Occurrence, origin, and fate of aqueous contaminants in Alberta groundwater

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PROJECT INFORMATION:

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PROJECT PARTNERS

The success of the project would not have been possible without the tremendous contributions of three essential project partners. The field sampling teams of Alberta Environment and Protected Areas (AEPA) were instrumental in obtaining highest-quality samples that yielded novel insights into the aqueous and gas geochemistry of groundwater in Alberta and its microbial populations involved in element cycling in aquifers. The hydrogeological, hydrogeochemical and mapping expertise of project partners at the Alberta Geological Survey (AGS) and AEPA was essential for arriving at many key findings of this 3-year project. Furthermore, this project would not have been possible without the willingness of Alberta Health (AH) to grant access to their extensive high-quality database of aqueous geochemistry compositions for Alberta groundwater. The Alberta Biodiversity Monitoring Institute (ABMI) also began supporting the project in 2022. The tremendous efforts by colleagues at AEPA, AGS, and AH to contribute to the success of this project are gratefully acknowledged.

EXECUTIVE SUMMARY

The availability of high-quality water is of key importance for Alberta's economic future development. The **objective** of this project was to determine the occurrence of key contaminants in groundwater throughout Alberta and to assess groundwater quality in a 3D aquifer framework. Where possible it was also attempted to understand the origin and potential fate of selected contaminants including methane, ethane, propane, nitrate, manganese, iron, sulfate, selenium, fluoride and radon.

During the 3-year project, the research team amalgamated a unified water quality database using archived water quality data from Alberta Health (AH), the Baseline Water Well Testing (BWWT) program, the Groundwater Observation Well Network (GOWN), the Alberta Water Well Information Database (AWWID), and data from Alberta Agriculture and Irrigation (AGI). This database was further complemented by analytical results for newly sampled groundwater obtained from GOWN wells. After careful quality assurance and quality control (QA/QC) procedures, this effort has yielded an unprecedented groundwater quality database with 131,491 samples from across Alberta with > 10 million water quality parameters. This unprecedented database for Alberta groundwater was subsequently used to assess the occurrence of select groundwater contaminants throughout Alberta.

Circa 65% of the groundwater samples have total dissolved solids (TDS) concentrations <1000 mg/L while 34% of the samples have TDS concentrations between 1,000 and 4,000 mg/L, and only 1% of the samples are saline (e.g., TDS >4,000 mg/L). A high proportion of groundwater samples were found to have mildly to highly reducing redox conditions ranging from post-oxic to sulfidic and methanic conditions. Consequently, circa 80% of the groundwater samples had negligible nitrate concentrations, while only 3% of the samples exceed 10 mg/L nitrate-N.

For manganese (Mn), 2,217 samples exceeded the maximum acceptable concentration (MAC) for drinking water of 0.12 mg/L, while arsenic (As) concentrations exceeded the MAC of 0.01 mg/L in 443 samples. Elevated Mn and As concentrations were mainly observed in shallow aquifers in sediments above bedrock characterized by post-oxic redox conditions.

The concentration of sulfate in Alberta groundwater is highly variable with 22% of the samples exceeding the aesthetic objective (AO) for drinking water of 500 mg/L. Oxidation of sulfide minerals in tills and shallow bedrock was identified as the predominant source of sulfate in groundwater. It was also found that a considerable number of groundwater samples in Alberta have fluoride (F) concentrations above the MAC of 1.5 mg/L. Hotspots of elevated F were always associated with groundwater having low Ca concentrations and Na-dominated water types. Only 25 samples exceeded the MAC for selenium (Se) of 0.05 mg/L.

Due to the often highly reducing conditions in some aquifers of Alberta, methane was detected in 1396 groundwater samples. Stable isotope analyses revealed that methane is predominantly of microbial origin. Radon was also found to be ubiquitous in groundwater obtained from 47 provincial groundwater observation well network (GOWN) wells but with comparatively low concentrations <65 Bq/L and is therefore not considered a significant health risk.

Microbiological analyses on samples obtained from GOWN wells revealed that older groundwaters, especially those from aquifers containing coal and shale, had surprisingly high numbers of bacteria sustaining productive microbial communities that are actively involved in cycling of oxygen, nitrate, sulfate and methane among others. Hydrogen was identified as a major energy source driving bacterial growth and cycling of methane in aquifers, while aquifer-internal formation of oxygen from nitric oxide was also revealed by metagenomic analyses.

The information compiled in this project was used to further advance the development of a 3D aquifer framework model for Alberta. This has resulted in an improved differentiation between different bedrock aquifers and aquifer-hosting sediments above bedrock including an updated stratigraphic framework for basal sand and gravel units that are part of the Empress group.

Outcomes of this project include an unprecedented knowledge of the spatial distribution of groundwater quality parameters across Alberta and an improved understanding of the province-wide occurrence, origin and fate of select groundwater contaminants having health implications for humans, livestock and ecosystems.

Key learnings are that there is astonishingly detailed information available on the quality of groundwater in Alberta based on the availability of 131,491 QA/QC'ed groundwater samples. This project has amalgamated this information into a unified dataset that reveals the spatial distribution of groundwater quality parameters across Alberta. This has provided an improved understanding of the occurrence, the origin and the fate of select groundwater constituents and contaminants in shallow groundwater of Alberta.

Broader benefits of the key learnings to users of groundwater in Alberta include a province-wide and systematic understanding of the quality of groundwater including its salinity, the water type, and the redox state of the groundwater. Salinity, water type and redox conditions are the key factors controlling the occurrence and fate of many groundwater constituents and contaminants including nitrate, manganese, arsenic, fluoride, sulfate and methane.

INTRODUCTION

Sector Introduction: The availability of high-quality water is of key importance for Alberta's economic future development. Shallow groundwater is a frequent source of water for domestic and livestock use in many rural areas. Groundwater also supports healthy aquatic ecosystems, for example by providing baseflow to sustain riverine flows. To ensure the future availability of high-quality groundwater in Alberta, it is important to better understand of the province-wide occurrence, origin, and fate of select groundwater contaminants.

