Evaluating the sustainable use of groundwater in Alberta: the Milk River aquifer

Project #212201911

Public Final Report

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The success of this project was enabled by diligent contributions of PhD candidate Avadhoot Date at the University of Calgary combined with an excellent collaboration with researchers from the University of Chicago (Dr. R. Yokochi), the University of Delaware (Dr. N. Sturchio), the University of Nevada (Dr. S. Wheatcraft) and the University of Bern in Switzerland (Dr. R. Purtschert), among various others. Financial matching support from the National Science Foundation (NSF) of the USA, the University of Chicago, and the University of Calgary is gratefully acknowledged. Sampling efforts were supported by members of the Milk River Watershed Council and field staff of Alberta Environment and Protected Areas, and we gratefully acknowledge this support.

A. EXECUTIVE SUMMARY

Providing sufficient amounts of high-quality water is of key importance for Alberta's economic future development. In regions of Alberta where surface water is fully allocated, groundwater can be used to supplement water availability, though groundwater source-water sustainability is often unknown. The objective of this project was to use a combination of novel and established groundwater age-dating tools to develop an accurate model of groundwater flow in the Milk River Aquifer (MRA) to determine the sustainable groundwater yield for this aquifer and to assess how groundwater quality in the MRA evolves with groundwater age.

Key results include the following:

^{81}Kr has emerged as an excellent tracer tool for dating of groundwater with mean residence times that are typical for the MRA (<50,000 to >500,000 years).

Groundwater in the areas near Skiff and Foremost, where significant groundwater abstraction from the MRA occurs, has tracer ages between 300,000 and 550,000 years.

FEFLOW finite element modeling indicated that the model-predicted hydraulic groundwater ages of 10 groundwater samples are in very good agreement with the corresponding ^{81}Kr tracer groundwater ages and hence the research project achieved the goal of an age-calibrated refined groundwater flow model for the MRA.

With increasing groundwater age, groundwater quality changes in a predictable fashion, displaying increasing Cl and total dissolved solid concentrations resulting in an increasing salinity of the groundwater. Sulfate concentrations decrease with increasing flow distance due to bacterial sulfate reduction followed by the microbial formation of methane as a result of methanogenesis.

The tracer-calibrated hydrological model revealed that circa one third of the groundwater flowing in the MRA north of the Milk River is derived by groundwater recharge via cross-formational flow through overlying units.

Calculations of sustainable groundwater yield for groundwater wells in the MRA north of the Milk River yielded a median Q_{20} value of 1350 m^3/d.

Key outcomes include a demonstration that ^{81}Kr is a highly suitable tracer for age-dating of old groundwater (<50,000 to >500,000 years). The newly obtained groundwater age data enabled the research team to achieve the goal of an age-calibrated refined groundwater flow model for a considerable portion of the MRA. Model calculations revealed that cross-formational flow through overlying units contributes a significant portion (circa one third) towards the groundwater flow in the MRA north of the Milk River, while groundwater salinity increase in a predictable fashion with increasing groundwater age. The age-calibrated refined groundwater flow model for the MRA also enabled the calculation of sustainable groundwater yields.

The **key benefits** are that the project has increased the understanding of the water sources that supply groundwater to the MRA, provided an estimate of sustainable groundwater yield for the MRA in

southern Alberta, and generated detailed knowledge of how groundwater quality in the MRA evolves with groundwater age. This information will be of benefit for the future use of this important groundwater resource.

B. INTRODUCTION

Sector Introduction: Providing sufficient amounts of high-quality water is of key importance for Alberta's future economic development and a considerable portion of the rural population in Alberta relies on groundwater for domestic and livestock use. Expanding the sustainable use of groundwater is a potential solution for addressing the regional scarcity of sufficient amounts of high-quality freshwater in some regions of Alberta. For example, parts of the South Saskatchewan River Basin (SSRB) are closed to new surface water licence applications and shallow groundwater can be a critical additional water source where high-quality water is available.

Knowledge and Technology Gaps: The Milk River Aquifer (MRA) is a transboundary aquifer, extending over 25,000 km^2 in southern Alberta, Canada, and northern Montana, USA. Intensive exploitation of the MRA in Alberta throughout the 20th century has resulted in a significant drawdown of the groundwater table in the MRA that was subsequently mitigated by better management following the MRA conservation program. However, the water tables remain considerably below the predevelopment condition in some highly exploited regions such as the area near Foremost. Recent research conducted by Petre and co-workers (2019) concluded that the MRA went through the transition from a predevelopment condition to a modern regime where a new sustainable hydrological condition has been attained as a result of reduced surface discharge and an increased cross-formational influx thereby compensating a significant fraction of the historical withdrawal over the past century. However, questions remain since their groundwater flow model remained unconstrained by accurate groundwater age and residence time measurements, while the impact of cross-formational water influx on the quality of groundwater in the MRA was also not fully predicted.

Numerical models of groundwater flow serve as an indispensable tool for a sustainable management of groundwater, but it is important that such models are calibrated using tracer-based information on groundwater residence times that provide unique information on the space- and time-integrated properties of subsurface water flow. Krypton-81 (half-life: 229,000 years, dating range up to 1 million years) is a noble gas radionuclide with an extremely low isotopic abundance (~10^{-12}) produced in the upper atmosphere. Since ^{81}Kr concentrations in rocks are very low compared to those in water, its isotopic abundance is minimally affected by water-rock interaction unlike more commonly used groundwater age tracers such as ^{14}C and ^{36}Cl. Krypton-81 decays at a constant and known rate, constituting an ideal tracer of old groundwater age. Therefore, ^{81}Kr has emerged as a novel and more accurate age-dating tracer where atmospheric Kr is incorporated in groundwater, and subsequently isolated from exchange with the atmosphere. This novel tracer can now routinely be measured owing to the development of the Atom Trap Trace Analysis (ATTA) technique at Argonne National Laboratory. This provided a new opportunity to use the novel groundwater age tracer ^{81}Kr in combination with more established tracer techniques to verify and calibrate an accurate numerical model of groundwater flow for the MRA.

C. PROJECT DESCRIPTION

In regions of Alberta where surface water is fully allocated, the question arises to what extent groundwater can be used to supplement the availability of high-quality water to sustain current and future economic growth. To provide accurate estimates regarding the sustainable yield of high-quality groundwater requires a) the availability of age-calibrated accurate groundwater flow models, and b) a detailed understanding of how groundwater quality evolves with increasing groundwater age. In the past, age-dating especially of old groundwater was mainly based on ^{14}C and ^{36}Cl and was associated with considerable uncertainties due to in-situ production and contamination issues. In consequence of the advent of novel highly sensitive measurement techniques such as atom trap trace analysis (ATTA), ^{81}Kr has recently emerged as a novel and highly accurate age-tracer especially for old groundwater.

The opportunity pursued in this project was to utilize a combination of novel (^{81}Kr) and more established groundwater age-dating tools (e.g., ^{14}C, ^{36}Cl, among others) to refine and calibrate an accurate numerical model of groundwater flow for the Milk River Aquifer (MRA). Application of this novel approach enabled the research team to make critical progress towards reaching two project objectives:
a) to determine the sustainable groundwater yield for the MRA in southern Alberta, and
b) to assess how groundwater quality in the MRA evolves with groundwater age, and in dependence on pumping and potential cross-formational flow.

No adjustments to the project objectives were required.

The performance metrics used to measure the success of this project include the following:
- the number of students trained over the course of the project;
- the number of publications and presentations derived from this project;
- the number of public-facing touch points to ensure knowledge mobilization to the end users;
- the number of trainees working in the sector.

