Groundwater Ages in Intertill and Buried Valley Aquifers in Saskatchewan, Canada

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Abstract

paleohydrogeology, glacial terrain, stable isotopes, radiogenic isotopes, dating techniques

Article Impact Statement

Shallow confined aquifers in Saskatchewan, Canada were recharged over a spectrum of times from late Pleistocene to present.

ABSTRACT

Continental glaciations during the Pleistocene Epoch created complex systems of aquifers and aquitards across many northern regions of the Earth. The low hydraulic conductivities of glacial till aquitards suggest that limited recharge will reach the underlying aquifers, potentially preserving old groundwaters. Here, we characterize the recharge history in intertill and buried valley aquifers in Saskatchewan, Canada using ^{14}C, ^{3}H, ^{4}He $\delta^{2}H$, $\delta^{18}O$ and major ions. Intertill aquifers with depths of <30 m had corrected ^{14}C ages ranging from 0 to 15.5 ka. These aquifers also contained ^{3}H and/or elevated NO_3 in some locations, indicating that a component of modern recharge had mixed with older water. A single sample from the Judith River bedrock aquifer in the region had a corrected ^{14}C age of 10.2 ka and elevated NO_3. Samples from buried valley aquifers with depths of 89 to 123 m contained older waters with ages >38 ka in some locations, indicating that recharge occurred before the last glacial advance over the region . While measuring tracers that cover a wide range of ages is necessary to understand these flow systems, $\delta^{2}H$ and $\delta^{18}O$ were less diagnostic because values of modern winter precipitation overlapped with groundwaters with a wide range of ages. The range of ages present in the intertill aquifers of the region indicate that these systems are currently being recharged, which indicates some development of groundwater resources is possible but also points to a need for groundwater protection measures.

INTRODUCTION

The bulk of the Earth's fresh groundwater is fossil (>12,000 years old) (Gleeson et al. 2016) and there has been debate about how strongly these waters are connected to the rest of the hydrologic cycle (Bierkens and Wada 2019; Cuthbert et al. 2023; Edmunds 2003; Ferguson et al. 2020; Margat et al. 2006). During Pleistocene glaciations, low permeability sediments (aquitards) were deposited in many regions, restricting the amount of recharge reaching underlying aquifers (Hendry et al. 2005; Ferris et al. 2020; Keller et al. 1988; van der Kamp 2001; Rodvang and Simpkins 2001; Gerber and Howard 1996). Glaciated areas also experienced large shifts in hydrologic boundary conditions with the advance and retreat of continental ice sheets (Lemieux et al. 2008; Person et al. 2007). Fossil groundwaters have been identified in various glaciated areas of the northern hemisphere (McIntosh et al. 2012; Person et al. 2007), including in relatively shallow aquifers in the Canadian Prairies (Grasby et al. 2000; Grasby and Chen 2005; Ruff et al. 2023; Grasby and Betcher 2002). The degree of isolation and potential for mixing with more recent recharge has been challenged recently by the widespread presence of both fossil and modern components in groundwaters in various locations globally (Jasechko et al. 2017). Here, we examine the ages of groundwaters in intertill and buried valley aquifers in Saskatchewan to improve our understanding of their connections to the rest of the hydrologic cycle.

There have been extensive efforts to understand the hydrostratigraphy of Pleistocene sediments in Saskatchewan (Christiansen 1992; MDH Engineered Solutions Ltd. 2011; Maathuis et al. 2011; Cummings et al. 2012) but understanding of groundwater flow patterns is limited due to the discontinuous nature of these aquifers and sparse spatial coverage of observation wells. Aside from the Dalmeny aquifer (Fortin et al. 1991), potentiometric surfaces have not been mapped at regional or subregional scales although there have been inferences made on flow directions and sources of recharge for individual wells in the SWSA observation well network (Meneley et al. 1979; Saskatchewan Water Security Agency 2024a). Modern recharge is thought to primarily occur through wetlands (Hayashi et al. 1998; Bam et al. 2020). Whether this recharge results in a substantial flux of water to intertill aquifers and buried valley aquifers is an open question, due to the low hydraulic conductivity of overlying unoxidized tills (Ferris et al. 2020). These tills contain water that has been interpreted as Pleistocene in age in many locations (Keller et al. 1988; Hendry et al. 2005; Hendry and Wassenaar 2011). The strength of the connection between aquifers confined by till aquitards and the rest of the hydrologic cycle remains unclear (Bam et al. 2020).

The presence of Pleistocene groundwaters in western Canada has often been identified with water stable isotopes, inferring that δ^2H and $\delta^{18}O$ values that plot along the global meteoric water line (GMWL), but are lower than modern precipitation or those in shallow or upgradient groundwater, originated as recharge from glacial sources (Ferguson et al. 2007; Ferguson and Jasechko 2015; Grasby et al. 2000; Grasby and Betcher 2002; Grasby and Chen 2005; Hendry et al. 2013). However, the use of δ^2H and $\delta^{18}O$ values to identify Pleistocene recharge could be complicated in some situations by overlap with older groundwater components with similar values that were recharged during interglacial periods (McIntosh et al. 2012; North Greenland Ice Core Project members 2004). δ^2H and $\delta^{18}O$ values may also provide inconclusive evidence of Pleistocene recharge in areas, such as Saskatchewan, where isotopically-depleted snowmelt forms a substantial portion of groundwater recharge (Bam and Ireson 2019; Hayashi et al. 1998). Seasonal weighted average $\delta^{18}O$ values of snow in the Saskatoon region vary between -23.1 and -19.7‰ (Koehler 2019), which is similar to the range of values that have been interpreted as glacial in origin in western Canada of -17 to -24‰ (Ferguson and Jasechko 2015; Grasby et al. 2000; Hendry et al. 2013; Ferguson et al. 2007). These $\delta^{18}O$ values overlap with the values of -15.5 to -19‰ that are found in shallow groundwater in Saskatchewan (Clark and Fritz 1997; Keller et al. 1988; Hendry et al. 2004; Hendry and Wassenaar 1999; Bam et al. 2020; McMonagle 1987), complicating interpretation of the timing of recharge. Variability in the water stable isotope values of modern recharge is largely attributable to seasonality rather than elevation of recharge areas, which likely varies by less than 100 m in the study area.

Uncorrected measurements of ^{14}C in groundwaters from glacial tills in Saskatchewan indicate recharge at 22.5 to 13.3 ka at the Warman site (Keller et al. 1988) and 31 to 25 ka at the King Site (Wassenaar and Hendry 2000), approximately corresponding to the LGM (Christiansen

1979; Dalton et al. 2022). Similar dates were estimated from ^{4}He concentrations in the Battleford Formation tills using transient diffusion models (Hendry et al. 2005). Numerical modeling of diffusion into shales from regional bedrock aquifers in the region suggest the presence of older groundwaters, perhaps as old as 300 ka (Hendry et al. 2013; Mowat et al. 2021). The behavior and sources of groundwater in Saskatchewan's intertill and buried valley aquifers throughout the Pleistocene and Holocene is less well-constrained. Here, we analyzed multiple age tracers (^{3}H, ^{14}C, and ^{4}He), noble gases, and water stable isotopes (δ^{18}O and δ^2H) of groundwater from Saskatoon Group intertill and Empress Group buried valley aquifers in Saskatchewan, Canada (Figure 1a). Results provide key insights into the distribution of groundwater ages in glaciated regions.

STUDY AREA

The Köppen-Geiger climate classification of the Saskatoon Region is a cold semi-arid type, typically featuring warm and dry summers with cold and dry winters (Peel et al. 2007). The Saskatoon region receives an average of 347 mm of precipitation annually (Environment and Climate Change Canada 2024). The majority of precipitation occurs during the late spring to early summer months, while approximately one-third of precipitation falls as snow during the winter months. Mean annual gross evaporation for the region, based on a 30-year period for the Canadian Prairies, ranges from 800–920 mm (Martin 2002), vastly exceeding precipitation amounts. The mean annual temperature is 2.4 °C and ranges from a mean monthly low of -17.5 °C in January to a mean monthly high of 19.0 °C in July (Environment and Climate Change Canada 2024). The Prairies are susceptible to drought conditions, having experienced many severe droughts over the past 500–1,000 years (Case and MacDonald 2003)

Saskatchewan has experienced eight to ten periods of substantial glacial advance and retreat over the past two million years, with the final glacial retreat between 17 ka to 10 ka (Christiansen 1979). These cycles of deposition and erosion produced a complex sequence of glacial till aquitards interlayered with sand and gravel aquifers (MDH Engineered Solutions Ltd. 2011). The lateral continuity of these strata is poorly understood in many cases, especially in terms of their hydraulic properties (Maathuis 2005; MDH Engineered Solutions Ltd. 2011).

The glacial and bedrock formations of interest are the Upper Cretaceous Lea Park, Judith River, and Bearpaw formations; the Empress Group ("buried valley aquifers"), which straddles the Neoogene-Quaternary boundary; and the Quaternary, Sutherland, and Saskatoon groups (Figure 2). The Upper Cretaceous formations are generally non-calcareous shales of varying marine clay, silt, and sand content, which are spatially variant due to erosion (Dawson et al. 1994; McLean 1971). The Tyner and Battleford Valleys were incised into bedrock predominantly during the late Neogene (Cummings et al. 2012). Substantial clastic deposits, carried by meltwater during the early Pleistocene, filled these valleys in the lowlands forming the Empress Group (Cummings et al. 2012; Whitaker and Christiansen 1972). The Hatfield Valley aquifer, which also contains Empress Group sediments, is underlain by till locally and is thought to have been incised by glaciofluvial processes during the Pleistocene (Cummings et al. 2012). Buried valley aquifers are an important groundwater supply in the region and are exploited by several small municipalities (MDH Engineered Solutions Ltd. 2011).

The overlying Sutherland Group, which was deposited prior to the Illinoian glaciation (Figure 2) is divided into the Mennon, Dundurn, and Warman units. These units are further subdivided into several till, intertill, and stratified units, that can be differentiated by carbonate and clay content, as well as the presence of paleo-oxidized horizons and/or intertill stratified deposits

(Christiansen 1992; MDH Engineered Solutions Ltd. 2011). The intertill units of the Mennon, Dundurn and Warman units are comprised of a range of sediment sizes from clay to gravel and form discontinuous aquifers, which are not typically targets for production wells (MDH Engineered Solutions Ltd. 2011).