Knowledge Gaps: Throughout the last few decades there have been a considerable number of groundwater studies investigating various aspects of groundwater quality in Alberta. Most of these studies were regionally restricted to specific sites and targeted only select contaminants of interest (e.g., nitrate, arsenic, methane). Individual government agencies created and maintained their own groundwater quality databases for their respective purposes, such as Alberta Health (AH), Alberta Environment and Protected Areas (AEPA), and Alberta Agriculture and Irrigation (AGI), among others. While this approach yielded numerous novel discoveries with respect to specific environmental issues and health-related questions regarding groundwater quality, it did not provide insights into regional patterns of groundwater quality and its evolution throughout the province.

By combining water quality information from five large data sources into a unified water quality database, with 131,491 groundwater samples, the research team has gained unprecedented insights into the spatial distribution of groundwater quality parameters in Alberta. This enabled the research team, for the first time to identify regional, spatial, and depth-related trends in current water types, redox conditions, and groundwater salinity variations, and explore natural and anthropogenic causes that impact groundwater quality. To our best knowledge, no other research team or government agency has a comparable data source that describes the current status of groundwater quality across the province in such a comprehensive fashion.

PROJECT DESCRIPTION AND METHODOLOGY

Knowledge Description: The objective of this project was to determine the occurrence of key contaminants in groundwater throughout Alberta and to assess groundwater quality in a 3D aquifer framework. Where possible, a further objective was to understand the origin and potential fate of selected contaminants including methane, ethane, propane, nitrate, manganese, iron, sulfate, selenium, fluoride and radon by combing geological, hydrogeological, geochemical, isotopic and microbiological information.

Updates to Project Objectives: There was no need to modify the project objectives during the research program.

Performance Metrics: The performance metrics that were targeted for this project were the following:

- 80,000 samples compiled and QA/QC-ed to generate a unified dataset.
- 360 samples analyzed for metagenomics including 180 existing samples
- 60 samples analyzed for radon contents
- The construction of a 3D aquifer framework model with groundwater samples allocated from the unified geochemical database
- The production of 5 aquifer-specific groundwater quality maps
- 4 highly qualified personnel trained
- 6 conference presentations given and 6 manuscripts to be published

The project was successfully completed using the methodology described in the original proposal. Task 1 was completed by compiling a high-quality groundwater database of 131,491 samples and by determining salinity, water type and redox state for all samples using excel-based calculations and aqueous geochemistry modeling software. Mapping of groundwater contaminants with a sufficient sample and data density was conducted using GIS techniques and yielded province-wide maps for various groundwater constituents (task 2). Sampling of GOWN wells to obtain samples for geochemical, isotopic, and microbial and metagenomic analyses (task 3) and radon measurements (task 4) was conducted with the fantastic support of the excellent field crews of AEPA. Identifying aquifer units for the sediments above bedrock and the development of 3D aquifer framework models was advanced by generating a 3D machine learning model of sand and/or gravel probability in the sediments above bedrock and 3D geostatistical models for select groundwater constituents such as sulfate and fluoride concentrations in aquifers in central and southern Alberta. Consequently, all sub-tasks and milestones were reached by the end of the 3-year project.

PROJECT RESULTS

Key Observations and Results

Task 1: The initial task of this 3-year project was the compilation and quality review of water chemistry data from approximately 190,000 groundwater samples from various sources (task 1, milestone 1). The water chemistry data were harmonized and subject to a thorough QA/QC assessment. The resulting product is a reliable, unified dataset with 131,491 high-quality groundwater samples from the 5 different major data sources: GOWN, BWWT, AH, AWWID and AGI. Figure 1a displays the number of groundwater samples per quarter township that passed the stringent QA/QC screening process. To our best knowledge, this has resulted in the most comprehensive and regionally extensive unified groundwater quality database available in Alberta.

For all groundwater samples, total dissolved solids (TDS) were calculated to assess groundwater salinity, and water types and redox states were assigned (task 1, milestone 2). Figure 1b shows the median TDS concentration per quarter township. 65% (85,977) of the 131,491 groundwater samples had TDS concentrations of less than 1000 mg/L, while 34% (44,298) of the groundwater samples had TDS contents ranging between 1000 and 4000 mg/L. Only 1216 groundwater samples were characterized by TDS concentrations >4000 mg/L and are hence classified as saline, representing only 1% of the 131,491 samples in the unified dataset.

