milk and St. Mary's Rivers isotopic composition by year of sampling.

Comparing isotope results upstream of the diversion, at the diversion (i.e., canal water) and downstream of the diversion we find the following:



- Significant isotopic seasonal variability, higher for the headwater basin and decreasing moving downstream
- A seemingly, although not well defined (due to a lack of data), inverse seasonal trend between the diversion (and downstream) and upstream basins, with the diversion water depleting through late summer/fall, and the headwater basin enriching
- Significant increase in enrichment downstream of the diversion in 2020, outside of the maximum enrichment seen in all previous years of record. Similarly, upstream of the diversion interestingly shows more enrichment (though smaller difference) from previous years in 2020.
- Diversion water in 2020 is consistent isotopically with previous years at a similar seasonal time frame

Figure 6. Time series isotopic compositions ($\delta^{18}\text{O}$ shown here) above, at and below diversion canal from 2016 to 2020.

Mapping Isotopic End Members

The second deliverable noted in our proposal was to

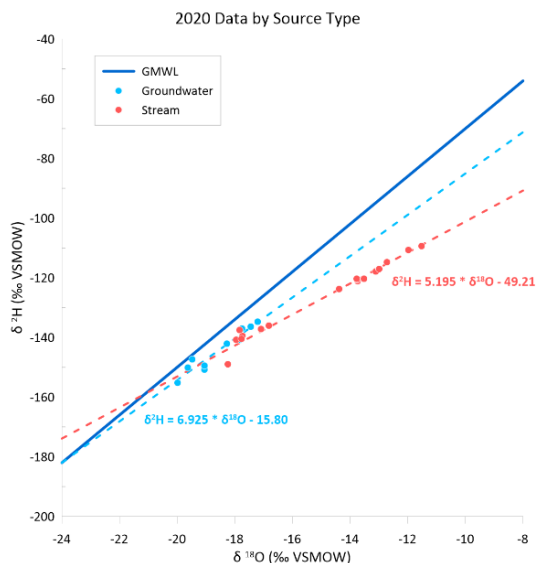
Map isotopic end members for this system using a dual isotopic framework approach relying on the historic and new stable isotope data

Our goal was to use the data available to first identify if isotopes were capable of seeing and differentiating the different components contributing to the Milk R water balance, and if yes, to subsequently attempt component separation using the available dataset and known methodologies. Through the analysis of isotope frameworks developed above (Figure 2 and Figure 3), it was determined that isotopes were capturing differences in evaporative fractionation, and regional source water differences (cause unknown) between, for example, the Milk and St. Mary's basins. Therefore, we further separated surface water and groundwater contributions using isotope frameworks (Figure 5), performed analytical estimations of water balance components (Table 1), and attempted an isotope hydrograph separation (IHS) analysis (Figure 7).

From the isotope framework source separation, surface water samples were plotted and regressed separately from those sampled by AEP from groundwater wells. All samples on Figure 5 were

from 2020, under zero-flow diversion, and such that a consistent period of sampling was used to assess isotopic differences. From the regression lines and slopes, we determine the following:

- Groundwater source tracks similarly to global meteoric waters, and even closer to known local meteoric water compositions (i.e., $\delta^2\text{H}=7.35 \delta^{18}\text{O} - 1.5$).



- This indicates moderate to little evaporative influence (through percolating surface water) of groundwater and suggests a deeper and/or older source originating from an upland recharge area near the border. This is consistent with the known hydrogeology of this region (Hendry and Schwartz, 1991; Pétré et al., 2015)

- Slight evaporative enrichment of groundwater does occur (i.e., a lower slope), but it is isotopically distinct from the amount of evaporative enrichment of surface waters

- Surface water undergoes significant evaporative enrichment in this region relative to meteoric inputs, and other Canadian river systems

- Groundwater was reasonably tightly

clustered and showed little variability among the different wells sampled

Figure 7. Isotopic data collected in 2020 mapped by source for river (red) and groundwater (blue) relative to global meteoric water (precipitation).