D. METHODOLOGY

Twenty-five high-quality samples were obtained for age-dating of groundwater and chemical, stable isotope, noble gas, and age dating analyses were conducted. Specialized field gas extraction devices and a Kr purification system for large gas quantities were used for collecting samples for radio-krypton dating of groundwater. A 7-collector Noblesse noble gas mass spectrometer (Nu Instruments) was used at the University of Chicago to analyze stable noble gas isotopes, which is essential in accurately interpreting the noble gas radionuclide data. The Atom Trap Trace Analyses (ATTA) instrument at

Argonne National Laboratory led by Dr. Mueller was used to determine ^{81}Kr groundwater tracer ages and low-level counting of ^{39}Ar and ^{36}Cl and determination of ^{14}C contents was conducted at the University of Bern (Switzerland) under the expert guidance by Dr. R. Purtschert.

The chemical compositions of the newly obtained groundwater samples were determined in the Applied Geochemistry group at the University of Calgary using state-of-the-art ion chromatography systems for cation and anion analyses, and an ICP-OES and an ICP-MS system for trace element analyses. Furthermore, the stable isotope compositions of water, nitrate, sulfate, bicarbonate, methane and ethane were determined using gas source isotope ratio mass spectrometry. In addition to the newly collected samples, 1429 groundwater quality records were assembled from various literature sources for interpretation of water quality trends.

The research team under the guidance of Dr. S. Wheatcraft used the FEFLOW finite element software to update the existing steady-state numerical groundwater model (Pétré et al., 2019) using newly acquired data on hydraulic heads and hydraulic conductivity. Numerous simulations using this equivalent porous media (EPM) model were run using a random walk particle tracking algorithm combined with a backward streamline particle tracking method to estimate hydraulic groundwater ages. The new high-quality groundwater age dates enabled the refinement of a groundwater flow model for the Milk River aquifer. In consequence, it was possible to assess how groundwater quality changes with groundwater age.

E. PROJECT RESULTS

During this project, the research team pursued 6 specific tasks with the following outcomes and key results:

Task 1: During several field sampling campaigns between 2021 and 2023, the research team, in some cases with help from staff of Alberta Environment and Protected Areas (AEPA), obtained 25 high-quality groundwater samples from wells completed in the Milk River aquifer (MRA) for water quality and age dating analyses. In addition, several surface water samples were obtained for water quality analyses. Field parameters were determined for all samples, and upon return to the laboratory, the concentrations of major cations and anions and minor ions were analyzed. This information was used to calculate total dissolved solids contents (TDS) and salinities and to determine water types and redox state of the obtained groundwater samples. In addition, the stable isotope compositions of water (H and O), dissolved inorganic carbon (C), and sulfate (S and O) were determined. Except for two samples, all obtained groundwaters contained some methane with C isotope ratios (expressed as $\delta^{13}C$ values) mostly between -57 and -76 ‰, and H isotope ratios ($\delta^{2}H$) between -168 and -312 ‰, consistent with a microbial methane source and highly reducing conditions in the aquifer facilitating methanogenesis.

In addition to the newly obtained samples, the research team accessed publicly available water quality records for groundwater and surface water samples, conducted a careful QA/QC screening, and for groundwater samples used well logging information to assign the aquifers in which the wells are completed. This resulted in 1429 additional groundwater samples from the MRA with high-quality aqueous geochemistry information, and 76 surface water samples from rivers, lakes and springs above the MRA with water quality information available for interpretation. In addition, data were obtained from various sources to construct hydraulic head contour maps and maps of transmissivity in the MRA. Figure 1 displays a map of hydraulic heads identifying recharge zones in the Sweet Grass Hills of Montana, and lowest hydraulic heads observed towards the northern edge of the MRA area confirming previously identified major groundwater flow paths in the MRA (Fig. 1 blue arrows) with some minor modifications (Fig. 1 green arrows).

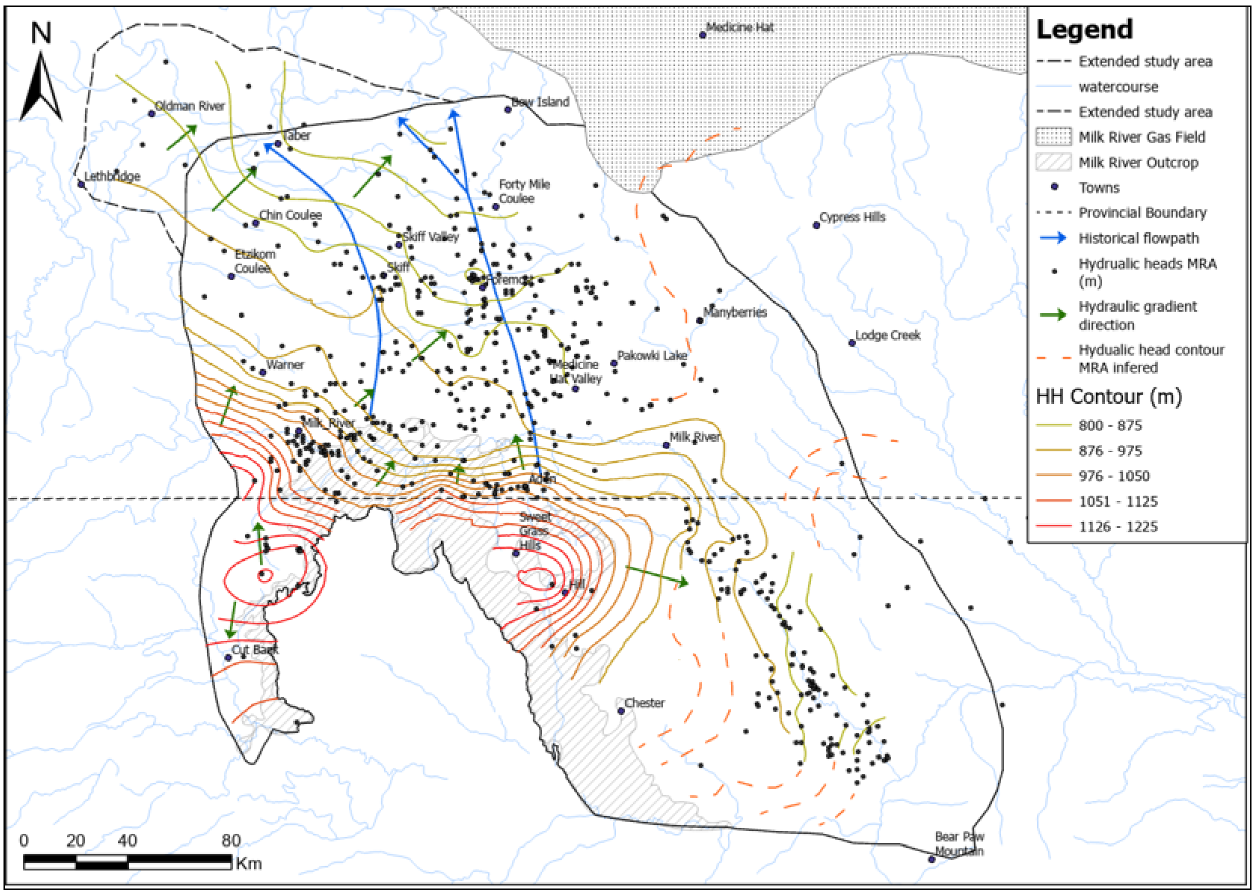

Figure 1: Potentiometric surface map for MRA groundwater with hydraulic head data depicted in meters and 50 m contour intervals.