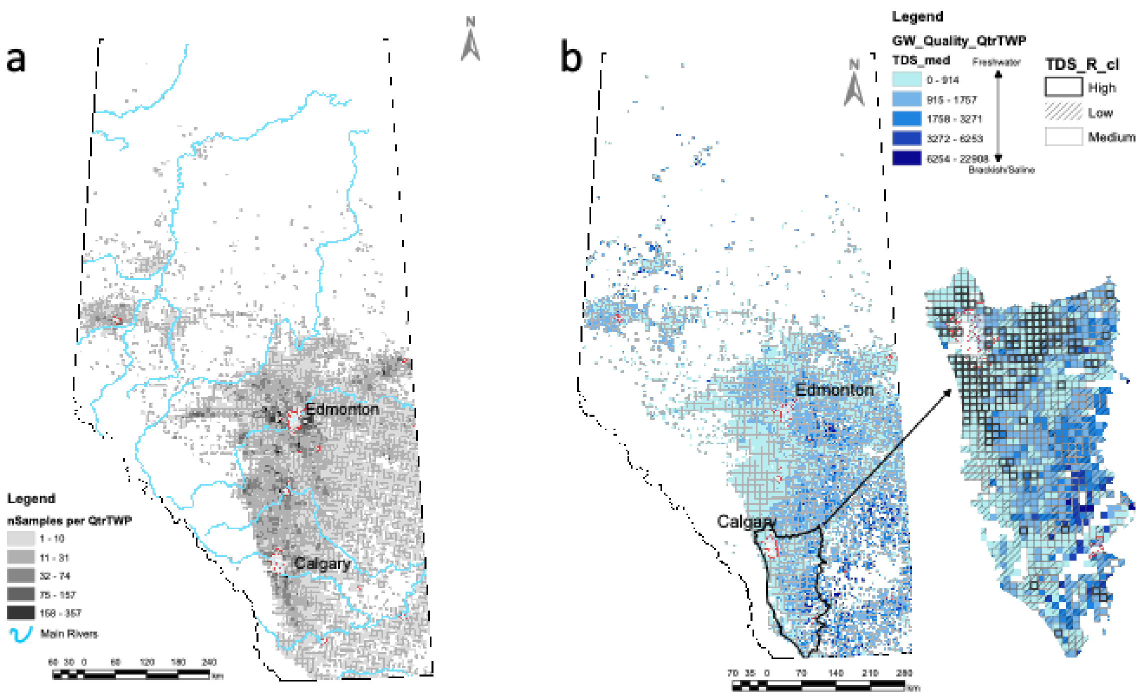


Figure 1: a) The number of groundwater samples per quarter township that passed the stringent QA/QC screening process. b) Median total dissolved solid concentration (mg/L) per quarter township and representativeness (high, low, and medium) of the median value based on the number of samples per quarter township and coefficient of variation.

During the 3-year project, the research team also evaluated groundwater quality evolution with respect to well depths and geological formation in which the water wells are completed (task 1, milestone 2) using the Calgary-Lethbridge Corridor (CLC) as a focus area. Despite local geochemical heterogeneities, the chemical evolution of groundwater follows a regional, topographically driven groundwater flow pattern. As shown in Figure 2A, groundwater evolves from a low TDS, near-neutral, Ca-Mg-HCO_3 water type with high Ca/Na ratios in the west, towards higher TDS, Na-SO_4 and Ca-SO_4 waters and alkaline Na-HCO_3 waters with low Ca/Na ratios in the east (Figure 2C). As shown later in this report, the evolution towards high TDS and SO_4-dominated water commonly occurs due to recharge through sulfide-bearing till, whereas the evolution towards low Ca/Na ratios of waters (Figure 2A) in the eastern CLC is mostly a result of cation exchange of Ca for Na, silicate weathering, and mixing with more saline formation waters (Figure 2B).

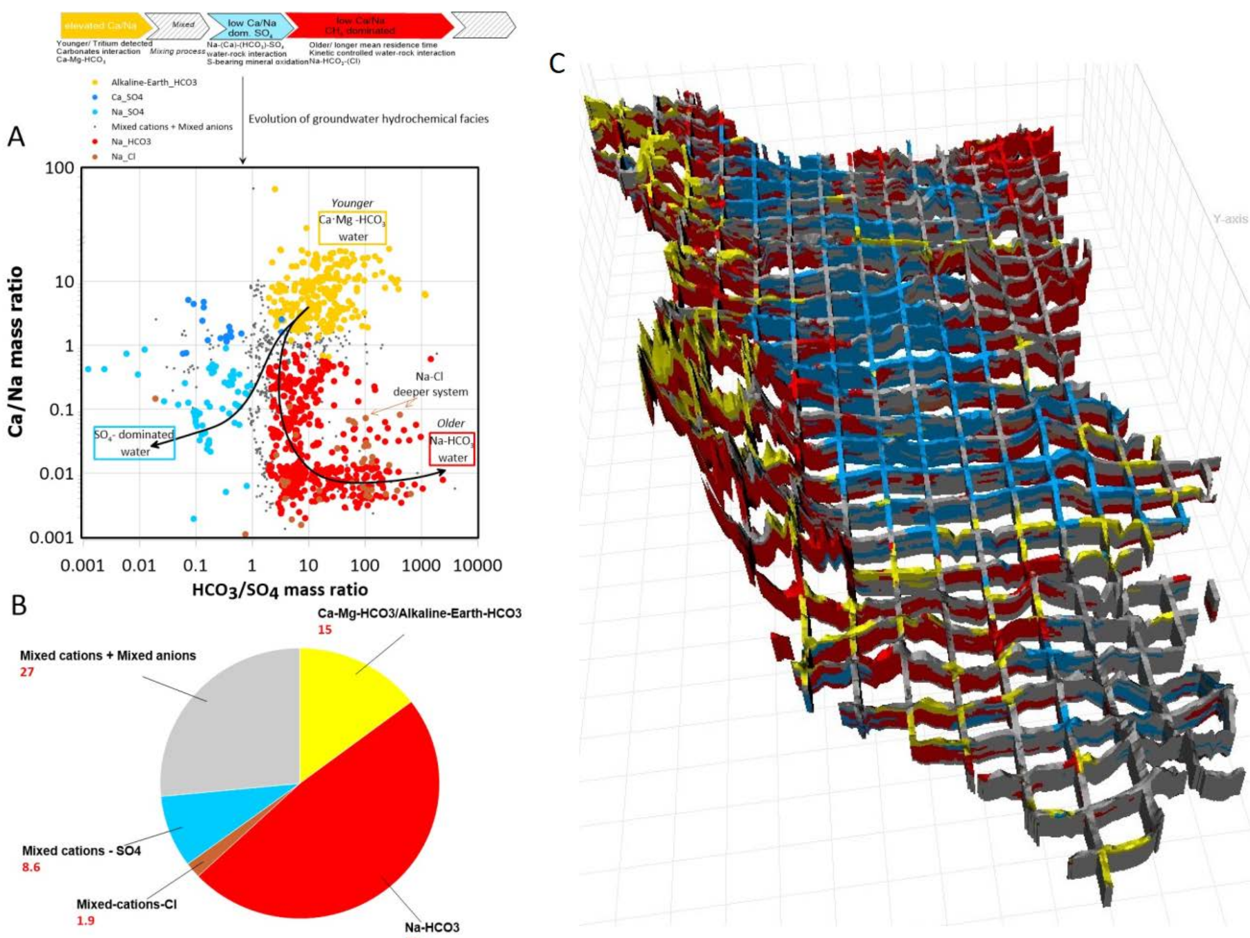
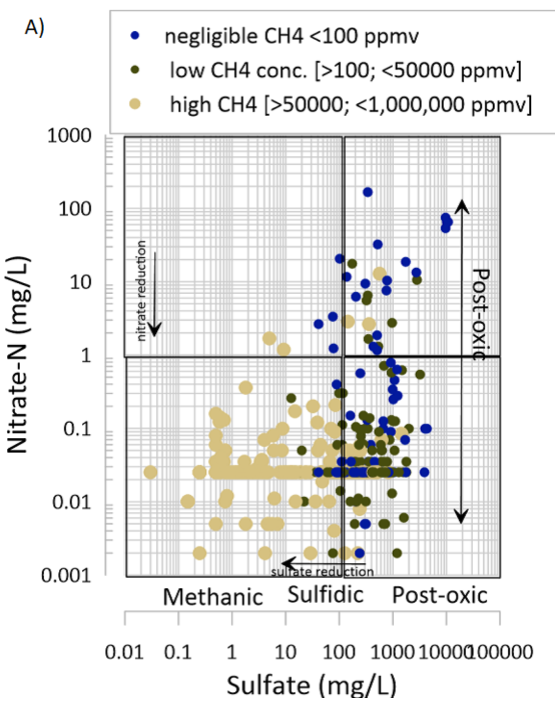