Baseflow separation from surface water was attempted using IHS methods given the isotope signatures between ground and surface water were sufficiently distinct (shown on Figure 5). Results shown on Figure 7 indicate percent surface water contributions >100%, which would result in discharge values (m^3/s) exceeding total streamflow. Contributions of surface water ranged from 0 to 729% ($\delta^{18}\text{O}$) and 0 to 244% ($\delta^2\text{H}$) for surface water; values exceeding 100% are not physically possible. Baseflow was numerically constrained between 0 (i.e., negative values were set to 0) and 100% (i.e., values exceeding were set to 100%). The main cause for this error was inadequate definition of a true baseflow isotopic composition; groundwater was used as a surrogate but based on Figure 6, was likely far too depleted to represent baseflow in the river. A second attempt at IHS was made using runoff (discharge-weighted streamflow samples) as baseflow, however these results were also unsatisfactory.

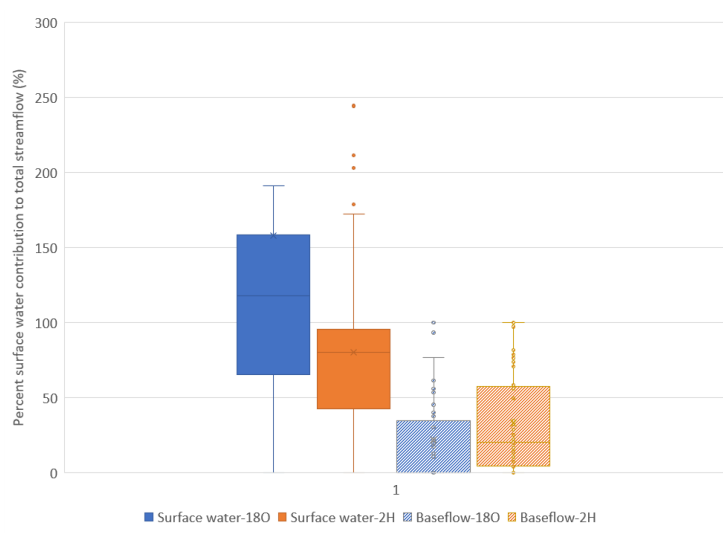


Figure 8. Results of the IHS separation between 'old' (baseflow) and 'new' (surface water) components.

Despite meeting the criteria for isotopically distinct end members, and generally only two contributing end members at any one time, this analysis clearly did not yield satisfactory results. The reasons for this are as follows:

- Sporadic, opportunistic sampling targeted early season data in some years when streamflow was still affected by snowmelt runoff. Hence the two-component only assumption was violated in some instances (e.g., March and April samples).
- Insufficient consistency and frequency of sampling, and poor seasonal coverage
- Inadequate description of the isotopic composition of baseflow (late ice-on periods) for the method separation: groundwater was too depleted and does not consistently contribute to hydrographs at the event scale, and rainfall was too enriched
- Low-flow periods were inadequately sampled, particularly in late fall prior to freeze up

It is likely that a sampling network and program designed with IHS in mind as a net result of sample collection could adequately fill these data gaps and provide more accurate baseflow separations in this region.

Analytical source water separations were performed on the isotope dataset in this study for the purposes of identifying individual water balance components (end members), such as evaporation loss relative to inflow (i.e., E/I), and transpiration relative to total evapotranspiration (i.e., T/ET), and overall water yield, or basin runoff (i.e., WY). Data were insufficient in resolution (over time) to perform monthly or even seasonal analyses, and therefore needed to be aggregated to the annual time scale. The focus here was to assess significant changes in the water balance between 2020 (i.e., zero-flow diversion) and other years with inter-basin diverted flow (Table 2).