One focus of the water quality data evaluation was on the distribution of chloride concentrations in groundwater of the MRA. Figure 2 reveals that chloride concentrations in groundwater close to the recharge areas near the Montana – Alberta border were typically < 25 mg/L. With increasing flow distance, concentrations of chloride increase progressively to levels of up to 150 mg/L in the areas near Foremost (Fig. 2). Much higher Cl concentrations reaching values >750 mg/L were only observed towards the northern border of the MRA (Fig. 2). This observation, in concert with various other water quality parameters and the isotopic composition of water (δ^2H and $\delta^{18}O$) suggest that freshwater that recharges the MRA progressively acquires increasing salinity (e.g., via diffusive exchange or possibly mixing) along the various flow paths. Towards the northern edge of the MRA, water-rock interactions and mixing with highly saline fluids causes a marked increase in salinity of the groundwater. Investigation of other water quality parameters reveals that groundwater flowing through the MRA becomes progressively reducing progressing towards regions where bacterial sulfate reduction and methanogenesis occur.

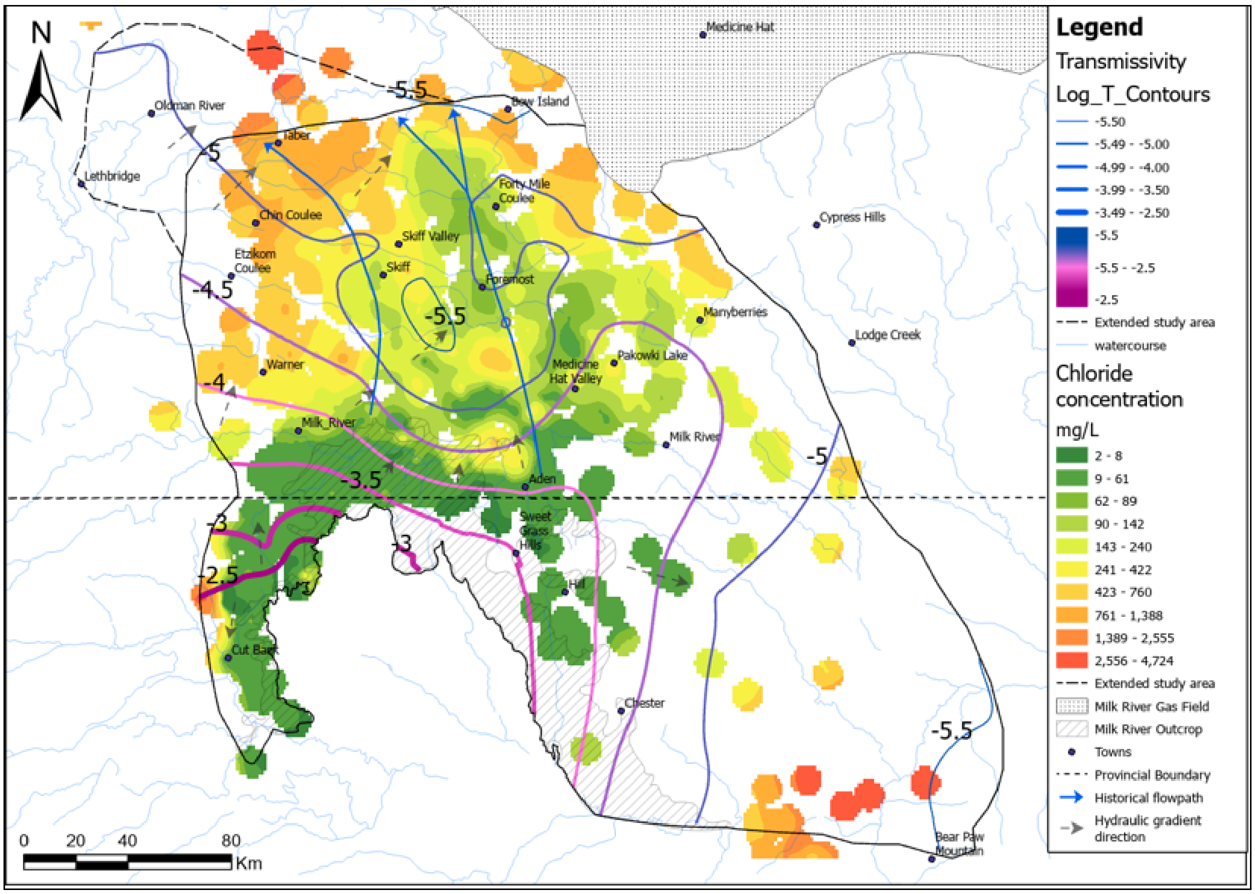

Figure 2: Map of chloride concentrations in groundwater of the MRA displaying increasing chloride concentrations along the groundwater flow paths.

Task 2: Age dating measurements of newly obtained groundwater samples included the following:

- ^{81}Kr measurements for 18 samples yielding groundwater tracer ages of up to 700,000 years,
- ^{36}Cl measurements for 22 samples,
- ^{14}C measurements for 21 samples, with 5 samples yielding groundwater ages of up to 36,000 years. The remaining 16 samples had ^{14}C abundances of < 1% modern carbon, and hence groundwater tracer ages > 40,000 years; and

- ^{85}Kr and $^{234/238}$U, $^{235/238}$U, ^{222}Rn and ^{232}Th measurements on select groundwater samples.

Using the newly obtained ^{81}Kr, ^{36}Cl and ^{14}C data enabled the research team to constrain the groundwater ages across wide regions of the Milk River Aquifer (MRA) in Alberta in unprecedented detail. Figure 3 shows the distribution of the newly obtained ^{81}Kr tracer ages of groundwater in the MRA. Figure 3 reveals that groundwater tracer ages are consistently below 65,000 years in the southern part of the Alberta portion of the MRA that is closest to the recharge area. With increasing flow distance towards the central and northern portions of the MRA in Alberta, groundwater tracer ages increase toward 544,000 years with one sample displaying a groundwater age of 708,000 years. These novel results confirm that groundwater ages progressively increase from the recharge area in the south towards the northern extent of the MRA in southern Alberta and provide unprecedented insights into the progressively increasing groundwater ages with flow distance within the MRA. In consequence, the novel tracer tools enabled for the first time an assessment of the approximate groundwater ages in select areas of the MRA. For instance, Figure 3 reveals that groundwater in the areas near Skiff and Foremost, where significant groundwater abstraction from the MRA occurs, has tracer ages between 240,000 and 550,000 years.