Figure 2: Evolution of groundwater types in the Calgary-Lethbridge Corridor (CLC): a) Water types illustrated in a cross-plot of Ca/Na and HCO_3/SO_4 ratios. B) Pie chart showing the distribution of different water types. C) 3-D groundwater model showing the occurrence of different water types in the CLC.

For all groundwater samples the redox status was determined (task 1, milestone 2) using threshold concentrations of redox sensitive species such as dissolved oxygen, nitrate, manganese, iron, sulfate and methane. Since concentrations of dissolved oxygen, manganese, iron and methane are often not reported, nitrate and sulfate were used as indicators to determine the prevailing redox conditions (Figure 3A). Where possible, additional redox sensitive species such as Mn, Fe and/or CH_4 were used to achieve a more refined redox zone classification based on the presence or absence of redox sensitive species in groundwater (Figure 3B). This analysis revealed that groundwater in the CLC is predominantly under moderate to highly reducing conditions with the following redox zone order: methanic (49%) > post-oxic (21%) > sulfidic (11%) > oxic-anoxic mixture (11%) > anoxic mixture zones (9%). As groundwater migrates away from the recharge zones, a systematic redox sequence is observed. Post-oxic redox zones, dominated by the denitrification of nitrate and reduction of manganese and iron were predominately found in groundwater samples collected from water wells completed in sediment above bedrock, and within the Paskapoo and Porcupine Hills formations. Groundwater samples collected from water wells completed within the Scollard and Willow Creek formations are predominantly associated with sulfidic zones, where bacterial sulfate reduction occurs facilitated by *Desulfomicrobium*, or methanic zones that were characterized by favorable conditions for methanogenesis enabling the formation of microbial methane as evidenced by high occurrences of *Methanobacterium* (task 3, milestone 1). The successful assignment of redox zones in the context of hydrogeological frameworks, as demonstrated here for the CLC, is of crucial importance for understanding the occurrence, sources, and fate of select groundwater contaminants.

A)



B)

Criteria used for assigning redox categories to groundwater in CLC area: identifying dominant ongoing redox process(es)				Oxygen	Nitrate	Manganese	Iron	Sulfate
			Threshold [mg/L]	1.0	1.0	0.04	0.2	100-400
General	Redox processes		Abbreviation					
Post-oxic	NO_3-reducing	Mixed process (NO_3-reducing/sulfate reducing or NO3reducing +pyrite oxidation)	NO_3red or NO_3red-SO_4red	<	≥	<	<	≥
Anoxic	Mn(IV)-reducing	Methanic	Mn(IV)red or CH4fm	<	<	≥	<	<
Anoxic	Fe(III)-reducing	Methanic	Fe(III)red or CH4fm	<	<	<	≥	<
Anoxic	SO_4-reducing		SO_4red	<	<	<	<	≥
Anoxic	Methanic		CH_4fm	<	<	<	<	<

Figure 3: Example of redox zone delineations for the CLC based on A) nitrate-sulfate-methane diagrams, and B) criteria used for assigning redox categories and probable dominant redox processes based on water chemistry threshold data.

Task 2: Mapping the occurrence of select groundwater contaminants at the provincial scale (task 2, milestone 1) was conducted using an innovative approach for spatial data representation in a fashion that is easily accessible for end-users and stakeholder groups. The geochemical mapping approach summarizes the median concentrations of select contaminants stratigraphically, by the geologic formation in which the water wells are completed, and spatially into quarter township polygons. For each quarter township, the median concentration of each groundwater constituent is determined along with a statistical summary consisting of minimum, maximum, median and quartile values. Variation in ion concentration around the median value in each ¼ township is measured using quartile data (Q1, Q3 and IQR) and, when combined with sample size, provides an indication of how well represented the median value is within the quarter township (Representativity Index, Figure 1b).