The Saskatoon Group, which was contains Illinoian through Late Wisconsinan-aged deposits (Figure 2), is divided into the Floral and Battleford units and surficial stratified deposits. The Floral and Battleford units can be differentiated from Sutherland Group units by their higher carbonate content and coarser lithology, and from one another as Floral Formation sediments can be delineated based upon the presence of paleo-oxidized horizons and/or intertill stratified deposits (MDH Engineered Solutions Ltd. 2011). The intertill stratified deposits of the Floral Formation form a discontinuous aquifer system in the region, including the Forestry Farm, Dalmeny, and Tessier aquifers (MDH, 2011) (Figure 1). These aquifers are a primary target for groundwater production in the region (MDH Engineered Solutions Ltd. 2011). The uppermost unit of the Saskatoon Group is the surficial stratified deposits, which are postglacial sediments lain by fluvial, lacustrine and aeolian processes (Christiansen 1992).

METHODS

Field Methods

Twelve monitoring wells were sampled June 9–17, 2022 (Figure 1). A submersible pump was used to purge a sufficient volume of water from the well to satisfy US Environmental Protection Agency low flow guidelines, which include stabilization of temperature, pH and electrical conductivity prior to sample collection (US EPA 2017). All parameters were measured using with a calibrated YSI Pro multi-parameter meter. All samples except for ^{14}C were field-filtered through a 0.45 μm nylon filter into pre-cleaned sample containers. Cation, anion, trace element, and alkalinity samples were collected into 30 mL high-density polyethylene (HDPE) bottles with minimal headspace. Cation and trace element samples were field-acidified with ultra-pure nitric acid to a pH < 2. Samples for $\delta^{18}O$ and $\delta^{2}H$ of water were collected into 30 mL glass vials with conic tops and no headspace. ^{3}H was collected into 1 L HDPE bottles and carbon-13 ($\delta^{13}C$) of dissolved inorganic carbon (DIC) into 30 mL glass serum vials crimp sealed with no headspace. Unfiltered samples were collected for ^{14}C into 1 L glass amber bottles. All samples were stored on ice in the field and refrigerated in the laboratory to remain at or below 4 °C. Noble gases were collected by pumping water into copper tubes, which were crimp sealed and shipped to the Noble Gas Laboratory at the University of Utah (Solomon and Cook 2000).

Laboratory Analysis

Alkalinity analysis was performed at the University of Arizona (UArizona)'s Department of Hydrology and Atmospheric Science using the Gran-Alk titration method (Gieskes and Rogers 1973) with an analytical precision of ± 0.6%. Anions, cations, and trace elements were quantified at the Analytical Geochemistry Laboratory in the Department of Geological Sciences at the University of Saskatchewan. Anions (SO_4, Cl, F, Br, and NO_3) were measured using a Thermo Dionex Integriong HPIC system fitted with an IonPac AS11-HC-4 µm column (analytical precision of ± 1%). Cations (Ca, Mg, Na, K, Si) were measured using a SPECTRO Analytical Instruments SPECTROBLUE ICP-OES system (analytical precision of ±2%). Trace elements (B, Fe, Mn, Sr) were measured using a Thermo Scientific iCAP TQe ICP-MS system (analytical precision of ±2%). Charge balances for all samples were within 5%.

^{3}H and $\delta^{13}C$-DIC analyses were performed at UArizona's Department of Geosciences Environmental Isotopes Laboratory. ^{3}H was analyzed using a Quantulus 1220 Spectrometer in an underground counting laboratory using electrolytic enrichment and liquid scintillation decay counting methods (Theodorsson 1996), with a detection limit of 0.5 TU. δ^{13}C-DIC was analyzed using a ThermoQuest Finnigan Delta PlusXL coupled with a Gasbench automated sampler with a precision of ±0.30‰ (VPDB).

δ^{18}O and δ^{2}H were analyzed at the USask's Hillslope Hydrology Lab using a Los Gatos Research liquid water Off-Axis Integrated-Cavity Output Spectrometer. Stable water isotope values are reported in parts per thousand (‰) relative to the Vienna Standard Mean Ocean Water and Standard Light Antarctic Precipitation (VSMOW-SLAP) standards. The 2-sigma uncertainties were ^{18}O (0.8‰) and δ^{2}H (2‰). ^{14}C analyses were performed at the University of Ottawa's Andre E. Lalonde AMS Laboratory on an Ionplus AG MICADAS (Mini Carbon Dating System). Uncertainty on ^{14}C results (1σ) ranged from 0.01–0.07 percent modern carbon (pmC).

Noble gases (^{4}He, ^{3}He/^{4}He, Ne, Ar, Kr, Xe) were measured at the University of Utah's Noble Gas Lab. Measurement of all noble gases except helium were completed using a Stanford Research SRS – Model RGA 300 quadruple mass spectrometer; helium was analyzed using a Mass Analyzers Products – Model 215-50 magnetic sector mass spectrometer. Analytical precision for total concentration of the gases was ^{3}He (±1%), ^{4}He (±1%), Ne (±2%), Ar (±2%), Kr (±4%) and Xe (±4%).

Radiocarbon Corrections

Uncorrected ^{14}C ages were corrected to account for geochemical reactions occurring in the subsurface—e.g., carbonate mineral dissolution—that impact ^{14}C activity by the addition of "dead carbon" (0 pmC ^{14}C), artificially increasing the apparent groundwater age (Clark and Fritz 1997). To make these corrections, NetpathXL (Parkhurst and Charlton 2008), a revised version of NETPATH (Plummer et al. 1994), was used. NetpathXL employs the revised Fontes and Garnier model (Han and Plummer 2013) and performs basic inverse modeling, based upon the major ion chemistry, δ^{13}C-DIC, and radiocarbon values. The program then plots sample points on a graph, which depending on where the samples plot, indicates whether the Tamers model, gas exchange model, or solid exchange model should be used in radiocarbon age corrections. In this study, the ^{14}C was assumed to be 100 pmC, and the ^{14}C and δ^{13}C of carbonate minerals were assumed to be 0 pmC and 0‰, respectively. The δ^{13}C of soil CO_2 was assumed to be -25‰, which is within the range of -22.9‰ to -26.8‰ found in soils in Saskatchewan (Landi et al. 2003).

Helium-4 Corrections

The contributions from atmospheric, mantle, and crustal sources to ^{4}He were deconvolved to assist with interpretation of ^{4}He concentrations. Crustal sources ($^4He_{rad}$), which accumulate in groundwater over time, are of primary interest in assessing groundwater ages in this study. Atmospheric ^{4}He contributions can be determined using the ^{4}He/^{20}Ne ratio, given that ^{4}He and ^{20}Ne have similar solubilities and assuming that ^{20}Ne is solely atmospheric using the following equation (Hilton 1996):

$$R_C = \frac{R_S X - R_A}{X-1} \qquad [1]$$

where $X = \left(\frac{^4He}{^{20}Ne}\right)_S / \left(\frac{^4He}{^{20}Ne}\right)_A$, R is the ^{3}He/^{4}He ratio, and the subscripts *C*, *S*, and *A* stand for the air-corrected, sample (i.e., measured), and air values, respectively. The ^{4}He/^{20}Ne of air ≈ 0.319; values close to this indicate greater atmospheric ^{4}He inputs, while samples with higher crustal ^{4}He inputs typically have a ^{4}He/^{20}Ne orders of magnitude higher than air (Ballentine et al. 1996). From here, the air-corrected ^{3}He/^{4}He ratio (R_C) can be used in an endmember mixing model to determine the mantle and crustal contributions, using the equation below:

$$R_C = f_m R_m + f_{rad} R_{rad} \qquad [2]$$

where subscripts *m* and *rad* represent the mantle and radiogenic crustal components, *f* is the fractional contribution to the measured sample from the mantle or crust, and R is $^3He/^4He$ ratio. Values in the literature suggest R_m ranges from 8–30 R_A (where R_A is the measured ratio in air; Saar et al. 2005), while R_{rad} ranges from 0.02–0.05 R_A (Castro et al. 2000). For the purposes of this research, and in line with past research, R_m = 8 and R_{rad} = 0.02. The in-situ production can be determined by removing contributions from air-saturated water ($^4He_{ASW}$) and the mantle ($^4He_{mantle}$) from the measured ^4He ($^4He_{total}$).

$$[\,^4He_{rad}] = [\,^4He_{total}] - [\,^4He_{ASW}] - [\,^4He_{mantle}] \qquad [3]$$

$^4He_{rad}$ can be used to estimate a groundwater age if *in situ* generation and diffusive fluxes into the aquifer can be estimated. Diffusive fluxes are variable and difficult to characterize in the study area because transport has not yet reached steady-state due to the relatively young ages of the sediments present (Hendry et al. 2005; Hendry and Wassenaar 2011). Due to this limitation, we use $^4He_{rad}$ concentrations to support interpretations of other tracers rather than estimating groundwater ages.

RESULTS

Field Parameters, Major Ions, Trace Elements

Field parameters (Table 1), alkalinity, and major ions of groundwater samples were measured at all 12 observation wells (Table 2). Temperature ranged from 5.9–10.6 °C, pH ranged from 7.10–8.42, and conductivity ranged from 1,300–4,389 µS/cm. Alkalinity ranged from 298–827 mg/L. Given that all samples had a pH < 9, bicarbonate (HCO_3) was assumed to be the dominant constituent of alkalinity. In general, four predominant groundwater types were observed: Ca-Mg-SO_4 (Saskatoon, Dalmeny, Tessier, Conquest 500, Conquest 502), Na-SO_4 (Tyner, Vanscoy, Nokomis), Ca-Mg-HCO_3 (Agrium, Unity, Lilac), and Na-HCO_3 (Hearts Hill) (Figure 3). Finally, nitrate (NO_3) was detected at the intertill wells at Dalmeny and Conquest 500, with concentrations ranging from 0.12–15.0 mg/L. Vanscoy was the only buried valley well with detectable NO_3, with a concentration of 1.14 mg/L. The bedrock well at Heart's Hill had a NO_3 concentration of 6.9 mg/L.