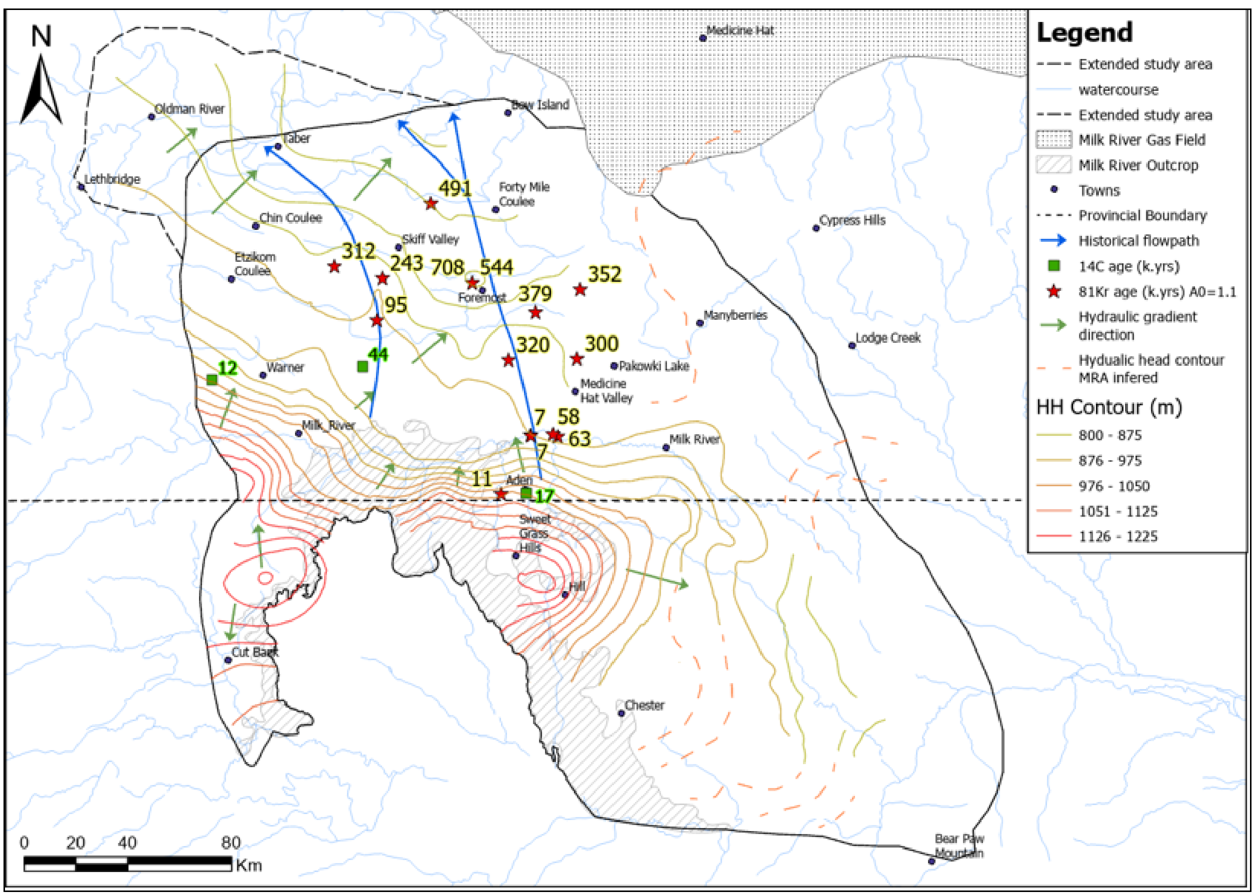

Figure 3. Map of the Milk River Aquifer depicting ^{81}Kr tracer groundwater ages (red stars; in k years; e.g. 312 = 312,000 years) for 14 locations assuming an initial ^{81}Kr/Kr ratio of 1.1 times the

atmospheric ratio. ^{14}C derived groundwater ages are shown for three locations (green squares) where groundwater is too young for accurate age dating with ^{81}Kr.

Task 3: The research team also investigated water quality in surface waters including lakes, rivers and springs in the area above the MRA. This included samples from Pakowki Lake, the Milk River, and data for 71 spring waters to assess the aqueous geochemistry of groundwater discharging to the surface environment. Figure 4 reveals that the highest chloride concentrations ranging between 162 and 245 mg/L in these surface water samples were observed in the north-western part of the MRA area near the town of Taber, while chloride concentrations in MRA groundwater in this area are one order of magnitude higher ranging from 1,395 to 2,555 mg/L. Also, it was found that dissolved sulfate was a key contributor to the total dissolved solids (TDS) of surface water samples in this area often with concentrations in excess of 1,000 mg/L, while sulfate concentrations in the groundwater of the underlying MRA are often low since bacterial sulfate reduction has occurred. These data do not provide strong evidence for cross-formational flow from deeper aquifers towards the surface in this part of the MRA.

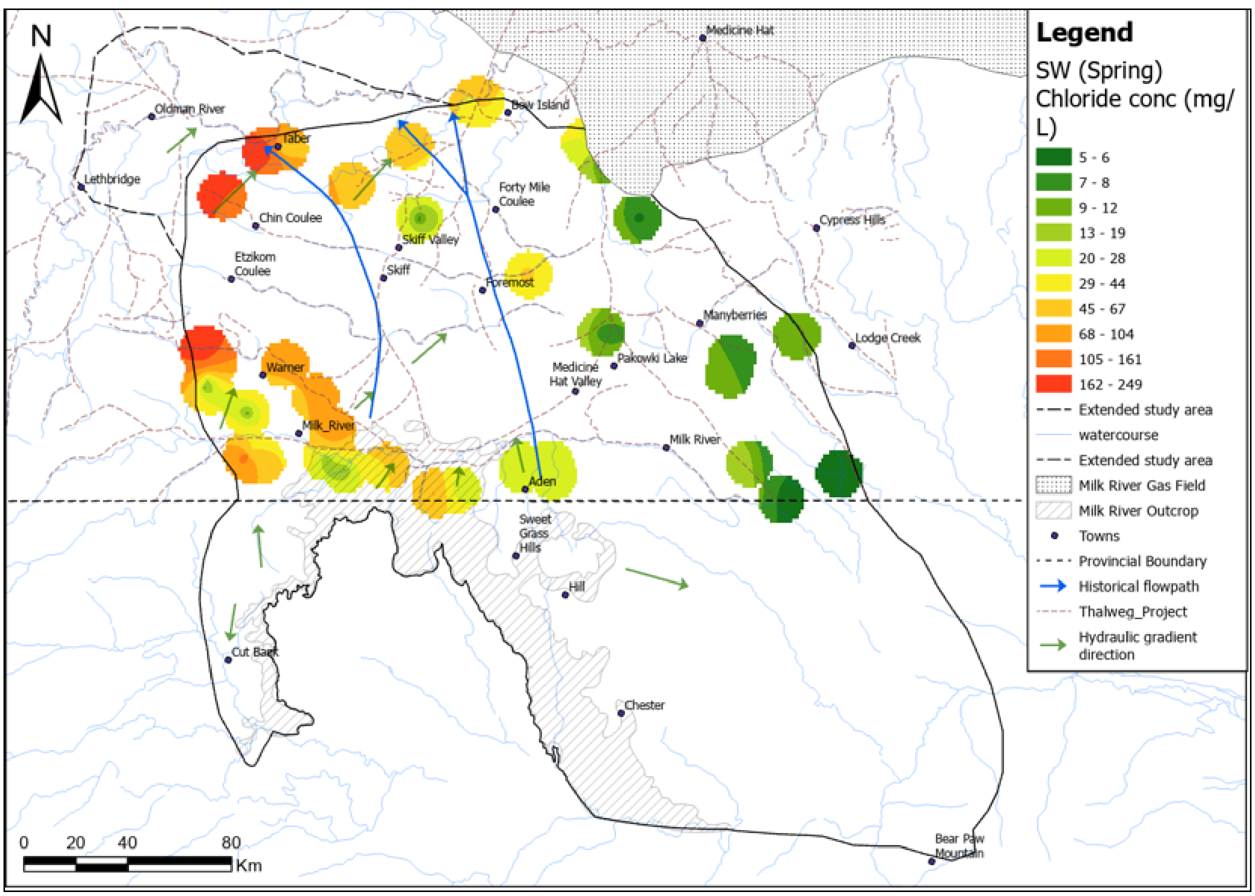

Figure 4: Map showing the chloride concentrations of 71 spring samples in the study area of the Milk River aquifer (MRA).