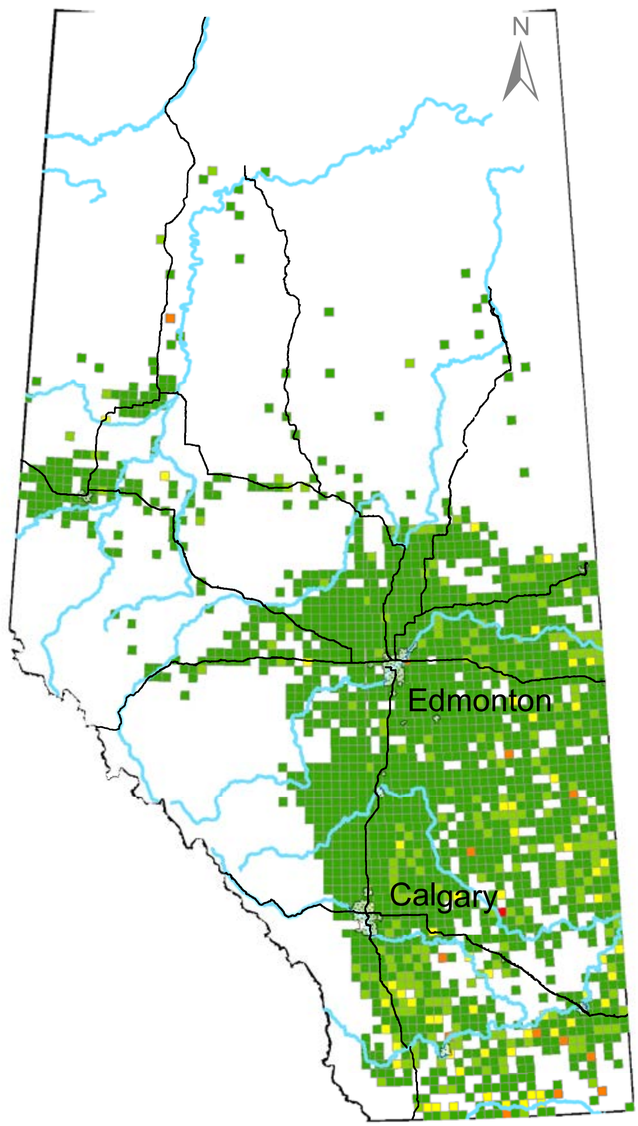


Figure 4: Median nitrate-N concentration (mg N/L) in groundwater per township at the provincial scale.

Nitrate concentration data are reported for 75,678 samples in the unified dataset and the regional distribution of median nitrate-N concentrations per quarter township is shown on Figure 4. Circa 66% of the samples (n=49,184) had negligible nitrate concentrations (e.g. below the analysis detection limit). This indicates that either nitrate never entered the aquifer or, in the case of aquifers with anoxic redox environments, previously occurring nitrate is not stable and has been removed via denitrification. When detected, nitrate is found in groundwater from both surficial sediments and bedrock formations with no statistically significant difference between them. Only

3.2% of the groundwater samples analyzed for nitrate (n=2,442) had nitrate-N concentrations above the Health Canada drinking water limit of 10 mg/L. Sources of nitrate were identified using N and O isotope ratios of a small number of nitrate-containing samples obtained from GOWN wells. Nitrate was shown to be derived from nitrification of soil organic matter in some groundwater samples, while in samples with the highest nitrate concentrations, it was shown to be frequently derived from manure. However, identification of nitrate sources using stable isotope techniques is often compromised by N and O isotope fractionation during partial denitrification, making it somewhat challenging to conclusively determine the initial isotopic fingerprint of the nitrate source.

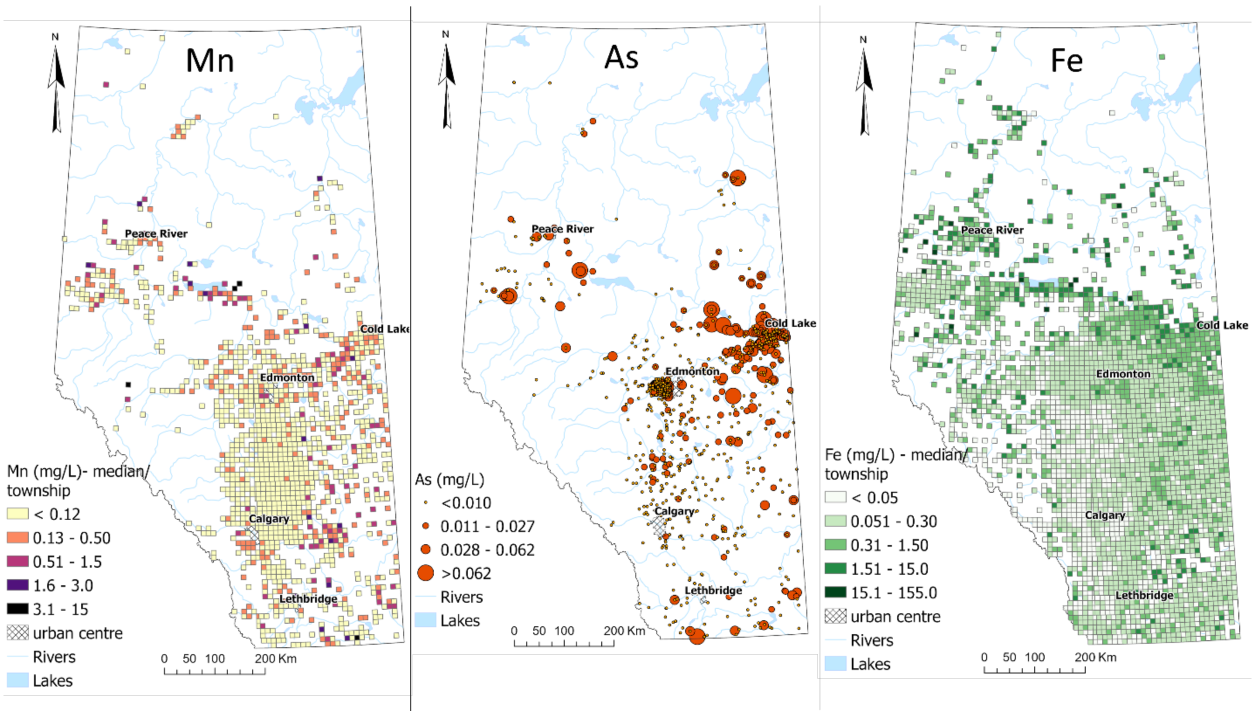


Figure 5: Spatial distribution of Mn (left), As (middle), and Fe (right) concentrations in groundwater samples of Alberta.