Table 2. Summary of water balance analyses for the Milk R basin. Values highlighted in red are physically impossible. Results are the average of both isotope tracers ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). Zero-flow diversion years highlighted in grey.

| Basin | WSC ID | Name | Area (km ²) | Year | WY (mm/yr) | E/I | T/ET |
|-------|---------|--|-------------------------|------|------------|-------|------|
| 1 | 11AA025 | Milk R at Western Crossing of International Boundary | 1054 | 2016 | 16.44 | - | - |
| | | | | 2017 | 68.68 | -0.01 | 1.01 |
| | | | | 2018 | 80.73 | -0.07 | 1.08 |
| | | | | 2019 | 84.49 | -3.67 | 5.05 |
| | | | | 2020 | 81.88 | 0.22 | 0.76 |
| 2 | 11AA001 | North Milk R near International Boundary | 239 | 2016 | 1248 | - | - |
| | | | | 2017 | 1382 | 0.05 | 1.05 |
| | | | | 2018 | 1261 | 0.01 | 1.03 |
| | | | | 2019 | 1389 | -0.08 | 0.85 |
| | | | | 2020 | 342.0 | 0.00 | 1.00 |
| 3 | 11AA005 | Milk R at Milk R | 1440 | 2016 | 111.6 | - | - |
| | | | | 2017 | 145.0 | 0.01 | 0.99 |
| | | | | 2018 | 150.8 | -0.04 | 1.04 |
| | | | | 2019 | 153.7 | -0.13 | 1.12 |
| | | | | 2020 | 63.35 | 0.12 | 0.87 |
| 4 | 11AA031 | Milk R at Eastern Crossing of International Boundary | 3793 | 2016 | 47.23 | - | - |
| | | | | 2017 | 58.20 | -0.03 | 1.03 |
| | | | | 2018 | 77.93 | -0.07 | 1.07 |
| | | | | 2019 | 59.35 | -0.13 | 1.13 |
| | | | | 2020 | 27.37 | 0.15 | 0.84 |

Similar limitations were experienced with the water balance component separation analysis as for the IHS baseflow separation: namely there were insufficient data to obtain accurate results for this analysis (note the red values in Table 2, which are physically impossible estimations). Some interesting findings did emerge from this analysis, however, that offer insight to the hydrologic functioning of this basin, and the potential for these methods should a more consistent isotope sampling program be established in the future:

- Transpiration losses likely exceed evaporation in this region
- Evaporation loss is small relative to inflow, indicating these basins are dominate through-flow basins (acting to convey flow, rather than store it)
- The impact of zero-flow diversion in 2020 was detected by the methods:
 - o Insignificant change in WY for basins unaffected by the diversion (11AA025) in 2020
 - o Up to a two-fold decrease in WY or runoff for basins downstream of the diversion (pre- to post-2020)
 - o A reduction in transpiration loss, accompanied by an increase in evaporation loss
- The impact of the diversion is seen on WY estimates at 11AA001, which has a very small drainage area by the highest effective WY estimates. WY can therefore identify and track changes in the amount of diverted water impacting this basin.
- Milk R at Eastern Crossing of International Boundary (11AA031) is particularly responsive to changing meteorologic conditions, with 2016 also being a very low flow year which was detected in the WY estimates, along with zero-flow diversion in 2020.

Summary of existing isotopic datasets

A third objective or deliverable of this work was to

Summarize existing isotopic datasets from WSC, long term regional networks and the USGS that can be leveraged for future studies.

In addition to the longitudinal survey of the Milk River conducted by Water Survey of Canada personnel during zero-diversion flow in 2020 (Figure 6), our team obtained previously sampled isotope data from a variety of sources, summarized here.



Figure 9. WSC longitudinal survey conducted in 2020 during zero-flow diversion along the Milk R.