Table 1: Well Details Including Location, Screening, Hydraulic Head, & Field Parameters

Well	Stratigraphic Unit	Aquifer Type	Date Sampled	Latitude	Longitude	Surface Elevation (masl)	Top of Screened Interval (masl)	Bottom of Screened Interval (masl)	Hydraulic Head (masl)
Agrium	Floral	Intertill	06/11/2022	52.026	-107.1	499.9	484.9	482.2	496.9
Conquest 500	Floral Formation	Intertill	06/13/22	51.574	-107.174	554.8	537.6	536	542.9
Dalmeny	Floral	Intertill	06/11/2022	52.261	-106.719	515.1	491.6	490.4	506.9
Saskatoon	Floral	Intertill	06/10/2022	52.172	-106.532	510.5	484.6	483.4	499.4
Tessier	Floral	Intertill	06/12/2022	51.881	-107.514	554.7	530	528.8	545
Unity	Intertill (unclassified)	Intertill	06/16/22	52.465	-108.955	672.1	646.5	645.3	657
Conquest 502	Saskatoon Group	Intertill	06/13/22	51.57	-107.314	571.6	554	552.8	562.1
Lilac	Empress	Buried Valley	06/15/22	52.758	-107.917	548.6	427.3	426.1	538.7
Nokomis	Empress	Buried Valley	06/17/22	51.505	-105.067	509.9	413	410	508.9
Tyner	Empress	Buried Valley	06/12/2022	51.024	-108.424	592.8	480.7	479.1	583.2
Vanscoy	Empress	Buried Valley	06/15/22	52.007	-107.049	512.1	426.7	423.4	507

Hearts Hill	Judith River	Bedrock	06/16/22	52.084	-109.564	688.8	613.5	612	680.8

Notes: All wells have a single screened interval; this section is the bottom/end of well construction. Hydraulic heads measured prior to purging.

Table 2: Field parameters and concentrations of anions, cations, and select trace elements for well samples. Units in mg/L for all analytes. F and Br are not included in table as they were below the method detection limit in all samples.

Well	pH	Temp	EC	Ca	Mg	Na	K	Si	B	Fe	Mn	Sr	Cl	HCO_3	SO_4	NO_3
Agrium	7.41	7.6	1459	111	36.9	106	7.79	10.4	0.58	2.69	0.19	0.77	19.6	595	207	<0.8
Conquest 500	7.71	9.2	3604	528	186	40.1	15.9	9.47	0.07	10.6	4.79	1.45	0.94	298	2000	15
Dalmeny	7.32	6.5	3272	367	181	95.4	11.8	10.9	0.56	10.8	0.28	2.31	6.59	827	1300	13.9
Saskatoon	7.10	8.8	4389	419	283	199	17.4	9.40	0.84	16.9	0.34	3.09	44.3	568	2240	<0.8
Tessier	7.23	10.4	1735	145	83.9	77.3	6.15	9.05	0.23	1.96	1.09	0.77	8.7	449	533	<0.8
Unity	7.16	6.6	1300	128	64	26.4	9.19	8.46	0.09	1.54	0.50	0.66	7.2	561	234	<0.8
Conquest 502	7.25	10.6	1875	193	78.3	71.8	10.2	11.7	0.43	1.77	1.36	1.08	20.2	417	622	<0.8
Lilac	7.94	6.8	1618	83.9	60	109	10.7	10.8	0.31	0.77	0.09	0.60	21.7	582	254	<0.8
Nokomis	7.46	7.0	4252	167	83.4	570	8.72	11.8	0.61	2.96	0.14	1.52	283	471	1270	<0.8
Tyner	8.18	6.9	3941	68.6	89.8	612	9.09	5.95	0.85	0.49	0.02	1.23	121	700	1210	<0.8
Vanscoy	8.42	6.7	3759	30.4	27.7	681	5.44	11.2	1.17	0.31	0.02	0.55	256	568	892	1.14

Heart's Hill	7.96	5.9	1506	16.1	14.5	258	8.93	8.97	0.55	0.25	0.05	0.58	5.7	635	210	6.79

Stable Isotopes

Stable water isotope values ranged from -21.1 to -16.2‰ and -163 to -137‰ for δ^{18}O and δ^{2}H, respectively (Table 3; Figure 4). Most samples plot on or below the Local Meteoric Water Line (LMWL) for Saskatoon (Koehler 2019), given by $\delta^{2}\mathrm{H} = (\delta^{18}\mathrm{O} \times 7.69 \pm 0.096) - 2.22 \pm 1.72$. The LMWL for Saskatoon has a lower slope and different y-intercept than the GMWL (Craig 1961), where $\delta^{2}\mathrm{H} = (\delta^{18}\mathrm{O} \times 8.0) + 10$, consistent with Saskatoon's semi-arid climate. Given the strong correlation between δ^{18}O and δ^{2}H values of groundwater samples ($R^2 = 0.967; P = 4.33x10^{-15}$), further discussion of stable water isotopes will be limited to δ^{18}O.

Table 3: Stable & Radioactive Isotopes. [a]Trace detection below method detection limit. For laboratory uncertainties, refer to the Methods section.

Well	δ^{18}O	δ^{2}H	^{3}H	δ^{13}C - DIC	^{14}C (raw)	^{14}C (uncorrected)	^{14}C (corrected)
	‰	‰	TU	‰	pmC	ka	ka
Agrium	-21.1	-163	ND/< 0.5	-12.6	16.1	14.7	10.1
Conquest 500	-19.7	-156	2.9	-11.9	34.3	8.6	3.5
Dalmeny	-19.1	-147	0.9	-12.2	15.9	14.5	10.3
Saskatoon	-19.6	-153	0.7	-13.0	8.8	19.5	15.5
Tessier	-19.3	-150	< 0.6[a]	-12.4	33.5	8.8	4.3
Unity	-16.2	-134	ND/< 0.5	-12.2	62.0	3.8	0

Conquest 502	-20.6	-160	ND/< 0.5	-12.0	21.2	12.5	8.0
Lilac	-16.9	-137	ND/< 0.5	-12.3	28.0	12.2	5.0
Nokomis	-18.5	-146	ND/< 0.5	-16.8	0.69	40.0	43.1
Tyner	-20.6	-162	ND/< 0.5	-18.8	< 0.51	> 42.5	> 42.5
Vanscoy	-19.5	-154	ND/< 0.5	-18.8	< 0.51	> 42.5	> 42.5
Hearts Hill	-18.4	-149	ND/< 0.5	-12.8	14.9	15.2	10.2

Radioactive Isotope Age Tracers

^{3}H was detected at four locations: Saskatoon (0.7 ± 0.28 TU), Dalmeny (0.9 ± 0.31 TU), Conquest 500 (2.9 ± 0.18), and Tessier (< 0.6 TU; apparent 0.3 ± 0.21 TU) (Table 3). In the other remaining wells, ^{3}H was below the detection limit. ^{14}C was detected at ten of twelve locations with uncorrected ^{14}C ranging from 0.69–62.0 pmC. At Tyner and Vanscoy, ^{14}C was non-detect (< 0.51 pmC). Geochemical modeling using NetPathXL (Parkhurst and Charlton 2008) produced corrected ^{14}C ‘ages’ ranging from modern to 43.1 ka; excluding Nokomis (43.1 ka), groundwater ^{14}C ages were much younger, ranging from modern to 15.5 ka (Figure 5).^{14}C ages were insensitive to the δ^{13}C value used with the exception of the use of low δ^{13}C values for the Nokomis sample, which would result in an ^{14}C age of 49.5 ka.

Noble Gases

Noble gas (He, Ne, Ar, Kr, Xe) concentrations were measured at all twelve locations, however the focus of this study pertains to the light noble gases (He, Ne, Ar) and their pertinent isotope relationships (^{3}He/^{4}He, ^{4}Ne/^{20}Ne, ^{40}Ar/^{36}Ar) (Table 4). Air corrected R_c/R_a values ranged from 0.008–0.332, with estimated mantle contributions of ^{4}He ranging from 0.0–3.9% (Table 4). $^{4}He_{rad}$ varied from 0.37 x 10^{-7} to 26.2 x 10^{-7} cm^3 STP/g in intertill aquifers. Samples from buried valley aquifers had higher concentrations (171 to 331 x 10^{-7} cm^3 STP/g), except for Lilac (13 x

10^{-7} cm^3 STP/g). This pattern of $^4He_{rad}$ concentrations is consistent with an expected increase associated with greater residence times. The $^{40}Ar/^{36}Ar$ in all samples are in excess of that expected in air-saturated water (366-819 vs 298.56): these excesses do not correlate with radiocarbon and are likely due to interactions with other fluids in the system. Noble gas recharge temperatures are not given for the aquifer due to their probabilities below the acceptable minimum (Jeung et al 2018).

Table 4: He, Ne, Ar Concentrations & Isotopic Ratios. [a]Air-corrected. [b]Correction not applied, results indicative of field or laboratory fractionation of noble gases. Concentrations for He and Ne are cm^3 STP/g. See methods section for analytical error associated with noble gases. R_c = air-corrected, f_{rad} = estimated fraction of crustal-derived ^4He, f_m = estimated fraction of mantle-derived ^4He.

Well	$^3He \times 10^{-13}$ cm^3 STP/g	$^4He \times 10^{-7a}$ cm^3 STP/g	R_c/R_a	$^{20}Ne \times 10^{-7}$ cm^3 STP/g	$^{22}Ne \times 10^{-8}$ cm^3 STP/g	$^{36}Ar \times 10^{-7}$ cm^3 STP/g	$^{40}Ar \times 10^{-4}$ cm^3 STP/g	f_{rad}	f_m	$^4He_{rad}$ 10^{-7} cm^3 STP/g
Conquest 500[b]	0.092	0.065	1.025	0.21	0.20	0.32	0.22	[c]	[c]	[c]
Agrium	10.9	26.41	0.274	2.17	2.05	13.4	4.90	0.968	0.032	25.57
Dalmeny	2.8	4.538	0.220	3.69	3.57	11.5	6.01	0.975	0.025	4.425
Saskatoon	11.4	27.06	0.275	2.82	2.61	9.24	4.66	0.968	0.032	26.19
Tessier	2.25	3.680	0.251	2.44	2.26	9.05	4.60	0.971	0.029	3.574
Unity	1.22	0.386	0.332	2.61	2.43	11.5	4.55	0.961	0.039	0.371
Conquest 502	1.73	3.082	0.219	2.00	1.90	8.85	4.38	0.975	0.025	3.005
Lilac	6.07	13.65	0.266	2.61	2.45	9.86	4.73	0.969	0.031	13.23
Nokomis	74.7	199.0	0.266	3.48	3.27	9.14	5.35	0.969	0.031	192.9
Tyner	49.0	174.5	0.195	4.94	4.68	12.1	9.91	0.978	0.022	170.7
Vanscoy	133	342.3	0.278	2.77	2.72	12.4	4.80	0.968	0.032	331.2
Hearts Hill	0.96	1.124	0.008	2.38	2.20	9.06	4.54	1.000	0.000	1.126

DISCUSSION

Interpretation of Sources of Recharge and Groundwater Flow Systems

Groundwater ages extend from modern to over 40,000 years, which includes the final advance of the Laurentide Ice Sheet over the region. The study area is thought to have been free of glacial ice for most of the period between ~75 to 30 ka (Dalton et al. 2022; Dredge and Thorleifson 1987; Wassenaar and Hendry 2000) and after ~12 ka (Christiansen 1979; Dalton et al. 2020) (Figure 6). All ^{14}C ages except one correspond to times when the region was ice free, suggesting that, in contrast to some bedrock aquifers in the region (Grasby et al. 2000; Grasby and Chen 2005; Ferguson et al. 2007), the bulk of groundwater present in these systems today did not originate as glacial recharge.