Manganese (Mn) concentrations were reported in 11,792 groundwater samples or 9% of the unified dataset with most of these samples collected after the year 2000. 20% of these samples (n=2,377) had Mn concentrations below the detection limit. Elevated Mn concentrations above the maximum acceptable concentration (MAC) guideline for drinking water (> 0.12 mg/L, Health Canada 2019) were observed in 19% (n=2,217) of the remaining Mn-containing groundwater samples. The mean and median concentrations of Mn in groundwater were 0.15 and 0.03 mg/L (n=9415), respectively. Figure 5 (left) shows the spatial distribution of median Mn concentrations in groundwater per township. Further investigations revealed that the highest proportion of groundwater samples with elevated Mn concentrations occurred in sediments above bedrock (32%), followed by aquifers in the Paskapoo (21%), Scollard (17%), and Horseshoe Canyon formations (13%). Elevated Mn concentrations occur primarily at depths of less than 50m below ground surface, especially in aquifers in sediments above bedrock that are characterized by mildly reducing conditions.

A total of 2871 samples have arsenic (As) concentrations reported in the unified dataset with 52% (n= 1,501) of the samples having As concentrations below the detection limits. The percentage of groundwater samples exceeding the Health Canada Drinking Water Guideline MAC of 0.01 mg/L for As is 15% (n=443) of all samples, and 32% of the samples with detected As concentrations (n= 1,370). Figure 5 (middle) shows the regional distributions of As concentrations in groundwater. Further analysis revealed that the highest proportion of groundwater samples with elevated As concentrations is associated with aquifers in sediments above bedrock. Low concentrations of arsenic are observed primarily in shallow Ca(Mg)-HCO_3 type groundwater (<30 mbgs). As groundwater evolves geochemically and becomes more reducing, the reductive dissolution of iron oxyhydroxides likely plays a key role in releasing reduced As species into groundwater, which likely explains elevated concentrations.

Although iron (Fe) in water is not considered a high-risk element affecting human health, elevated concentrations can negatively impact water well infrastructure as well as other household items. Therefore, in Canada the aesthetic water quality objective for iron is 0.3 mg/L. Fe concentrations in groundwater varied considerably from not detected (<0.01 mg/L) to up to 200 mg/L. The percentage of groundwater samples from the unified dataset exceeding the aesthetic objective of 0.3 mg/L was 32% (n=42,710) from a total of 131,491 samples in the unified dataset. Figure 5 (right) shows that elevated Fe concentrations in groundwater occur predominantly in the eastern and northern portion of the province, especially in aquifers in sediments above bedrock that are characterized by post-oxic reducing conditions.

Sulfate occurrence in groundwater at the provincial scale is shown in Figure 6. Sulfate commonly contributes to high TDS in Alberta's groundwater and varies considerably geographically, even at the sub-watershed scale. In the prairies of southern and central Alberta, sulfate concentrations vary from below the detection limit to >10,000 mg/L (n=34) with 22% of the samples above the drinking water aesthetic objective of 500 mg/L. The highest sulfate concentrations were often found in aquifers in the sediments above bedrock and higher median sulfate concentrations were predominantly detected towards the southeastern portion of the province. The source of sulfate is interpreted to be predominantly from recharge through oxidized, pyrite-rich till or shallow bedrock, which is supported by S and O isotope ratios from GOWN well samples showing that sulfate is predominantly derived from the oxidation of sulfur-bearing minerals such as pyrite. Furthermore, S and O isotope ratios of sulfate provided evidence for the occurrence of bacterial sulfate reduction in several aquifers. These findings indicate that both sulfur oxidation and bacterial sulfate reduction play a key role in governing the occurrence of sulfate in aquifers throughout Alberta. This observation was supported by amplicon sequencing of bacterial 16S rRNA genes that demonstrated the prevalence of sulfur oxidizing *Sulfurimonas* and *Sulfuricurvum* as well as sulfate reducing bacteria represented by *Candidatus* Desulforudis and *Desulfatirhabdium* (task 3, milestone 1).