AITF Innotech: long-term sampling dating back to the late 1980's has been conducted by Innotech Alberta (Calgary office) in this basin and around this basin, with a specific focus on water

chemistry and quality. As part of their sampling protocol, stable water isotopes were sampled within the Milk R basin (Figure 7). These data were shared with our team for the period 2016-2018 and were occasional, opportunistic samples (non-continuous in time). These data were not sampled with an eye on source separation in the Milk River but were used in this study to attempt source separation during time periods where flow was being diverted from the St. Mary's basin.

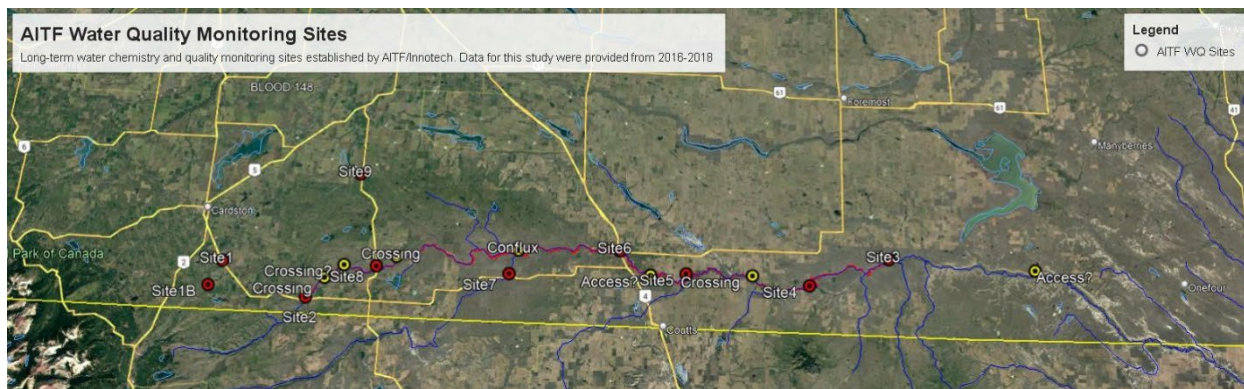


Figure 10. Long-term AITF/Innotech water chemistry and quality monitoring sites where isotope data were obtained from 2016-2018 for this study.

AEP Groundwater: Alberta Environment and Parks (AEP) has been sampling groundwater in this region also since the late 1980's at various Provincial, public and private well sites. In 2020, when the longitudinal survey was being arranged during zero-flow diversion, our team reached out to AEP and asked if they could simultaneously conduct a groundwater survey. Samples were retrieved by AEP personnel and analysed from September and October of 2020 for our source separation analysis (Figure 8).



Figure 11. AEP long-term groundwater monitoring sites within the Milk R basin region that were sampled in 2020 for this study.

We did not locate any nearby isotope in precipitation (USNIP) or isotope in river sampling sites (USGS) with the American network that would be useful for studies in this region. The combination of all data, at all locations, used in our study is provided in Figure 11a, with sample counts for each location provided in Figure 11b.