Groundwater in the intertill aquifers had corrected ^{14}C ages ranging from 0.0–10.3 ka, aside from one well (Saskatoon) with an age of 15.5 ka and $^{4}He_{rad}$ in these wells are up to 26.19 x 10^{-7} cm3 STP/g (Figure 5). These ages are younger than the youngest glacial tills in the study area (Christiansen 1979, 1992), indicating that recharge has been occurring throughout the Holocene. Pleistocene waters are retained in tills in some locations in Saskatchewan (Wassenaar and Hendry 2000) but the ages measured here indicate that these tills do not prevent recharge to the underlying intertill aquifers at regional scales. The presence of ^{3}H at Saskatoon, Dalmeny, Conquest and Tessier, which was sourced from nuclear weapons testing in the 1960s (Clark and Fritz 1997; Gleeson et al. 2016; Lindsey et al. 2019), indicates that modern recharge is present in some areas. NO_3, which commonly indicates that groundwater has been affected by fertilizer and/or manure application in agricultural areas (Burow et al. 2010; Power and Schepers 1989; Wick et al. 2012), is present at elevated concentrations of 6.79, 13.9, 15.0 mg/L at Heart's Hill, Dalmeny and Conquest 500 respectively, which is also indicative of the presence of modern recharge. The measured NO_3 at Vanscoy (1.1 mg/L) likely has an anthropogenic source. Past sampling of this well has found NO_3 concentrations as high as 15.5 mg/L in 1977 followed by non-detects in the

1980s and another increase to 9.2 mg/L in 2004 (Saskatchewan Water Security Agency 2024a). Such variations could be the result of recharge through leaky wells. Mixing of modern waters at other locations could also be the result of leaky wells (Jasechko et al. 2017), diffusion of older groundwater from adjacent aquitards (Bethke and Johnson 2002) or contributions of young and old groundwaters by the different flowpaths intersected along a well screen (Jurgens et al. 2012).

The major ion chemistry is consistent with the expected geochemical evolution of groundwater with age (Palmer and Cherry 1984). Intertill aquifers contain Ca-Mg-HCO_3 and Ca-Mg-SO_4 waters (Figure 3), which are typical for younger waters. Na-HCO_3-SO_4 waters are found in buried valley samples except Lilac, where Ca-Mg-HCO_3 water is found along with much younger ages than other buried valley samples. The bedrock sample from Heart's Hill contains Na-HCO_3 water, which is consistent with other lower salinity samples from the Judith River Formation in Saskatchewan (Ferris et al. 2017; McMonagle 1987). Piper plots using larger datasets from the region show considerable variability in the major ion composition of groundwater found in both intertill and buried valley aquifers (MDH Engineered Solutions Ltd. 2011; McMonagle 1987). Whether this variability can be related to groundwater age for these larger datasets, where age tracers were not measured or reported, is unclear.

Groundwater ages closer to the LGM are present at the Saskatoon well, and have also been observed in Sutherland Group tills in the study area, where uncorrected ^{14}C ages ranging from 19.9–24.8 ka were observed (Keller et al. 1988). The range of ages in this study indicates there has been active subregional groundwater flow systems in these aquifers since they became confined during the deposition of Late Wisconinan tills. For example, the Dalmeny aquifer has a modern hydraulic gradient of ~0.001 to 0.002 over a flow system ~ 10 km in length (Fortin et al. 1991). The aquifer has a typical porosity of 0.30 and hydraulic conductivity of 10^{-6} to 10^{-3} m/s (MDH

Engineered Solutions Ltd. 2011; Meneley et al. 1979). This gradient, hydraulic conductivity, and porosity provide a groundwater velocity of ~0.1 to 200 m/yr. These velocities result in aquifer transit times that are of 50 to 100,000 years. This 10.3 ka ^{14}C age found near the Dalmeny aquifer's southeast discharge area suggests that the effective hydraulic conductivity is in the lower part of the range of hydraulic conductivities, assuming a piston flow model. The presence of elevated NO_3 suggests that the bulk age is a mixture of older groundwaters and modern recharge and that piston flow may not accurately describe the flow system. The increase in hydraulic gradients toward the discharge zones shown by Fortin et al. (1991) suggest that recharge is occurring through the overlying tills over much of the aquifer. The mixed groundwater ages may reflect the presence of younger water associated with flowpaths intersected in the upper portion of the well screen, while the lower part of the well screen samples older groundwater. This mixing process has been explored in detail by Jurgens et al (2012). This may provide a conceptual model for other intertill aquifers in the study area that have similar ^{14}C ages along with contributions of modern recharge.

Recharge reaching intertill aquifers must pass through overlying tills. A compilation of hydraulic conductivities for tills in Saskatchewan revealed in situ values of 5.5×10^{-9} m/s for measurements at depths of less than 10 m, 1.9×10^{-9} m/s for depths between 10 and 23 m 1.8×10^{-10} m/s at depths greater than 23 m, with the reduction in permeability attributed to the transition between oxidized and unoxidized conditions (Ferris et al. 2020). Values in the upper two depth intervals were much more variable than those in the lower interval due the presence of fractures. Estimates of Darcy velocities in the deeper tills are as low as 10^{-4} m/yr, which is corroborated by diffusion-dominated transport (Hendry and Wassenaar 1999). In the higher hydraulic conductivity oxidized tills, Darcy velocities a few orders of magnitude greater are possible. Hydrostratigraphic cross-sections of the region indicate that oxidized tills directly overlie Floral Formation aquifers in some areas (MDH Engineered Solutions Ltd. 2011). These areas are possible pathways for recharge, especially if they correspond with upland wetlands.

The persistence of older water in the Tyner Valley (Tyner and Vanscoy) and Hatfield Valley aquifers (Nokomis) indicates that the aquifers have not been flushed during or since the LGM, perhaps due to presence of older tills during the Late Wisconsinan glaciation. Groundwater age does not have an obvious relationship with what can be inferred about the regional groundwater flow systems in these aquifers from the limited data available. In the Tyner Valley aquifer, the sample from Tyner has a $^{4}He_{rad}$ concentration of 170.7 x 10^{-7} cm^3 STP/g and the sample from Vanscoy, which is ~150 km to the northeast, has a concentration of 331.2 x 10^{-7} cm^3 STP/g. At Nokomis, a $^{4}He_{rad}$ value of 192.9 x 10^{-7} cm^3 STP/g was measured, suggesting that the age of the groundwater at Tyner is just beyond the limit of ^{14}C dating and that ages at Vanscoy could be considerably older. Hydraulic head is ~582 masl at Tyner and ~508 masl at Vanscoy which could indicate that the higher ^{4}He concentrations are present in the downgradient location. However, the dearth of hydraulic head and tracer measurements create some uncertainty around this interpretation. Groundwater flow at Tyner could be southwards towards the South Saskatchewan River (Meneley et al. 1979), which has a hydraulic head value of ~554 masl at that location. However, responses of this aquifer to pumping nearby suggest the presence of low permeability barriers that may prevent regional flow (Maathuis 2005). Groundwater flow at Vanscoy is thought to be northward (Meneley et al. 1979) but the discharge area is unclear. The South Saskatchewan River has an elevation of ~470 masl at Saskatoon while a well Warman has a hydraulic head value of 452 masl, suggesting downward flow from the South Saskatchewan River towards the Tyner Valley aquifer. There is little pumping in this area (Saskatchewan Water Security Agency 2024b), suggesting that gradients are the result of background conditions.

Discharge appears to occur further to the northeast downstream of the confluence of the North and South Saskatchewan rivers. Little is known about the flow system within Hatfield Valley aquifer at Nokomis. Discharge from this system may be occurring into Last Mountain Lake to the east (Meneley et al. 1979) or to the Qu'Appelle River Valley to the south.

The one bedrock aquifer sample taken in this study was from the Judith River Formation and had a corrected ^{14}C age of 10.2 ka and a NO_3 concentration of 6.79 mg/L, indicating a component of modern recharge. Flow in this region was previously thought to be to the northeast (Meneley et al. 1979) but more recent mapping of the potentiometric surface in this region indicates that groundwater flow is towards the south in this region with discharge occurring to the South Saskatchewan River approximately 20 km south of the well that was sampled (Ferris et al. 2017). Till covers much of the region surrounding this well and recharge likely occurs in areas where aquitards are thinner due to nondeposition or erosion but this region has yet to be mapped in detail.

Use of δ^2H and $\delta^{18}O$ as Groundwater Tracers in Saskatchewan

Multiple studies of groundwater in bedrock aquifers in the Canadian Prairies have used a shift in δ^2H and $\delta^{18}O$ values similar to those in modern recharge to lower values as an indication of the presence of Pleistocene meltwater (Ferguson et al. 2007; Grasby et al. 2000; Grasby and Chen 2005) but such a shift is not obvious in the data collected in this study (Figure 7). In intertill aquifer samples, $\delta^{18}O$ values range from -21.1 to -16.2‰. In samples with ^{14}C ages < 5 ka, $\delta^{18}O$ values are between -19.7 and -16.2‰, while the Saskatoon sample, with ^{14}C age of 15.5 ka has a $\delta^{18}O$ value of -19.6‰. $\delta^{18}O$ values associated with older groundwater samples in buried valley aquifers have values of -20.6 to -18.5‰. Aside from the samples with the highest $\delta^{18}O$ values at

Lilac and Unity, which appear to be affected by evaporation, there is considerable overlap in the $\delta^{18}O$ values from samples with ages corresponding to the Pleistocene and Holocene.

Values of approximately -21 to -18‰ have been interpreted as Pleistocene in age within glacial tills based on groundwater ages and transport modelling (Hendry et al. 2004; Keller et al. 1988) but this also overlaps with modern precipitation in the Saskatoon region (Koehler 2019), as well as shallow groundwater (Clark and Fritz 1997; Keller et al. 1988; Hendry et al. 2004; Hendry and Wassenaar 1999; Bam et al. 2020; McMonagle 1987). Groundwater $\delta^{2}H$ and $\delta^{18}O$ in the region, including previous analyses of intertill aquifers and buried valley wells sampled in this study, have been explained by recharge from modern precipitation without a need to consider a paleo-recharge component (McMonagle 1987).