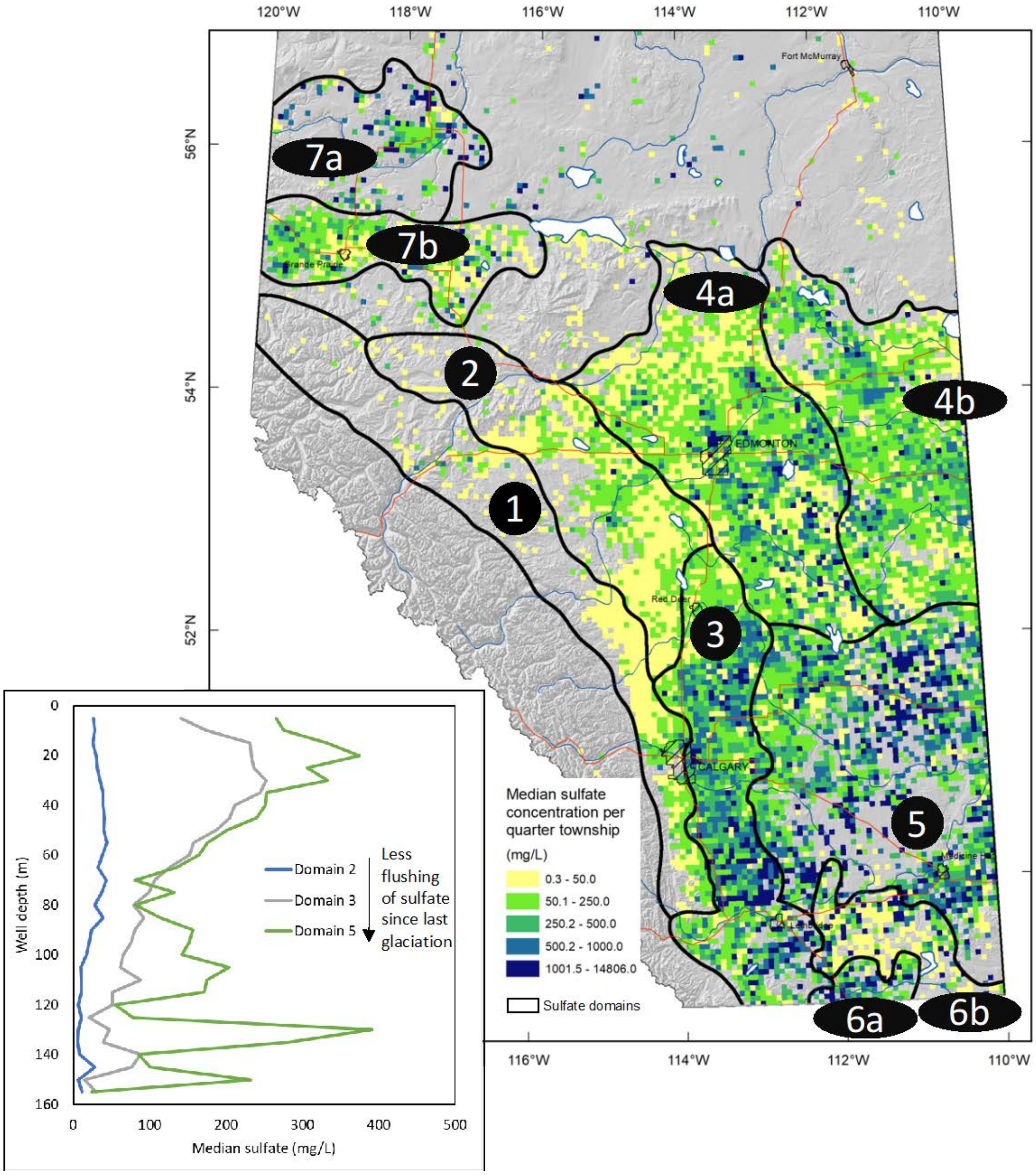


Figure 6: Median sulfate concentrations per quarter township in the uppermost aquifer (i.e., sediments above bedrock or bedrock).

Table 1: Provincial domains governing the concentration of sulfate in groundwater.

Domain	Description
1	**Lack of sulfate source** • Cordilleran ice sheet till low in sulfate due to a low abundance of sulfur-bearing minerals in the Rocky Mountain source area.
2	**Lack of sulfate source and/or higher flushing** • Laurentide ice sheet till low in sulfate due to low abundance of sulfur-bearing minerals in local bedrock (Paskapoo Formation). • And/or wetter climate and higher recharge and groundwater circulation. Water in the shallow subsurface is relatively young and flushed of sulfate.
3	**Sulfate from till and coal?** • Laurentide ice sheet till with no clear source area of sulfur-bearing minerals considering the last glacial maximum ice flow from the northwest across the Paskapoo Formation. • Perhaps sulfate-bearing till from an unrecognized glacial ice flow direction prior to the last glacial maximum or from coal deposits? Or climate and permeability lowers flushing rate compared to domain 2?
4	**Sulfate from till with local bedrock source** • Highly variable sulfate concentrations. • Sulfate from till with shale bedrock sources (Lea Park Formation and small portion of Bearpaw formation). • Shallow coals may contribute to sulfate generation either from entrenchment within till or in-situ oxidization.
5	**Sulfate from shallow shale bedrock and till, low flushing** • Sulfate directly from Bearpaw Formation where sediments are thin, and from till with local Bearpaw Formation source. • Thicker sediment with deep redox depth may generate more sulfate. • Dry climate, low recharge. • Low flushing of sulfate but high sulfate at depth.
6	**Shallow sulfate from till, very low sulfate at depth** • High sulfate from till in the recharge area of the Milk River Formation where groundwater is relatively young (6a). • Decrease in sulfate to very low values in the deeper, downgradient portion of the Milk River Formation where groundwater is old (6b). • Domain 6b underlies domain 5.
7	**Sulfate from till with local bedrock source** • Higher sulfate in domain 7a closer to shale bedrock source and drier climate.

This project revealed the key controls on sulfate concentrations in shallow aquifers at a provincial scale, where geology, ice flow trajectory, geochemical processes, climate, permeability, recharge/discharge conditions, and flow systems vary to a considerable extent spatially. To identify major controls on the level of sulfate concentrations in aquifers from local to provincial scales, we used the unified geochemical database, a 3D model of sandiness above bedrock (task 5), regional mapping of the depths of redox zones, ice flow and a principal component and cluster analyses of hydro-chemical and hydro-physical parameters relating to sulfate mobilization. At the provincial scale, geology, glacial history, ice flow trajectory and climate largely explain variations in sulfate distribution in shallow aquifers, with sulfate concentrations increasing towards the drier southeast (Figure 6). A more detailed investigation between Calgary and Strathmore revealed lower sulfate concentrations in shallow aquifers where deeper regional groundwater is moving upwards towards the surface. Although sulfate originates predominantly from the tills, glacial ice flow trajectories impact the amount of sulfur-bearing material in the near-surface sediments. For example, till from the Laurentide ice flow over the northern part of the Paskapoo Formation is low in sulfur-bearing minerals due to their low abundance in the bedrock of the source region. At a watershed scale, low sulfate concentrations in aquifers are generally associated with greater proportions of sandiness, higher recharge, and proximity to depressions, where sulfate has presumably been flushed to discharge zones or to deeper groundwater where bacterial sulfate reduction occurs. Although the distribution of sulfate in shallow groundwater is highly variable, it was possible to defined geographical domains based on regional characteristics influencing sulfate occurrence and fate in shallow aquifers throughout Alberta (Figure 6, Table 1).