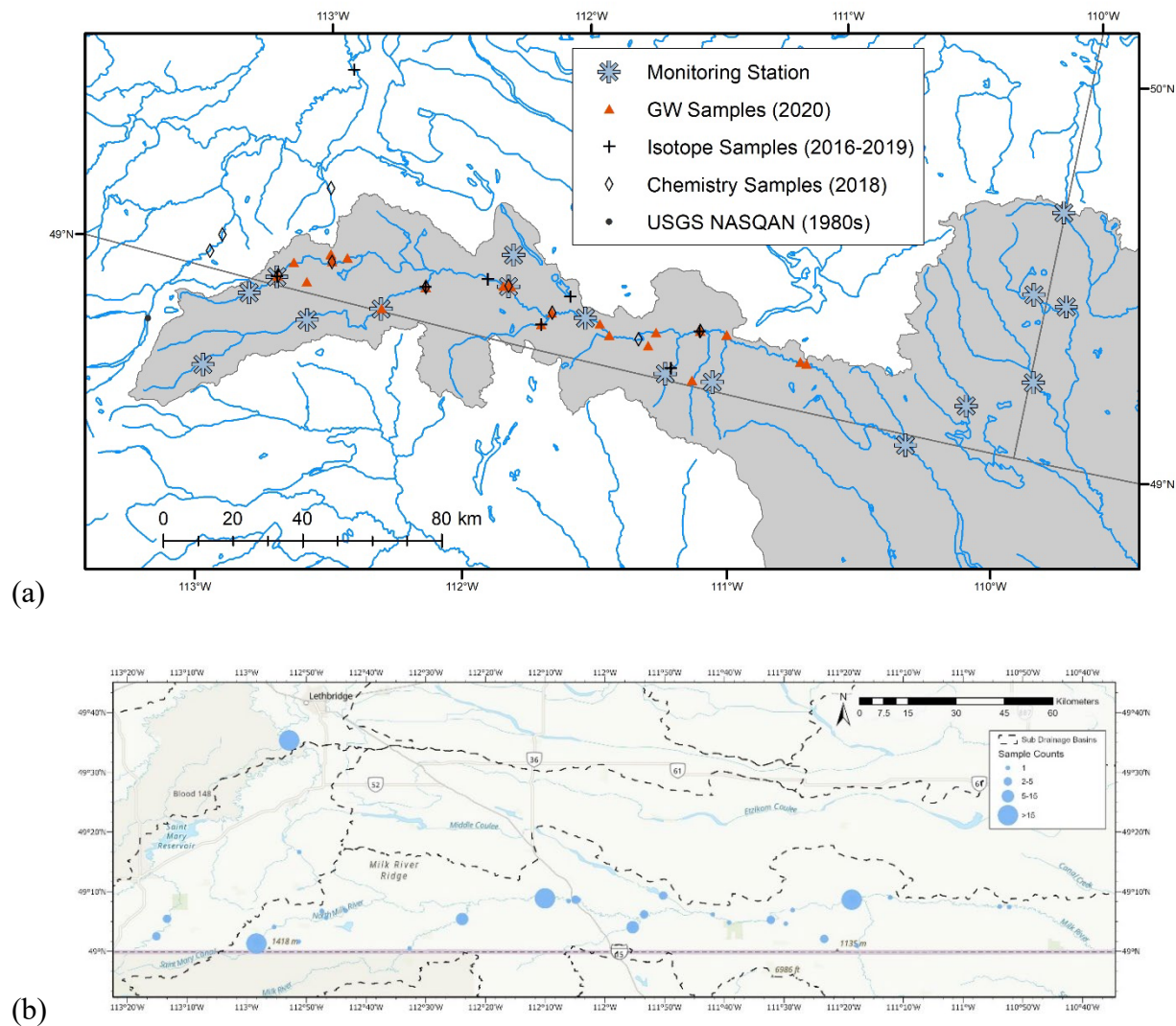


Figure 12. Spatial summary of combined data sources obtained for these analyses: (a) Isotope samples (2016-2018) + Chemistry samples (2018) were retrieved from AITF; GW samples (2020) were collected by AEP partnership during zero-diversion flows; Hydrometric stations were sampled in 2020 by WSC personnel in a longitudinal survey during zero-diversion flow. Panel (b) indicates the sample count used for these analyses at each site.

Design of possible future monitoring

The final deliverable of this study was to

Provide recommendations for the design of an isotopic monitoring program for this system to aide in understanding hydrologic sources and sinks along the Milk River.