Seasonal changes in hydraulic head have been invoked as evidence of the timing of recharge to both intertill and buried valley aquifers (McMonagle 1987). Subsequent research in Saskatchewan, including some of the wells sampled by McMonagle (1987), has shown that these variations in hydraulic head are the result of downward hydraulic diffusion of changes in total stress from soil moisture loading rather than recharge reaching confined aquifers (van der Kamp and Maathuis 1991; Anochikwa et al. 2012; van der Kamp and Schmidt 1997). This is corroborated by corrected ^{14}C ages from the current study indicating that a considerable fraction of groundwater at these locations is not modern recharge. This suggests that either the climate and recharge mechanisms have been relatively stable throughout the Holocene and late Pleistocene or that different climates and recharge mechanisms have resulted in similar $\delta^{2}H$ and $\delta^{18}O$ values.

Conditions during the early Holocene were more arid than those currently observed (Wolfe et al. 2002), which would have also emphasized winter precipitation in recharge. Increased aridity conditions may explain the presence of $\delta^{2}H$ and $\delta^{18}O$ values that plots beneath the GMWL associated with an early Holocene corrected ^{14}C date at the Lilac well. δ^2H and $\delta^{18}O$ values at the Saskatoon well, which has a corrected ^{14}C date that coincides with a time when the region was glaciated, is similar to modern winter precipitation in the Saskatoon region. The climate conditions associated with the much older groundwater ages at Vanscoy, Nokomis and Tyner have not been characterized in detail. The similarity with other δ^2H and $\delta^{18}O$ values could indicate similar climate conditions. Coincidence of δ^2H and $\delta^{18}O$ values in groundwater with modern precipitation is not an indicator that modern recharge is present. δ^2H and $\delta^{18}O$ values are similar for groundwater with a wide range of groundwater ages, making these measurements less useful in the study area than they are in other regions.

Implications for Groundwater Management

The geochemical and isotopic measurements made in this study indicate that a range of groundwater ages, from fossil to modern, exist in intertill and buried valley aquifers in the Saskatoon region. Modern recharge and much older groundwater are often present the same wells, underscoring the need to use multiple tracers that provide information over different age ranges. Recharge to confined intertill aquifers is occurring despite the widespread presence of low hydraulic conductivity tills and lack of obvious recharge areas. This underscores a need for groundwater protection measures in Saskatchewan and more generally.

The presence of a continuum of groundwater ages including modern recharge indicates that groundwater resources in the region could be renewable if developed at a suitably low level. Groundwater age is a function of both recharge rate and distance from the point of recharge along a flowpath (Ferguson et al. 2020). The sparsity of the observation well network and lack of other reliable hydraulic head measurements make it difficult to determine the position of observation wells relative to recharge areas. As a result, groundwater recharge rates cannot reliably be determined with the groundwater ages estimated in this study. Additionally, recharge rates themselves are insufficient to assess whether groundwater is renewable because they are not critical to predicting hydraulic responses of groundwater to pumping (Cuthbert et al. 2023; Konikow and Leake 2014). However, the presence of modern recharge is generally considered to be a minimum requirement to allow for development of groundwater resources, particularly where older groundwaters are present (Margat et al. 2006; Bierkens and Wada 2019).

Understanding what level of development is possible will require more detailed hydraulic characterization of aquifers in the region to understand the potential impacts of pumping to hydraulic heads in existing and future wells and groundwater-surface water interactions.

Single well tests were conducted at most SWSA observation wells in the region (Meneley et al. 1979) but these tests may not be sufficient to capture the spatial variability of hydraulic conductivity due the limited number of wells. Published data for these aquifers is also relatively limited (MDH Engineered Solutions Ltd. 2011). An additional challenge is that single wells tests do not provide estimates of storage coefficients (Cooper et al. 1967; Halford et al. 2006), which are necessary to predict the spatial and temporal distribution of drawdown resulting from pumping. Additional multiwell testing in an expanded observation network would improve our understanding of these aquifers. Expansion of the observation well network would also provide opportunities to improve the spatial coverage of hydraulic head and tracer measurements for use in calibrating numerical models that could be used to predict changes in hydraulic head associated with pumping.

SUMMARY & CONCLUSIONS

This study used groundwater age tracers of varying timescales (^{3}H, ^{14}C, ^{4}He), stable water isotopes and major ions to examine the recharge history of intertill and buried valley aquifers in southern Saskatchewan, Canada. The majority of groundwater present throughout Saskatoon group intertill aquifers was recharged after the LGM (i.e., < 10.3 ka), and in several areas contains a component of modern recharge (< 60 years old). Pleistocene glacial water, still retained in adjacent till aquitards in the region (Hendry and Wassenaar 1999; Keller et al. 1988), must have been flushed or mixed with younger water by regional groundwater flow in intertill aquifers. Regional flow appears to have been operating in shallow intertill aquifers throughout the Holocene based on the range of radiocarbon ages present in these aquifers. This suggests that groundwater in these aquifers is being replenished under current conditions, although at low rates. Groundwater in the buried valley aquifers of the Empress Group is substantially older than the overlying Saskatoon groups, with recharge likely occurring during interglacial periods from 75–40 ka when southern Saskatchewan was ice-free. Groundwater in the underlying Judith River Bedrock is similar in age to the Saskatoon Group, suggesting a similar recharge mechanism.

No trends were observed in $\delta^{18}O$ and $\delta^{2}H$ values compared to groundwater age. This could indicate that recharge mechanisms similar to those observed today have been occurring over millennial timescales but may also reflect different sources of recharge with similar $\delta^{18}O$ and $\delta^{2}H$ values. ^{3}H and NO_3 provided clearer evidence that a component of modern groundwater is being recharged to these aquifers. ^{4}He measurements were not straightforward to interpret due to issues related to diffusion profiles that have not had time to reach steady state in the Pleistocene sediments of the region, along with noble gas contributions from other fluids. The presence of groundwater with ages measured in millennia and modern groundwater at the same wells underscore the importance of using multiple tracers to characterize groundwater age distributions.

Acknowledgments

Funding for this research was provided by the Geological Survey of Canada. We thank Erin Schmeling from the University of Saskatchewan for providing field equipment for sampling. We would also like to acknowledge Kei Lo and Anatoly Melnik from the Saskatchewan Water Security Agency who provided background information and logistical support in accessing the monitoring well network.

References

Anochikwa, C. I., G. van der Kamp, and S. L. Barbour. 2012. Interpreting pore-water pressure changes induced by water table fluctuations and mechanical loading due to soil moisture changes. *Canadian Geotechnical Journal* 49, no. 3: 357–66, https://doi.org/10.1139/t11-106.

Ballentine, C. J., R. K. O’Nions, and M. L. Coleman. 1996. A Magnus opus: Helium, neon, and argon isotopes in a North Sea oilfield. *Geochimica et Cosmochimica Acta* 60, no. 5: 831–49.

Bam, E. K., and A. M. Ireson. 2019. Quantifying the wetland water balance: a new isotope-based approach that includes precipitation and infiltration. *Journal of Hydrology* 570: 185–200.

Bam, E. K., A. M. Ireson, G. van Der Kamp, and J. M. Hendry. 2020. Ephemeral ponds: Are they the dominant source of depression-focused groundwater recharge? *Water Resources Research* 56, no. 3: e2019WR026640.

Bethke, C. M., and T. M. Johnson. 2002. Paradox of groundwater age. *Geology* 30, no. 2: 107–10.

Bierkens, M. F., and Y. Wada. 2019. Non-renewable groundwater use and groundwater depletion: a review. *Environmental Research Letters* 14, no. 6: 063002.

Burow, K. R., B. T. Nolan, M. G. Rupert, and N. M. Dubrovsky. 2010. Nitrate in Groundwater of the United States, 1991−2003. *Environmental Science & Technology* 44, no. 13: 4988–97, https://doi.org/10.1021/es100546y.

Case, R. A., and G. M. MacDonald. 2003. Tree Ring Reconstructions of Streamflow for Three Canadian Prairie Rivers. *JAWRA Journal of the American Water Resources Association* 39, no. 3: 703–16, https://doi.org/10.1111/j.1752-1688.2003.tb03686.x.

Castro, M. C., M. Stute, and P. Schlosser. 2000. Comparison of 4He ages and 14C ages in simple aquifer systems: implications for groundwater flow and chronologies. *Applied Geochemistry* 15, no. 8: 1137–67.

Christiansen, E. A. 1979. The Wisconsinan deglaciation, of southern Saskatchewan and adjacent areas. *Canadian Journal of Earth Sciences* 16, no. 4: 913–38.

Christiansen, E. A. 1992. Pleistocene stratigraphy of the Saskatoon area, Saskatchewan, Canada: an update. *Canadian Journal of Earth Sciences* 29, no. 8: 1767–78.

Clark, I. D., and P. Fritz. 1997. *Environmental isotopes in hydrogeology*. CRC press.

Cooper, H. H., J. D. Bredehoeft, and I. S. Papadopulos. 1967. Response of a finite-diameter well to an instantaneous charge of water. *Water Resources Research* 3, no. 1: 263–69.

Craig, H. 1961. Isotopic variations in meteoric waters. *Science* 133, no. 3465: 1702–3.

Cummings, D. I., H. A. Russell, and D. R. Sharpe. 2012. Buried-valley aquifers in the Canadian Prairies: geology, hydrogeology, and origin 1 1 Earth Science Sector (ESS) Contribution 20120131. *Canadian Journal of Earth Sciences* 49, no. 9: 987–1004.

Cuthbert, M. O., T. Gleeson, M. F. P. Bierkens, G. Ferguson, and R. G. Taylor. 2023. Defining renewable groundwater use and its relevance to sustainable groundwater management. *Water Resources Research* 59, no. 9: e2022WR032831.

Dalton, A. S., M. Margold, C. R. Stokes, L. Tarasov, A. S. Dyke, R. S. Adams, S. Allard, H. E. Arends, N. Atkinson, and J. W. Attig. 2020. An updated radiocarbon-based ice margin chronology for the last deglaciation of the North American Ice Sheet Complex. *Quaternary Science Reviews* 234: 106223.

Dalton, A. S., C. R. Stokes, and C. L. Batchelor. 2022. Evolution of the Laurentide and Innuitian ice sheets prior to the Last Glacial Maximum (115 ka to 25 ka). *Earth-Science Reviews* 224: 103875.