In **Task 4** the research team used the FEFLOW finite element software to update the existing steady-state numerical groundwater model (Pétré et al., 2019) using newly acquired data on hydraulic heads and hydraulic conductivity. Numerous simulations using this equivalent porous media (EPM) model were run using a random walk particle tracking (RWPT) algorithm along with a backward streamline particle tracking method to estimate hydraulic groundwater ages. Particle seeds were positioned at sample locations where groundwater tracer ages were available as shown in Figure 3. Figure 5 shows one example for sample ETZ located in the town of Etzikom, which is 11 km northwest of Pakowki Lake. The determined hydraulic model age for this groundwater sample flowing from A to A’ in Figure 5 is 341,000 years, which is in excellent agreement with the ^{81}Kr apparent tracer age of 352,000 years.

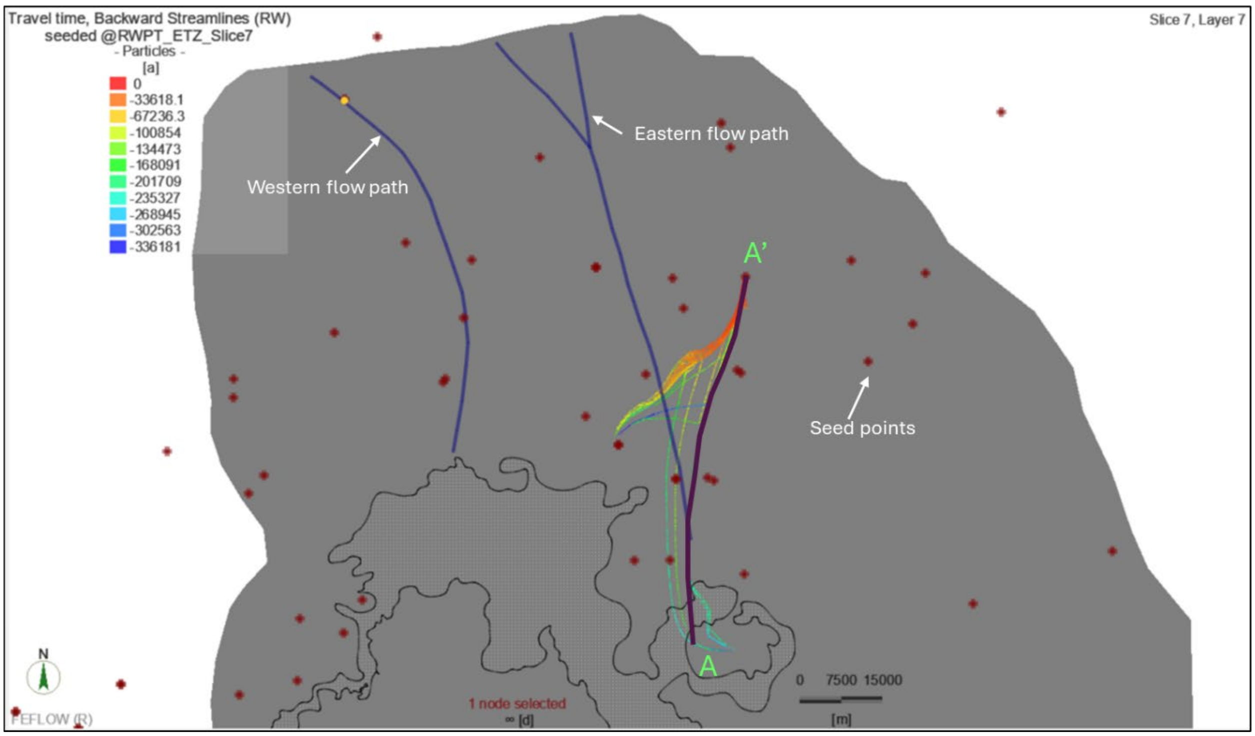

Figure 5: Map of MRA showing a backward streamline produced using the random walk particle tracking (RWPT) algorithm for the steady state numerical flow model. The seed point is sample ETZ whose hydraulic model age is 341,000 years. This hydraulic model age is in excellent agreement with the ^{81}Kr apparent tracer age of 352,000 years.

Initial simulations using the FEFLOW finite element software indicated that the model-predicted groundwater ages predominantly range from 50,000 to 700,000 years. To improve the agreement of the initial hydraulic groundwater ages with the measured ^{81}Kr tracer ages for groundwater, the hydraulic conductivity values of the existing steady-state numerical groundwater model (Pétré et al., 2019) were multiplied by a factor of two (on average 3.4×10^{-6} m/s). Additionally, a sensitivity analysis was conducted to assess the influence of porosity on the estimated hydraulic groundwater ages. Several simulations were conducted, where the effective porosity was increased in steps of 0.04, starting from the initial porosity of 0.10 up to a maximum of 0.30. It was observed that increasing effective porosity led to a decrease in seepage velocity, which, in turn, increased the model-predicted groundwater ages. A similar exercise was performed on a modified model with an average hydraulic conductivity of 3.4 x 10^{-6} m/s. Increasing the effective porosity also resulted in higher model-predicted groundwater ages. Based on these observations, it was decided to run the particle tracking algorithm using the initial effective porosity of 0.10. Further research is required to assess the effects of changing vertical anisotropy, longitudinal dispersivity, and transverse dispersivity in the aquitards including the Pakowki Formation and the upper part of the Colorado Shale on the model-predicted groundwater ages.