An expression of interest to establish a longer-term isotope monitoring network, and to conduct modelling and analysis studies in this region was submitted to the Request for Project Ideas (RFPI) issued by the International Watersheds Initiative (IWI) in February 2022. Our overall recommendations here would guide any future work/studies, and there is sufficient evidence from this study to support on-going isotope monitoring in support of

- Tracking contributions from the St. Mary's and Milk R systems and subsequent downstream mixing.
- Source water separation targeting more informed estimation of evaporation losses.
- Baseflow separation and quantification; and
- Early climate change detection (i.e., a shift in water balance components or component ratios)

Based on the above analyses, results, limitations and findings, the following recommendations are made with regards to a possible future isotope monitoring network:

- Continued and sustained monitoring of isotopes in streamflow for (at a minimum) the basins and gauges identified and used in this study.
- Working in partnership with AEP to collect occasional (i.e., once, or twice a year) samples from two or three local groundwater wells to track changes in groundwater composition.
- Working in partnership with the USGS, establish a long-term CNIP or GNIP rainfall monitoring station to collect water isotopes in rainfall within the Milk and St. Mary's basins
- Temporally consistent sampling of river flows that targets sampling across all seasons.
- Capturing snowmelt-induced high flows, rainfall-driven summer flows, and fall recessions.
- At least one winter ice-on low-flow river sample a year obtained from above and below the diversion to track and identify baseflow compositions

The following sampling resolution is recommended to provide the most complete coverage for IHS and source estimation:

- *Groundwater*: 2 or 3 wells sampled up to 2x per year
- *Precipitation*: 1 rainfall sample per month x 2 stations (one in Canada, one in the US) x 12 months (monthly sample collection). Snow collection will not be necessary.
- *Streamflow*: 4 basins x 1 or 2 streamflow sample/basin/month (during ice-off) x 8 months of the year
- *Baseflow*: 1 ice-on streamflow sample/year in January or February x 4 basins

Table 3 provides an annual cost estimation to implement a long-term isotope monitoring network for the Milk/St. Mary's basins that will inform water balance estimation and potential long-term modelling under climate change.

Table 3. Cost estimate for annual isotope sampling network in the Milk/St. Mary's River basin, assuming a unit cost of sample analyses at \$25/sample for both isotopes.

| No. of Locations | Source | Samples per location per year | Total samples per year | Sub-total |
|-------------------------|---------------|--------------------------------------|-------------------------------|-------------------|
| 2 | Groundwater | 2 | 4 | \$100 |
| 2 | Precipitation | 12 | 24 | \$600 |
| 4 | Streamflow | 12 | 48 | \$1200 |
| 4 | Baseflow | 1 | 4 | \$100 |
| | | | 80 | \$2,000/yr |

Conclusions & Recommendations

Based on the findings reported in this study, we can conclude the following:

1. The St. Mary's and Milk R source waters are isotopically distinct and can be traced using stable water isotope analysis
2. The headwater basin of the Milk R, and the St. Mary's basin, are isotopically similar to meteoric (and groundwater) isotopic compositions and undergo much less evaporation and mixing than downstream tributaries and basins.
3. The Milk R experienced more evaporation in 2020 than in previous years analysed
4. We find groundwater and surface water sources to be isotopically distinct
5. Surface waters were isotopically distinct in 2020, under zero-flow diversion from the St. Mary's basin
6. In 2020, surface water in the Milk R downstream of the diversion underwent significant evaporative enrichment, more than was observed in previous years of record analysed
7. Sufficient isotopic distinction exists between surface and groundwater sources such that isotope hydrograph separation (IHS) is possible to identify time series baseflow contributions
8. There were insufficient isotope data in this study to perform accurate baseflow separations; long-term and more targeted (seasonal and component) monitoring is needed
9. Water Yield water balance estimations were capable of detecting wet/dry cycles and zero-flow diversion differences in basin runoff
10. E/I and T/ET water balance estimations resulted in physically meaningless quantitative estimations as a result of a lack of isotope data available for the basins, specifically the inconsistent nature in the time series of sample collection
11. Water balance estimations revealed that transpiration is more dominant than evaporation loss in this region
12. Despite combining several sources of existing data, the sporadic and discontinuous nature of isotope sampling from 2016-2020 limits the application of analytical modelling to separate and quantify source contributions and water balance components
13. Isotope separations and water balance estimations appear to be promising tracers for this region should an investment in a longer-term isotope monitoring network be made.