Dawson, F., C. Evans, R. Marsh, and R. Richardson. 1994. Uppermost Cretaceous and Tertiary strata of the Western Canada sedimentary basin. *Geological Atlas of the Western Canada Sedimentary Basin, Canadian Society of Petroleum Geologists and Alberta Research Council, Calgary*, 18.

Dredge, L. A., and L. H. Thorleifson. 1987. The Middle Wisconsinan history of the Laurentide ice sheet. *Géographie physique et Quaternaire* 41, no. 2: 215–35.

Edmunds, W. M. 2003. Renewable and non-renewable groundwater in semi-arid and arid regions. In *Developments in water science*, 50:265–80. Elsevier.

Environment and Climate Change Canada. 2024. Canadian Climate Normals 1991-2020 Data - Climate, 2024, https://climate.weather.gc.ca/climate_normals/results_1991_2020_e.html?searchType=stnProv&lstProvince=SK&txtCentralLatMin=0&txtCentralLatSec=0&txtCentralLongMin=0&txtCentralLongSec=0&stnID=265000000&dispBack=0.

Ferguson, G., R. N. Betcher, and S. E. Grasby. 2007. Hydrogeology of the Winnipeg Formation in Manitoba, Canada. *Hydrogeology Journal* 15, no. 3: 573–87, https://doi.org/10.1007/s10040-006-0130-4.

Ferguson, G., M. O. Cuthbert, K. Befus, T. Gleeson, and J. C. McIntosh. 2020. Rethinking groundwater age. *Nature Geoscience* 13, no. 9: 592–94.

Ferguson, G. and Jasechko, S., 2015. The isotopic composition of the Laurentide Ice Sheet and fossil groundwater. *Geophysical Research Letters 42*, no. 12: 4856-4861.

Ferris, D. M., M. Lypka, and G. Ferguson. 2017. Hydrogeology of the Judith River Formation in southwestern Saskatchewan, Canada. *Hydrogeology Journal* 25, no. 7: 1985–95, https://doi.org/10.1007/s10040-017-1611-3.

Ferris, D. M., G. Potter, and G. Ferguson. 2020. Characterization of the hydraulic conductivity of glacial till aquitards. *Hydrogeology Journal* 28: 1827–39.

Fortin, G., G. Van Der Kamp, and J. Cherry. 1991. Hydrogeology and hydrochemistry of an aquifer-aquitard system within glacial deposits, Saskatchewan, Canada. *Journal of Hydrology* 126, nos. 3–4: 265–92.

Gerber, R. E., and K. W. Howard. 1996. Evidence for recent groundwater flow through Late Wisconsinan till near Toronto, Ontario. *Canadian Geotechnical Journal* 33, no. 4: 538–55, https://doi.org/10.1139/t96-080-302.

Gieskes, J. M., and W. C. Rogers. 1973. Alkalinity determination in interstitial waters of marine sediments. *Journal of sedimentary research* 43, no. 1: 272–77.

Gleeson, T., K. M. Befus, S. Jasechko, E. Luijendijk, and M. B. Cardenas. 2016. The global volume and distribution of modern groundwater. *Nature Geoscience* 9, no. 2: 161–67.

Grasby, S. E., and R. N. Betcher. 2002. Regional hydrogeochemistry of the carbonate rock aquifer, southern Manitoba. *Canadian Journal of Earth Sciences* 39, no. 7: 1053–63.

Grasby, S. E., and Z. Chen. 2005. Subglacial recharge into the Western Canada Sedimentary Basin—Impact of Pleistocene glaciation on basin hydrodynamics. *Geological Society of America Bulletin* 117, nos. 3–4: 500–514.

Grasby, S. E., K. Osadetz, R. N. Betcher, and F. Render. 2000. Reversal of the regional-scale flow system of the Williston Basin in response to Pleistocene glaciation. *Geology* 28, no. 7: 635–38.

Halford, K. J., W. D. Weight, and R. P. Schreiber. 2006. Interpretation of transmissivity estimates from single-well pumping aquifer tests. *Groundwater* 44, no. 3: 467–71.

Han, L.-F., and L. N. Plummer. 2013. Revision of Fontes & Garnier's model for the initial 14C content of dissolved inorganic carbon used in groundwater dating. *Chemical Geology* 351: 105–14.

Hayashi, M., G. van der Kamp, and D. L. Rudolph. 1998. Water and solute transfer between a prairie wetland and adjacent uplands, 1. Water balance. *Journal of Hydrology* 207, nos. 1–2: 42–55.

Hendry, M. J., S. L. Barbour, K. Novakowski, and L. I. Wassenaar. 2013. Paleohydrogeology of the Cretaceous sediments of the Williston Basin using stable isotopes of water. *Water Resources Research* 49, no. 8: 4580–92.

Hendry, M. J., C. J. Kelln, L. I. Wassenaar, and J. Shaw. 2004. Characterizing the hydrogeology of a complex clay-rich aquitard system using detailed vertical profiles of the stable isotopes of water. *Journal of Hydrology* 293, nos. 1–4: 47–56.

Hendry, M. J., T. G. Kotzer, and D. K. Solomon. 2005. Sources of radiogenic helium in a clay till aquitard and its use to evaluate the timing of geologic events. *Geochimica et Cosmochimica Acta* 69, no. 2: 475–83.

Hendry, M. J., and L. I. Wassenaar. 1999. Implications of the distribution of δD in pore waters for groundwater flow and the timing of geologic events in a thick aquitard system. *Water Resources Research* 35, no. 6: 1751–60.

Hendry, M. J., and L. I. Wassenaar. 2011. Millennial-scale diffusive migration of solutes in thick clay-rich aquitards: evidence from multiple environmental tracers. *Hydrogeology Journal* 19, no. 1: 259.

Hilton, D. R. 1996. The helium and carbon isotope systematics of a continental geothermal system: results from monitoring studies at Long Valley caldera (California, USA). *Chemical Geology* 127, no. 4: 269–95.

Jasechko, S., D. Perrone, K. M. Befus, M. B. Cardenas, G. Ferguson, T. Gleeson, E. Luijendijk, J. J. McDonnell, R. G. Taylor, and Y. Wada. 2017. Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. *Nature Geoscience* 10, no. 6: 425–29.

Jurgens, B.C., Böhlke, J.K., and Eberts, S.M., 2012, TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data: U.S. Geological Survey Techniques and Methods Report 4-F3, 60 p.

Kamp, G. van der. 2001. Methods for determining the in situ hydraulic conductivity of shallow aquitards–an overview. *Hydrogeology Journal* 9: 5–16.

Kamp, G. van der, and H. Maathuis. 1991. Annual fluctuations of groundwater levels as a result of loading by surface moisture. *Journal of Hydrology* 127, nos. 1–4: 137–52.

Kamp, G. van der, and R. Schmidt. 1997. Monitoring of total soil moisture on a scale of hectares using groundwater piezometers. *Geophysical Research Letters* 24, no. 6: 719–22, https://doi.org/10.1029/97GL00521.

Keller, C. K., G. Van Der Kamp, and J. A. Cherry. 1988. Hydrogeology of two Saskatchewan tills, I. Fractures, bulk permeability, and spatial variability of downward flow. *Journal of Hydrology* 101, nos. 1–4: 97–121.

Koehler, G. 2019. Snow gauge undercatch and its effect on the hydrogen and oxygen stable isotopic composition of precipitation. *Isotopes in Environmental and Health Studies* 55, no. 4: 404–18.

Konikow, L. F., and S. A. Leake. 2014. Depletion and Capture: Revisiting "The Source of Water Derived from Wells." *Groundwater* 52, no. S1: 100–111.

Landi, A., D. W. Anderson, and A. R. Mermut. 2003. Organic carbon storage and stable isotope composition of soils along a grassland to forest environmental gradient in Saskatchewan. *Canadian Journal of Soil Science* 83, no. 4: 405–14, https://doi.org/10.4141/S02-021.

Lemieux, J., E. Sudicky, W. Peltier, and L. Tarasov. 2008. Dynamics of groundwater recharge and seepage over the Canadian landscape during the Wisconsinian glaciation. *Journal of Geophysical Research: Earth Surface (2003–2012)* 113, no. F1.

Lindsey, B.D., Jurgens, B.C., and Belitz, K., 2019, Tritium as an indicator of modern, mixed, and premodern ground-water age: U.S. Geological Survey Scientific Investigations Report 2019–5090, 18 p., https://doi.org/10.3133/sir20195090

Maathuis, H. 2005. Review of Pumping and Recovery Data for the Tyner Valley Aquifer and Impact of Pumping on the Tessier Aquifer. SRC Publication No. 10417-2E05.

Maathuis, H., B. T. Schreiner, A. Karvonen, J. Fahlman, and N. Shaheen. 2011. Regional geological and groundwater mapping in Saskatchewan: a historical perspective. In *Geohydro 2011 Conference*, 2011. Quebec City, Canada.

Margat, J., Foster, S. and Droubi, A. 2006. Concept and Importance of Non-Renewable Resources. In: Foster, S. and Loucks, D.P., Eds., Non-Renewable Groundwater Resources: A Guidebook on Socially-Sustainable Management for Water-Policy Makers, IHP-VI, Series on Groundwater No. 10, UNESCO, Paris, 13-24.

Martin, F. R. J. 2002. *Gross Evaporation for the 30 Year Period 1971-2000 in the Canadian Prairies*. Agriculture and Agri-Food Canada, Prairie Farm Rehabilitation Administration. Hydrology Report 113, 69 p.

McIntosh, J. C., M. Schlegel, and M. Person. 2012. Glacial impacts on hydrologic processes in sedimentary basins: evidence from natural tracer studies. *Geofluids* 12, no. 1: 7–21.

McLean, J. R. 1971. Stratigraphy of the Upper Cretaceous Judith River Formation in the Canadian Great Plains. Saskatchewan Research Council Geology Division. Report no. 11. 96 p.

McMonagle, A. L. 1987. Stable isotope and chemical compositions of surface and subsurface waters in Saskatchewan, https://harvest.usask.ca/items/59516875-0525-491c-943e-ec73d9f21b03.

MDH Engineered Solutions Ltd. 2011. Hydrogeology Mapping of NTS Mapsheet Saskatoon 73B.

Meneley, W. A., H. Maathuis, E. J. Jaworski, and V. F. Allan. 1979. *SRC observation wells in Saskatchewan, Canada: Introduction, design and discussion of accumulated data*. Vol. 3. 19. Saskatoon, Canada: Saskatchewan Research Council.

Mowat, A. C., D. J. Francis, J. C. McIntosh, M. B. Lindsay, and G. A. Ferguson. 2021. Variability in timing and transport of Pleistocene meltwater recharge to regional aquifers. *Geophysical Research Letters* 48, no. 20: e2021GL094285.