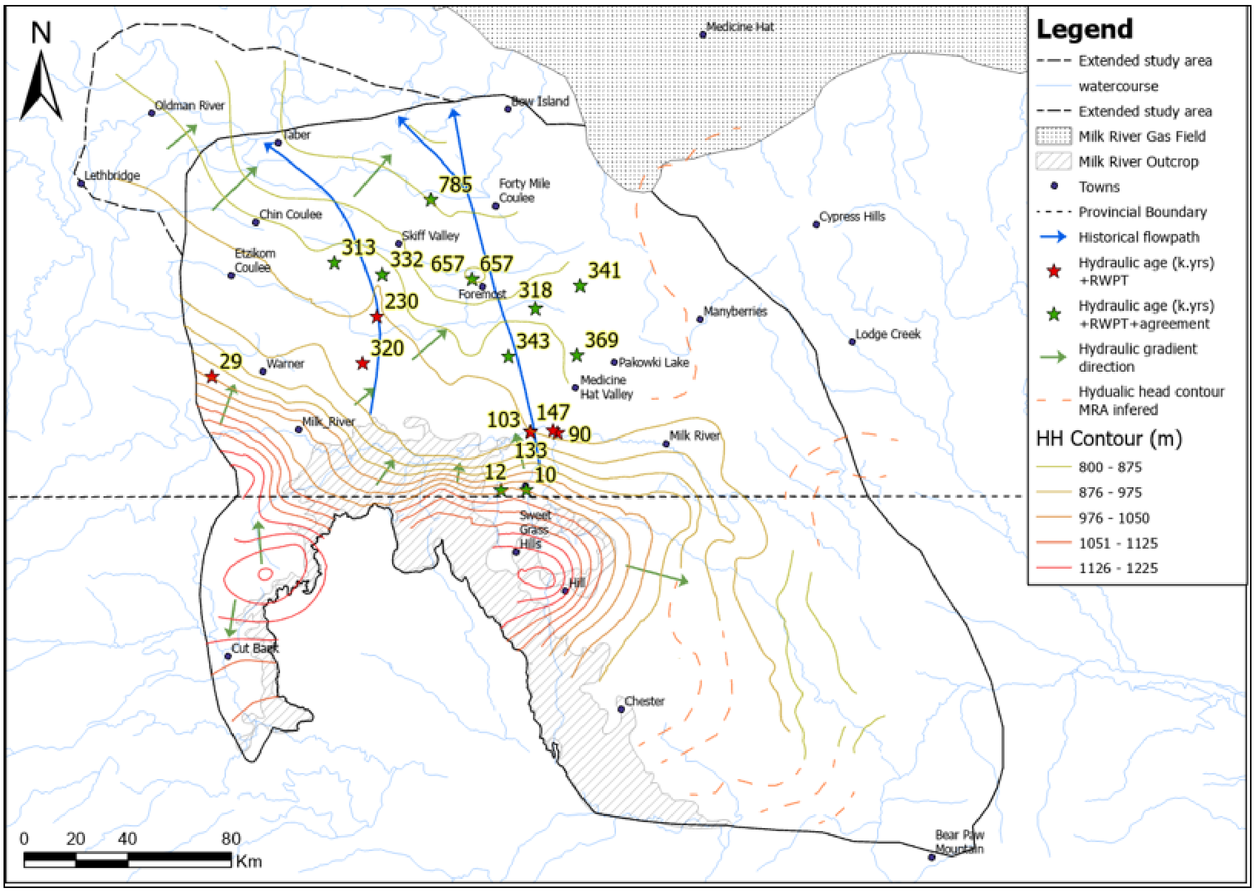

Figure 6. Map of the Milk River Aquifer depicting hydraulic groundwater ages (k years) for 14 sampling locations. Green stars (n=10) represent those sampling locations where hydraulic groundwater ages are in good agreement with apparent ^{81}Kr tracer ages. At locations indicated by red stars, marked discrepancies were observed between hydraulic groundwater ages and apparent ^{81}Kr tracer ages. RWPT = Random Walk Particle Tracking.

Figure 6 shows the hydraulic groundwater ages based on the revised groundwater model data. It was found that the hydraulic ages of 10 groundwater samples are in good agreement with the corresponding ^{81}Kr tracer groundwater ages. In this region, the research project achieved the goal of an age-calibrated refined groundwater flow model for the MRA. However, hydraulic model ages for three samples located within 20 km of the recharge zone are much older than the respective ^{81}Kr tracer ages. All three sampling locations are located near the Milk River and hence active surface water - groundwater interaction appears to be a cause for the observed disagreement at these three sites. The potential presence of secondary porosity, particularly fracture porosity, is an alternate potential explanation for the observed discrepancy that should be further explored especially where fractured bedrock is present.

Model-predicted groundwater ages on the northern edge of the MRA range from 500,000 to 700,000 years. In this area, the aquifer thickness decreases, and the aquifer dips to the north, where groundwater wells are completed at increasing depths. This suggests that groundwater flow velocities are very low, resulting in very old groundwater towards the northern boundary of the MRA.

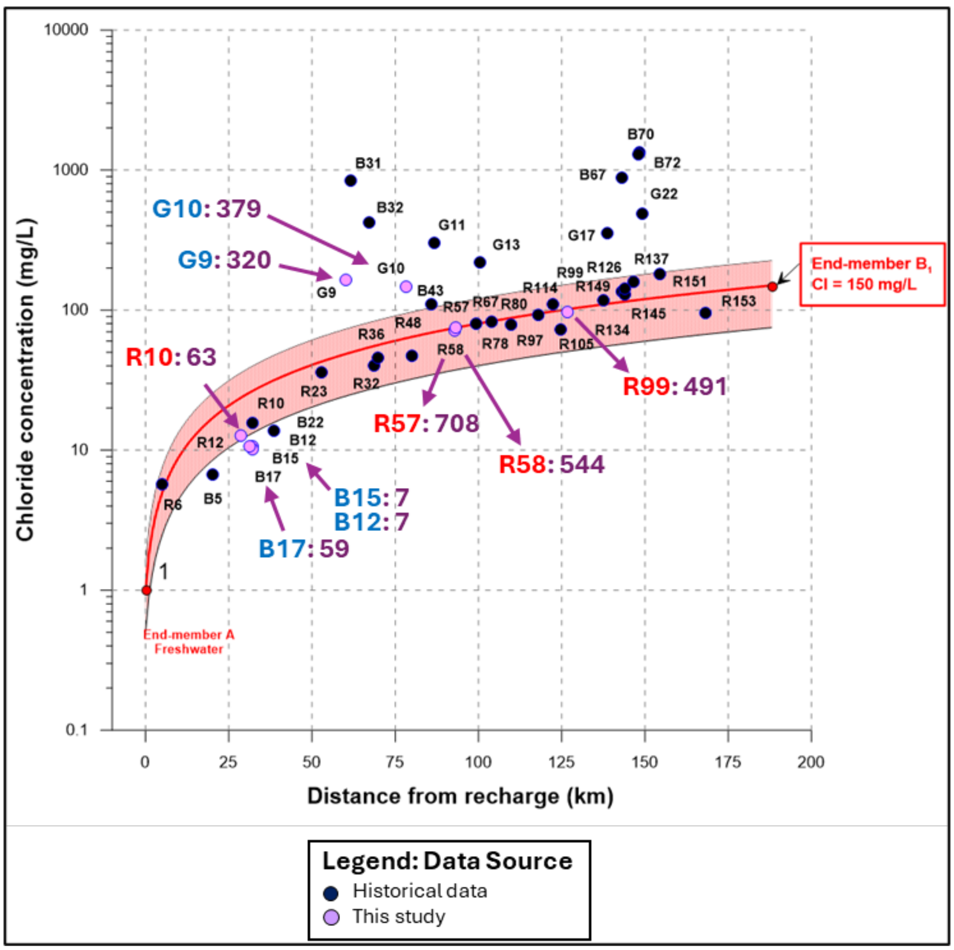

Figure 7. Chloride concentrations in groundwater with distance from the recharge zone along the eastern flow path. Samples with ^{81}Kr apparent groundwater ages (shown as purple numbers in k years) are marked using arrows.

Using the age-calibrated refined groundwater flow model, the research team was for the first time able to constrain how groundwater chemistry changes with groundwater age in the MRA. Figure 7 reveals that the majority of groundwater samples from the MRA plot on a curved trend with chloride concentrations of <10 mg/L near the recharge area and Cl concentrations progressively increasing with distance towards an endmember with a Cl concentration of 150 mg/L. Chloride concentrations were consistently < 20 mg/L in groundwater samples that were less than 100,000 years old. Groundwater with tracer ages approaching 500,000 years progressed towards Cl concentrations of 100 mg/L or more. Such a trend can be explained either by (a) mixing of recharged groundwater with increasing proportions of a brackish water from incomplete flushing of formation fluids, (b) input of chloride via diffusion from shale layers within the MRA, c) input of chloride via cross-formational flow through overlying and underlying aquitards, or (d) a combination of the above options.

There are six samples shown in Figure 7 that reveal anomalously high concentrations of chloride at distances between 60 and 100 km from the recharge zone. Water flux rate budget calculations indicate a water influx to the MRA from the aquitards above (Pakowki Formation) for four samples and from below (Colorado Shale) for two samples at these sampling locations. Calculations from the steady-state numerical model suggest that the net water inflow (flux) ranges from 0.1 to 3.5 m^3/d at these six locations and the major proportion of net influx is due to flow from the overlying Pakowki Formation into the porous media of the MRA. In contrast, the Colorado Shale acts predominantly as a sink, with net water flux directed from the MRA into the underlying aquitard. Vertical hydraulic gradient calculations also indicate that there is a net water influx from the MRA into the Colorado Shale.

Figure 7 also displays five samples with elevated chloride concentrations at the distal end of the MRA. Using a steady-state numerical flow model, net water flux (m^3/d) calculations were performed for all five samples. The results indicate water inflow from the overlying Pakowki Shale into the porous media of the MRA (net inflow fluxes < 1 m^3/d). Additionally, it was observed that there is a net outflow of groundwater from the MRA into the Colorado Shale, which acts as a sink. Previous calculations of vertical hydraulic gradients between the MRA and Colorado Shale also suggest that there is a net water flux from the MRA into the underlying aquitard.