The results of this 1-year pilot project, there is sufficient evidence, in our opinion, to justify establishing a long-term isotope monitoring network in the milk/St. Mary's basins to support water balance and hydrologic estimation. Such a monitoring program could be supported by both Water Survey of Canada and USGS hydrometric technicians during their regular site visits to these gauges, by Alberta Environment and Parks for groundwater monitoring, and joint Canada-USA participation in rainfall monitoring. Coupled iso-hydrologic modelling offers the opportunity to gap fill time series of hydrologic analyses, component separations and isotope records, and permits projections under future climate conditions. Furthermore, isotope data can be used to support and improve hydrologic model calibration (Holmes et al., 2020; Stadnyk and Holmes, 2020), which would support identification of climate change projections on water balance in this region to support operational decisions regarding water licencing, diverted flow, and withdrawals.

References

- Benettin, P., Volkmann, T.H.M., Von Freyberg, J., Frentress, J., Penna, D., Dawson, T.E., Kirchner, J.W., 2018. Effects of climatic seasonality on the isotopic composition of evaporating soil waters. *Hydrol. Earth Syst. Sci.* 22, 2881–2890. <https://doi.org/10.5194/HESS-22-2881-2018>
- Delavau, C., Chun, K.P., Stadnyk, T., Birks, S.J., Welker, J.M., 2015. North American precipitation isotope ($\delta^{18}\text{O}$) zones revealed in time series modeling across Canada and northern United States. *Water Resour. Res.* 51, 1284–1299. <https://doi.org/10.1002/2014WR015687>
- Gat, J.R., Mook, W.G., Meijer, H.A., 2001. Environmental isotopes in the hydrologic cycle, principles and applications. Volume II: Atmospheric Water, in: *Environmental Isotopes in the Hydrologic Cycle, Principles and Applications*. IAEA IHP-V, Vienna, AU, p. 167.
- Gibson, J.J., Holmes, T., Stadnyk, T.A., Birks, S.J., Eby, P., Pietroniro, A., 2021. Isotopic constraints on water balance and evapotranspiration partitioning in gauged watersheds across Canada. *J. Hydrol. Reg. Stud.* 37, 100878. <https://doi.org/10.1016/j.ejrh.2021.100878>
- Gibson, J.J., Holmes, T., Stadnyk, T.A., Birks, S.J., Eby, P., Pietroniro, A., 2020. ^{18}O and ^2H in streamflow across Canada. *J. Hydrol. Reg. Stud.* 32, 100754. <https://doi.org/10.1016/j.ejrh.2020.100754>
- Hendry, M.J., Schwartz, F.W., 1991. Hydrogeology and hydrochemistry of the Milk River aquifer system, Alberta, Canada: a review*. *Appl. Geochemistry* 6, 369.
- Holmes, T., Stadnyk, T.A., Kim, S.J., Asadzadeh, M., 2020. Regional Calibration With Isotope Tracers Using a Spatially Distributed Model: A Comparison of Methods. *Water Resour. Res.* 56, e2020WR027447. <https://doi.org/10.1029/2020WR027447>
- Pétre, M.A., Rivera, A., Lefebvre, R., 2015. Three-dimensional unified geological model of the milk river transboundary aquifer (Alberta, Canada – Montana, USA). *Can. J. Earth Sci.* 52, 96–111. <https://doi.org/10.1139/CJES-2014-0079/ASSET/IMAGES/LARGE/CJES-2014-0079F10.JPEG>
- St Amour, 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. Process.* 19, 3357–3381. <https://doi.org/10.1002/hyp.5975>
- Stadnyk, T.A., Holmes, T.L., 2020. On the value of isotope-enabled hydrological model calibration. *Hydrol. Sci. J.* 65, 1525–1538. <https://doi.org/10.1080/02626667.2020.1751847>