North Greenland Ice Core Project members. 2004. High-resolution record of northern hemisphere climate extending into the last interglacial period. *Nature* 431: 147–51.

Palmer, C. D., and J. A. Cherry. 1984. Geochemical evolution of groundwater in sequences of sedimentary rocks. *Journal of Hydrology* 75, nos. 1–4: 27–65.

Parkhurst, D.L., and Charlton, S.R., 2008, NetpathXL—An Excel® interface to the program NETPATH: U.S. Geological Survey Techniques and Methods 6-A26, 11 p.

Peel, M. C., B. L. Finlayson, and T. A. McMahon. 2007. Updated world map of the Köppen-Geiger climate classification. *Hydrology and Earth System Sciences* 11, no. 5: 1633–44.

Person, M., J. McIntosh, V. Bense, and V. Remenda. 2007. Pleistocene hydrology of North America: the role of ice sheets in reorganizing groundwater flow systems. *Reviews of Geophysics* 45, no. 3.

Plummer, L. N., E. C. Prestemon, and D. L. Parkhurst. 1994. An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, version 2.0. *Water-Resources Investigations Report* 94: 4169.

Power, J. F. Y., and J. S. Schepers. 1989. Nitrate contamination of groundwater in North America. *Agriculture, ecosystems & environment* 26, nos. 3–4: 165–87.

Rodvang, S., and W. Simpkins. 2001. Agricultural contaminants in Quaternary aquitards: A review of occurrence and fate in North America. *Hydrogeology Journal* 9: 44–59.

Ruff, S. E., P. Humez, I. H. de Angelis, M. Diao, M. Nightingale, S. Cho, L. Connors, O. O. Kuloyo, A. Seltzer, and S. Bowman. 2023. Hydrogen and dark oxygen drive microbial productivity in diverse groundwater ecosystems. *Nature Communications* 14, no. 1: 3194.

Saskatchewan Water Security Agency. 2024a. Groundwater Observation Well Network, 2024, https://www.wsask.ca/Water-Info/Ground-Water/Observation-Wells/.

Saskatchewan Water Security Agency. 2024b. Water Wells GIS Site, 2024, https://gis.wsask.ca/Html5Viewer/index.html?viewer=WaterWells.WellsViewer/.

Solomon, D. K., and P. G. Cook. 2000. 3H and 3He. In *Environmental tracers in subsurface hydrology*, 397–424. Springer.

Theodorsson, P. 1996. *Measurement of weak radioactivity*. River Edge, New Jersey: World scientific.

US EPA Region 1. 2017. Low stress (low flow) purging and sampling procedure for the collection of ground water samples from monitoring wells. *EQASOP-GW4*, 30 p.

Wassenaar, L. I., and M. J. Hendry. 2000. Mechanisms controlling the distribution and transport of 14C in a clay-rich till aquitard. *Groundwater* 38, no. 3: 343–49.

Whitaker, S., and E. Christiansen. 1972. The Empress Group in southern Saskatchewan. *Canadian Journal of Earth Sciences* 9, no. 4: 353–60.

Wick, K., C. Heumesser, and E. Schmid. 2012. Groundwater nitrate contamination: factors and indicators. *Journal of environmental management* 111: 178–86.

Wolfe, S. A., J. Ollerhead, and O. B. Lian. 2002. Holocene eolian activity in south-central Saskatchewan and the southern Canadian prairies. *Géographie physique et Quaternaire* 56, no. 2: 215–27.

Figures

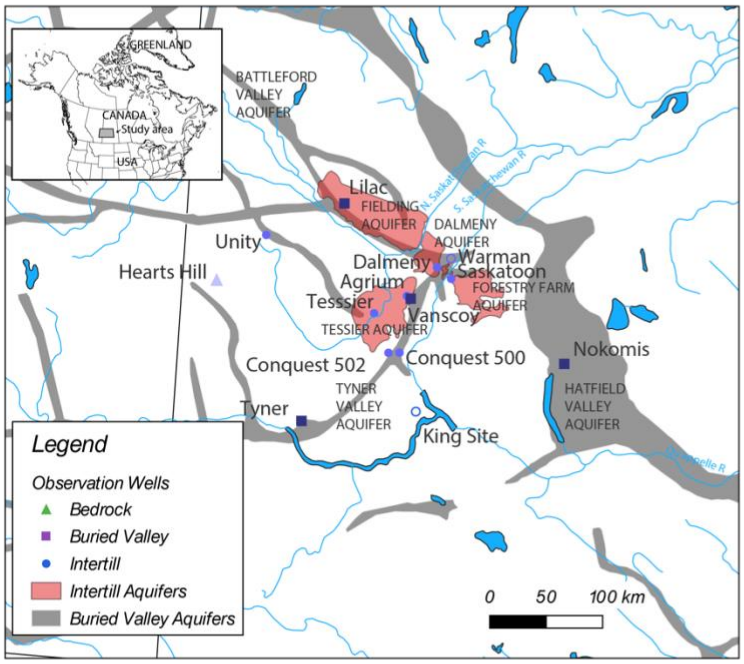

Figure 1: Site map (a) showing sampled wells, aquifer type, and the approximate extent of buried valley aquifer locations (buried valley aquifer shape file modified from Cummings et al. 2012)

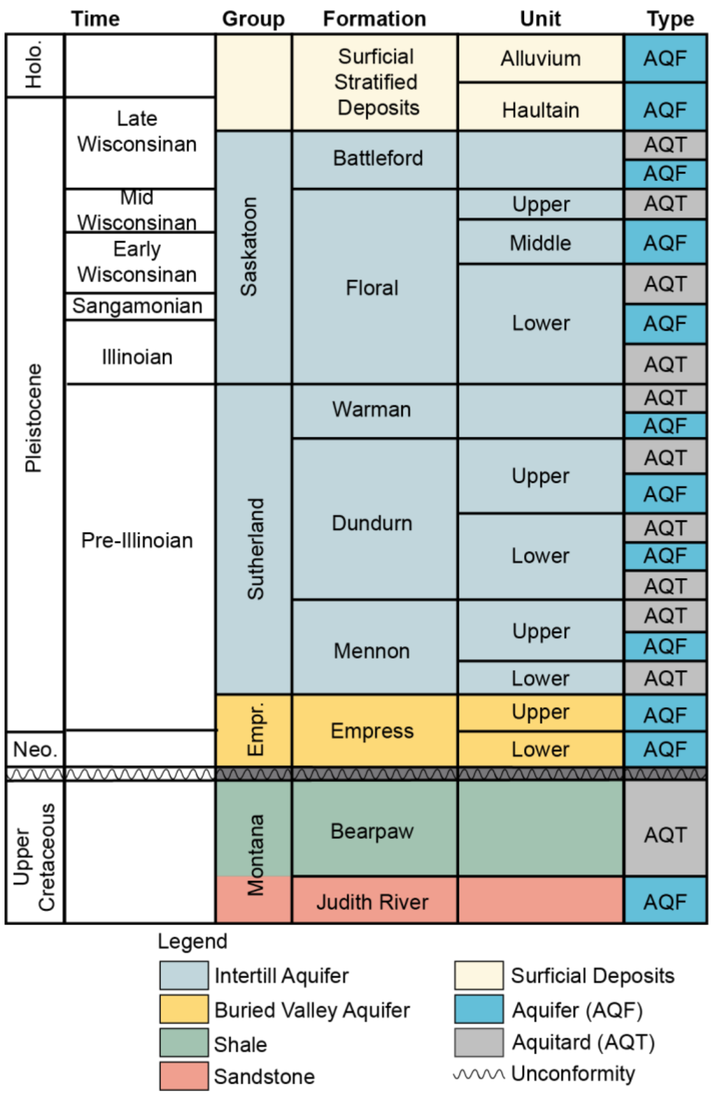

Figure 2: Generalized stratigraphic column (b) showing time, group, formation, unit, and type (aquifer/aquitard) of the study area. Based on Christiansen (1992) and MDH (2011).

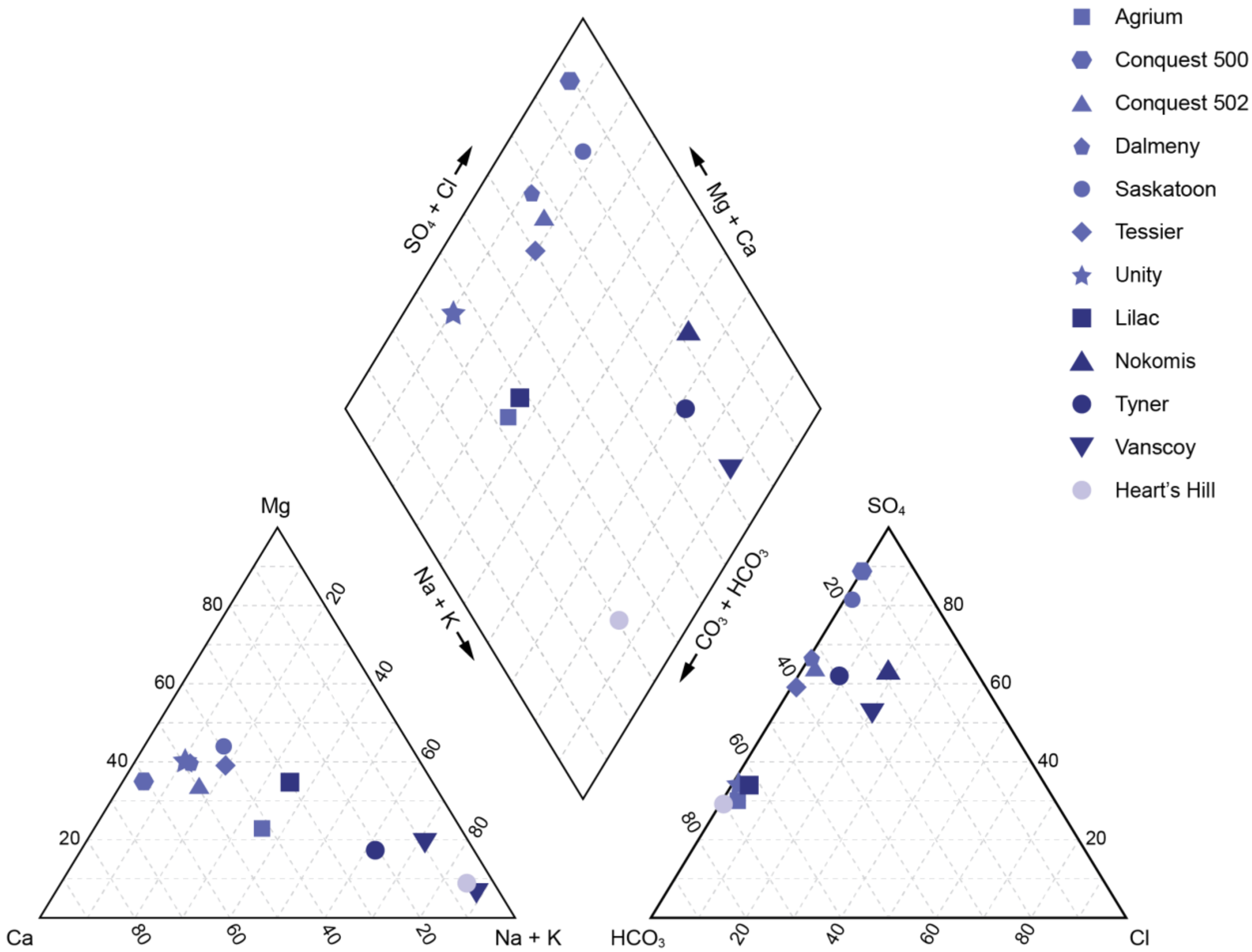

Figure 3: Piper plot showing the distribution of major ions in samples analyzed in this study. Samples higher in Na and Cl tend to be buried valley samples, while intertill aquifers have a range of dominant cations with very little Cl relative to HCO_3 and SO_4.