In **Task 5**, the research team used the tracer-calibrated hydrological flow model in an attempt to estimate the sustainable yield of the MRA. Figure 8 displays a summary of the estimated water budget for the MRA according to the age-calibrated groundwater flow model used in this study. Recharge zones are primarily located in the Sweet Grass Hills of Montana enabling a recharge rate of approximately 17,000 m^3/day into the unconfined portions of the MRA where mean residence times of groundwater are <50,000 years. A considerable portion of this recharged water (circa 88%) subsequently discharges to the Milk River and other surface waters in the southern part of the Alberta portion of the MRA. The remaining recharged water, circa 2,100 m^3/d, sustains the flow in the confined portion of the MRA north of the Milk River, where groundwater ages vary from 50,000 to >500,000 years. Furthermore, this study found that the MRA is supplied in this area by additional groundwater input via cross-formational flow through overlying units of circa 1,200 m^3/d (Fig. 8), constituting approximately 37% of recharge to the aquifer. Model calculations also revealed that some MRA water (up to 500 m^3/d) is lost to underlying aquitard formations. Considering these refined water flux data obtained through the age-calibrated groundwater flow model, it is estimated that the current net groundwater influx to the region of the MRA located north of the Milk River totals approximately 2750 m^3/d.

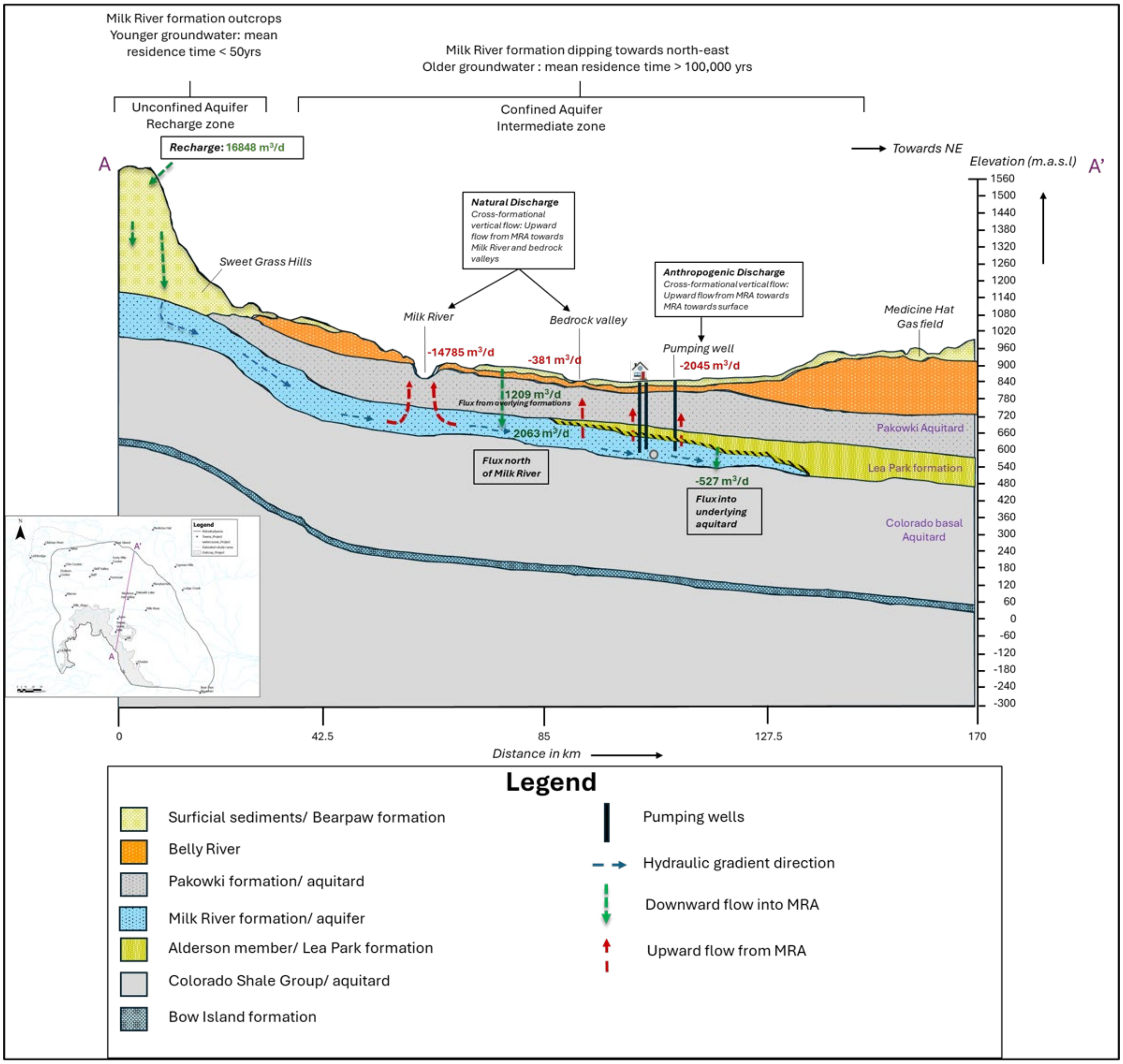

Figure 8. Schematic cross section summarizing water budget results obtained from the age-calibrated groundwater flow model used in this study.

Calculations of sustainable groundwater yield were conducted using the method by Farvolden (1959) as recommended by the Alberta Energy Regulator (AER) using available transmissivity data and head data calculated as potentiometric elevation minus top of the well screen elevations for different zones of the MRA. For the three zones containing the majority of the groundwater wells in the MRA north of the Milk River, calculated median Q_{20} values ranged from 220 to 550 m^3/d, while the cumulative median Q_{20} value for all six zones north of the Milk River was estimated at 1350 m^3/d. This value is approximately 33% lower than the anthropogenic discharge through groundwater pumping that was estimated by Pétré et al. (2016) indicating that there are limitations for additional groundwater abstraction from the MRA according to current model estimates.

Task 6 was to assess the transferability of the approach tested in this project for the MRA to other aquifers in Alberta. It was demonstrated that the novel ^{81}Kr age dating approach combined with more established groundwater age dating tools (e.g., ^{14}C, ^{36}Cl) allows for the first time an assessment of groundwater tracer ages that range from less than 100,000 to more than 500,000 years. These groundwater age dates are of importance for refining and calibrating numerical models of groundwater flow for confined aquifers. This in turn is of key importance for estimating sustainable groundwater yields and for determining how groundwater quality evolves with groundwater age, and in dependence on pumping and cross-formational flow. Therefore, the novel approaches utilized in this project are transferrable to other confined aquifers in the province (and elsewhere) for which detailed geological and hydrogeological information exists, that contain groundwater in excess of 50,000 years and have sufficient well access to sample the groundwater for age-dating and water quality assessment purposes.

References:

Farvolden, R.N. (1959): Groundwater supply in Alberta. Alberta Research Council, unpublished report, 12 pp.

Pétré, M.-A., Rivera, A., Lefebvre, R., Hendry, M. J., & Folnagy, A. J. (2016). A unified hydrogeological conceptual model of the Milk River transboundary aquifer, traversing Alberta (Canada) and Montana (USA). *Hydrogeology Journal*, *24*(7), 1847-1871.

Pétré, M.-A., Rivera A. & Lefebvre R. (2019): Numerical modeling of a regional groundwater flow system to assess groundwater storage loss, capture and sustainable exploitation of the transboundary Milk River Aquifer (Canada–USA). *Journal of Hydrology* 575 (2019): 656-670.

F. KEY LEARNINGS

The key learnings from this project were:

^{81}Kr has emerged as an excellent tracer tool for dating of groundwater with mean residence times that are typical for the MRA and range from less than 50,000 to more than 500,000 years.

Groundwater in the areas near Skiff and Foremost, where significant groundwater abstraction from the MRA occurs, has tracer ages between 300,000 and 550,000 years.

FEFLOW finite element modeling indicated that the model-predicted hydraulic groundwater ages of 10 groundwater samples are in very good agreement with the corresponding ^{81}Kr tracer groundwater ages and hence the research project achieved the goal of an age-calibrated refined groundwater flow model for the MRA.

With increasing groundwater age, groundwater quality changes in a predictable fashion, displaying increasing Cl and total dissolved solids concentrations resulting in an increasing salinity of the groundwater. Sulfate concentrations decrease with increasing flow distance due to bacterial sulfate reduction followed by the microbial formation of methane as a result of methanogenesis.

The tracer-calibrated hydrological model revealed that circa one third of the groundwater flowing in the MRA north of the Milk River is derived from groundwater recharge via cross-formational flow through overlying units.

Calculations of sustainable groundwater yield for groundwater wells in the MRA north of the Milk River yielded a median Q_{20} value of 1350 m^3/d.

G. OUTCOMES AND IMPACTS

The project demonstrated that ^{81}Kr is a highly suitable tracer for age-dating of old groundwater (<50,000 to >500,000 years). The newly obtained groundwater age data enabled the research team to achieve the goal of an age-calibrated refined groundwater flow model for a considerable portion of the MRA. Model calculations revealed that cross-formational flow through overlying units contributes a significant portion (circa one third) towards the groundwater flow in the MRA north of the Milk River, while groundwater salinity increases in a predictable fashion with increasing groundwater age. The age-calibrated refined groundwater flow model for the MRA also enabled the calculation of sustainable groundwater yields.

The key benefits are that the project has increased the understanding of the water sources that supply groundwater to the MRA. An estimate of sustainable groundwater yield was obtained for the MRA in southern Alberta, and detailed knowledge of how groundwater quality in the MRA evolves with groundwater age was obtained. This information will be of benefit for the future use of this important groundwater resource.

The project achieved for the most part the predicted project metrics. At the University of Calgary, two PhD students, one part-time postdoctoral fellow, and one part-time research associate were trained and contributed major scientific insights to this project. Several conference presentations were given or are scheduled at major international conferences including the following:

Mayer, B., Thistle, S., Plata, I., Humez, P., Date, A., Nightingale, M., Kim, J.-H., Purtschert, R., Musy, S., Duran, N., Yokochi, R., McClain, C. & Ligget, J. (2023): Understanding the regional occurrence of select groundwater contaminants based on novel and established tracer measurements in age-dated groundwater samples in Alberta, Canada. – 2023 Goldschmidt Conference, Lyon, France, July 9-14, 2023.

Purtschert, R. and Musy, S., (2024): The use of radio-noble gases ^{39}Ar and ^{81}Kr in hydrological science: Accomplishments and puzzling inquiries. Goldschmidt 2024, August 18-23, 2024, Chicago, Illinois, USA.

Date, A. V., B. Mayer, P. Humez, M. Nightingale, P. Mueller, M. Bishof, J Lantis, C. Vockenhuber, J. Corcho, R. Purtschert, R. Yokochi, N. Sturchio, P. Abdrakhimova, S. Wheatcraft (2024): Evaluation of changes in groundwater quality in dependence of flow path and groundwater age in the Milk River Aquifer. – AGU Fall Meeting, December 9-13, 2024, Washington, USA.

In the next 12 months, the research team plans the publication of three peer-reviewed papers in international peer-reviewed scientific journals.

H. RECOMMENDATIONS AND NEXT STEPS

The research team used the FEFLOW finite element software to update a previous steady-state numerical groundwater model (Pétré et al., 2019). This product is an equivalent porous media (EPM) model. While it was determined that hydraulic groundwater ages in some regions of the MRA were in good agreement with the corresponding ^{81}Kr tracer groundwater ages, significant discrepancies were observed in some other portions of the MRA. This raises the question to what extent fracture porosity and groundwater flow through fractures contributes to groundwater flow in some portions of the MRA, especially where fractured bedrock is present? Hence, it is recommended to investigate the role of fracture flow in the MRA in more detail in the near future. If fracture-based groundwater flow is found to play a significant role in portions of the MRA, it will be of key importance to expand the current version of the groundwater flow model, that is solely based on equivalent porous media (EPM), with a fracture flow component.

I. KNOWLEDGE DISSEMINATION

Knowledge mobilization occurred via several presentations to stakeholders including the following:

Mayer, B.: Groundwater quality in Alberta and the impact of agricultural activities. – Presentation given to members of the Alberta Institute of Agrologists, April 28, 2022.

Mayer, B.: Occurrence, sources, and fate of select groundwater contaminants in Alberta. – Seminar presentation given to staff members of Alberta Environment and Protected Areas, April 20, 2023.

Mayer et al.: Determining the sources of contaminants and the age of groundwater in Alberta's aquifers using isotope techniques. – Alberta Innovates Water Innovation Series: Using isotopes to study climate-related changes in our water resources, October 17, 2023.

J. CONCLUSIONS

Providing sufficient amounts of high-quality water is of key importance for Alberta's economic future development. In regions of Alberta where surface water is fully allocated, groundwater can be used to supplement water availability, though groundwater source-water sustainability is often unknown. The objective of this project was to use a combination of novel and established groundwater age-dating tools to develop an accurate model of groundwater flow in the Milk River Aquifer (MRA) to determine the sustainable groundwater yield for this aquifer and to assess how groundwater quality in the MRA evolves with groundwater age.

Key results include the following:

^{81}Kr has emerged as an excellent tracer tool for dating of groundwater with mean residence times that are typical for the MRA ranging from less than 50,000 to more than 500,000 years.

FEFLOW finite element modeling indicated that the model-predicted hydraulic groundwater ages in parts of the MRA are in very good agreement with the corresponding ^{81}Kr tracer groundwater ages and hence the research project achieved the goal of an age-calibrated refined groundwater flow model.

With increasing groundwater age, groundwater quality changes in a predictable fashion, displaying increasing Cl and total dissolved solids concentrations resulting in an increasing salinity of the groundwater.

The tracer-calibrated hydrological model revealed that circa one third of the groundwater flowing in the MRA north of the Milk River is derived by groundwater recharge via cross-formational flow through overlying units.

Calculations of sustainable groundwater yield for groundwater wells in the MRA north of the Milk River yielded a median Q_{20} value of 1350 m^3/d.

Key outcomes include a demonstration that ^{81}Kr is a highly suitable tracer for age-dating of old groundwater (<50,000 to >500,000 years). The newly obtained groundwater age data enabled the research team to achieve the goal of an age-calibrated refined groundwater flow model for a considerable portion of the MRA. Model calculations revealed that cross-formational flow through overlying units contributes a significant portion (circa one third) towards the groundwater flow in the MRA north of the Milk River, while groundwater salinity increase in a predictable fashion with increasing groundwater age. The age-calibrated refined groundwater flow model for the MRA also enabled the calculation of sustainable groundwater yields.

Next steps should include a more detailed investigation of the role of fracture flow in the MRA.

The **key benefits** of the project are an increased understanding of the water sources that supply groundwater to the MRA, an estimate of sustainable groundwater yield for the MRA in southern

Alberta, and detailed knowledge of how groundwater quality in the MRA evolves with groundwater age. This information will be of benefit for the future use of this important groundwater resource.