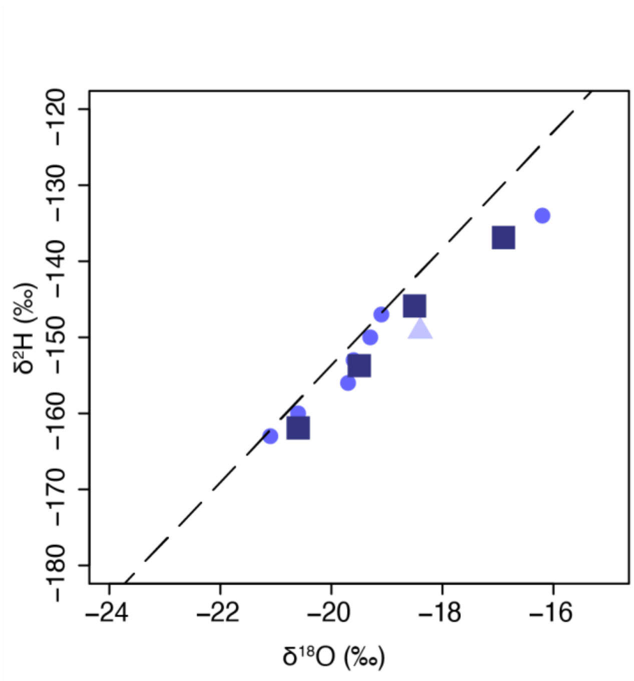

Figure 4: Stable water isotope values of intertill (*blue circles*), buried valley (*purple squares*), and bedrock (*green triangle*) aquifers relative to the Local Meteoric Water Line (*dashed black line*) (Koehler 2019).

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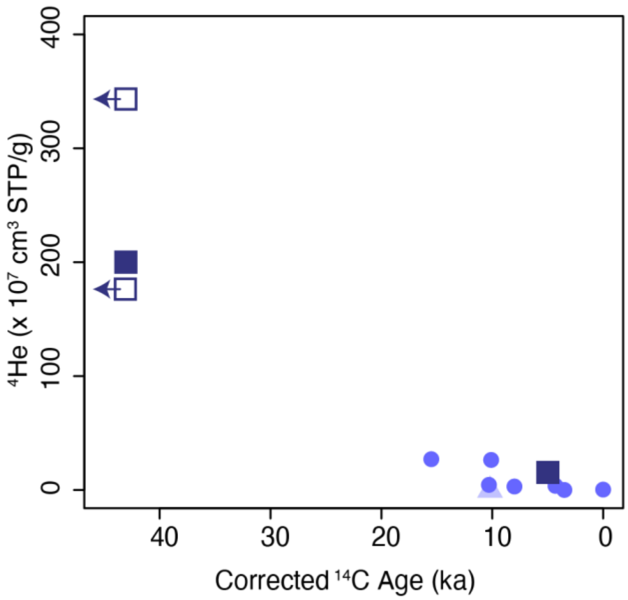

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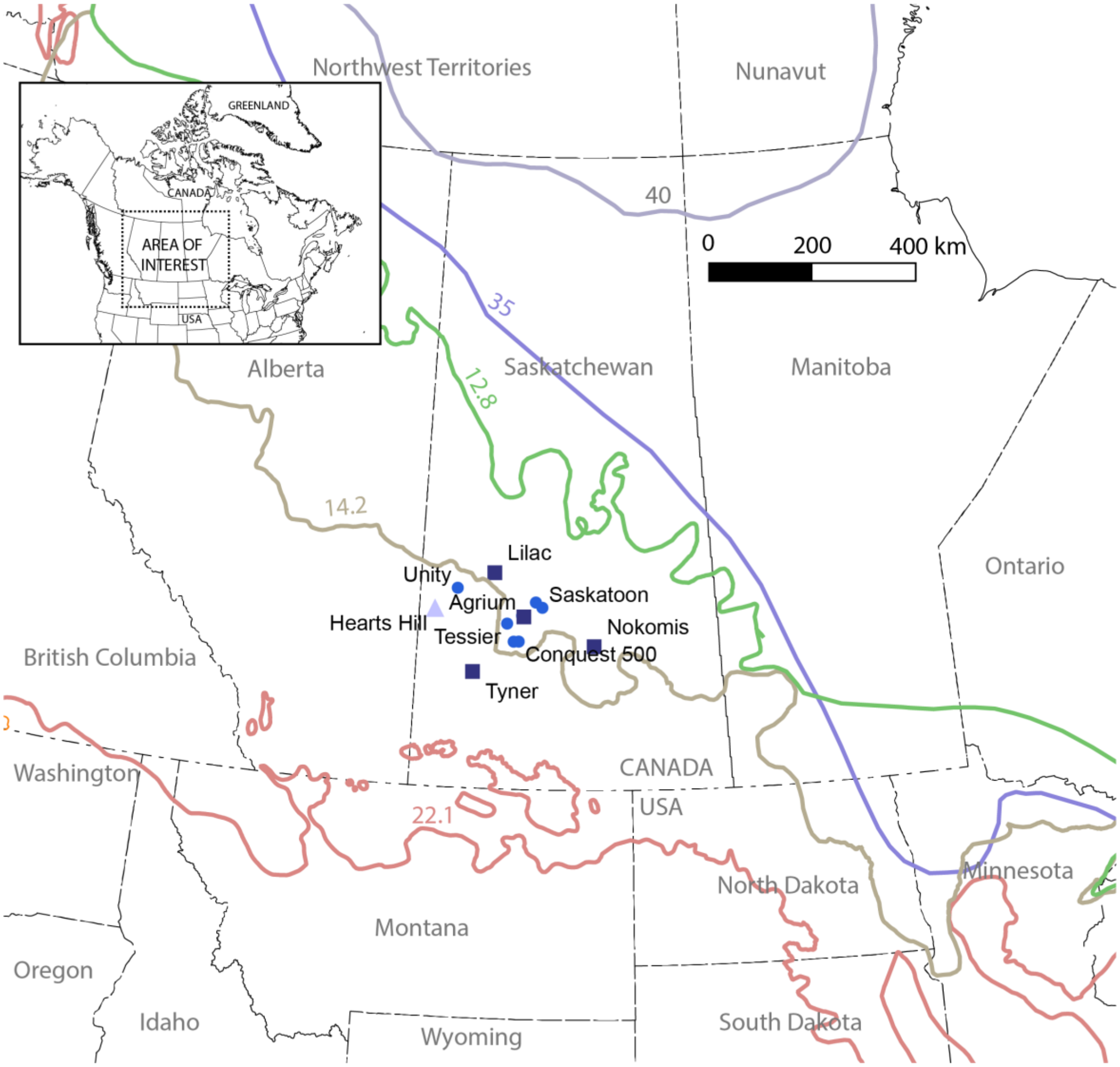
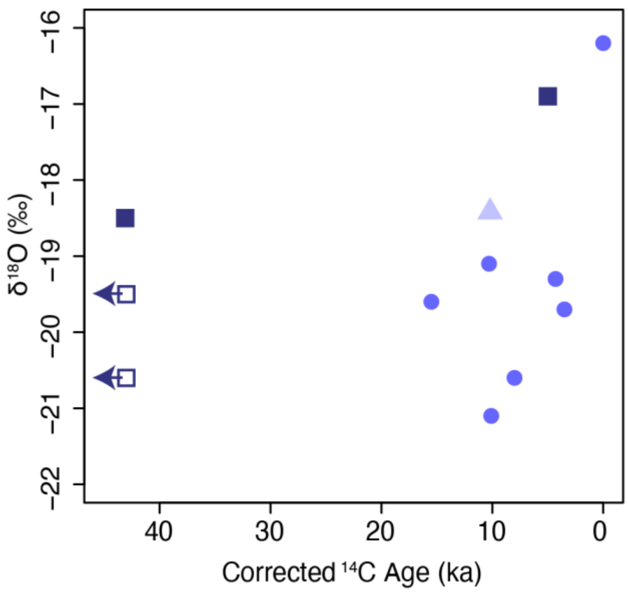
753 **Figure 5**: Air-corrected radiogenic ^{4}He (cm^3 STP/g) versus corrected ^{14}C age (ka) of intertill (*blue*
754 *circles*), buried valley (*purple squares*), and bedrock (*green triangle*) aquifers. Open purple
755 squares indicate ^{4}He values for samples with no detectable radiocarbon.



756
757
758 **Figure 6**: Study area showing the southern extent of the Laurentide Ice Sheet (ages in ka)
759 (Dalton et al. 2020, 2022). The region was glaciated during the LGM (i.e., 22.1 to 14.2 ka) for
760 intertill (*blue circles*), buried valley (*purple squares*), and bedrock (*green triangle*) aquifers. The
761 study area has been ice-free since at least 12.8 ka and prior to 30 ka back to at least 65 ka.

762 

763 **Figure 7**: $\delta^{18}O$ values (‰) show no clear relation with corrected groundwater radiocarbon age

764 for intertill (*blue circles*), buried valley (*purple squares*), and bedrock (*green triangle*) aquifers.

765 Note: open purple squares indicate $\delta^{18}O$ values for samples with non-detect ^{14}C.