Fluoride has a MAC of 1.5 mg/L according to the Canadian Drinking Water Quality Guidelines (Health Canada, 2019). A total of 130,227 out of 131,491 samples have fluoride concentrations reported in the unified dataset with 85% of these samples (n=112,067) having a F concentration below 1.5 mg/L. Mapping revealed hotspots of elevated fluoride concentrations (>4 mg/L) in three regions of Alberta (Figure 7). Occurrence of elevated fluoride concentrations was found to be dependent on the groundwater type that is affected by groundwater flow system dynamics. Samples with elevated fluoride concentrations were always associated with groundwater discharge areas. Low concentrations of fluoride are associated with groundwaters having high calcium and low sodium concentrations. In contrast, groundwaters with high concentrations of fluoride are associated with low Ca and high Na concentrations, and elevated pH values. Aquifers containing the mineral fluorite with groundwater that has evolved towards very low Ca/Na ratios appears to be at the highest risk of fluoride concentrations exceeding the MAC of 1.5 mg/L.

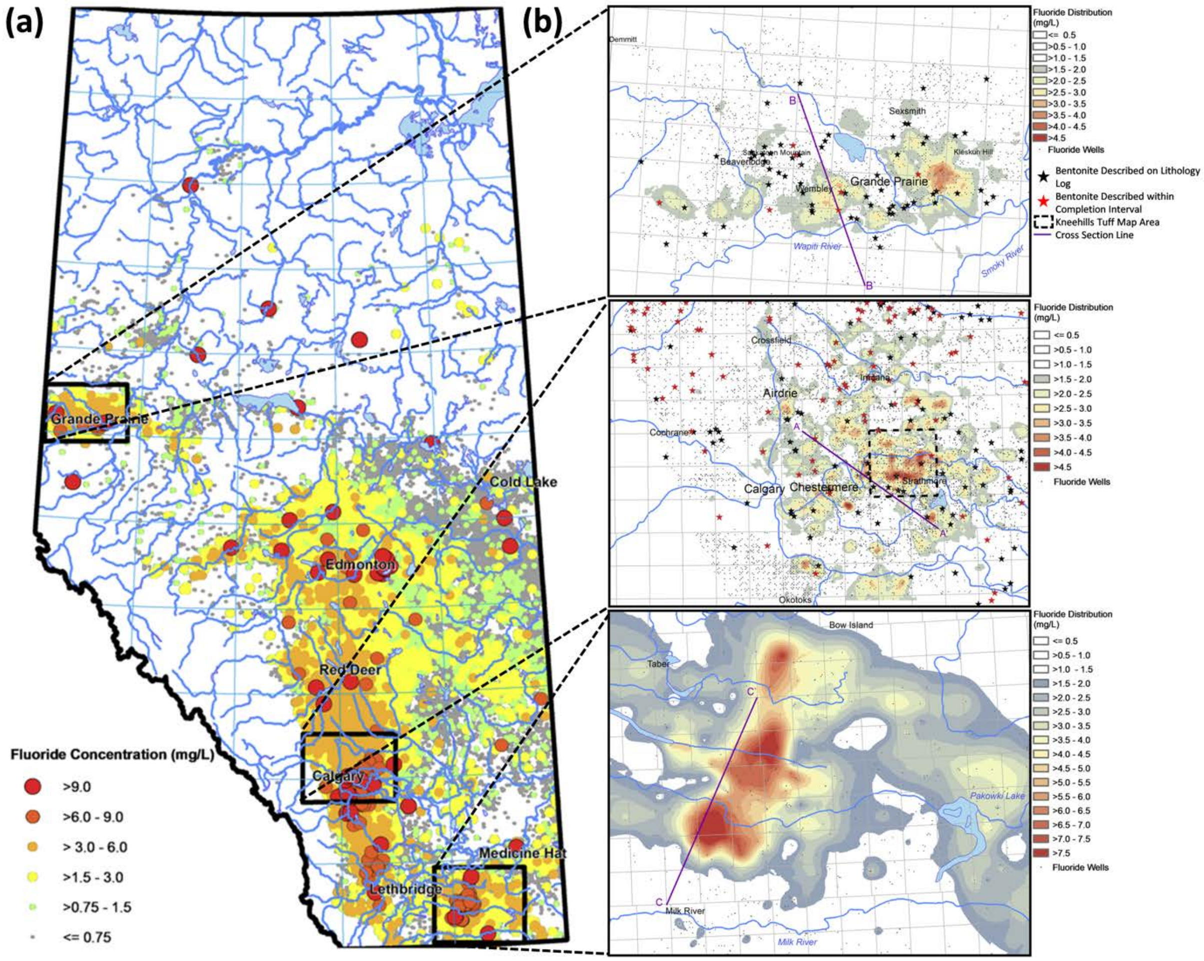


Figure 7: Spatial distribution of F concentrations in groundwater samples of Alberta.

The unified dataset contains 3,340 groundwater samples with reported selenium (Se) concentrations. About 79% of the samples (n=2,649) had Se concentrations below the detection limits, while 1% of the samples (n=25) exceeded the drinking water MAC of 0.05 mg/L for Se (Health Canada, 2019). Figure 8 displays the regional distribution of Se in groundwater of Alberta. There appear to be two possible sources of elevated selenium (>0.05 mg/L) in groundwater. Elevated Se concentrations in group 1, shown in Figure 8, are found in groundwater samples (n=15) from deeper water wells ranging from 40 to 231 m below ground surface and are mainly associated with highly evolved groundwater of Na-HCO_3 and Na-Cl water types. Elevated Se concentrations from group 2 (n= 10, Figure 8) were found in groundwater from wells shallower than 40 m and in Ca-HCO_3 to Na-SO_4 water types. Water wells screened in aquifers containing coal seams such as the Belly River Group, the Scollard and Horseshoe Canyon formations were commonly associated with groundwater samples (~70%, n=17) containing elevated Se concentrations.

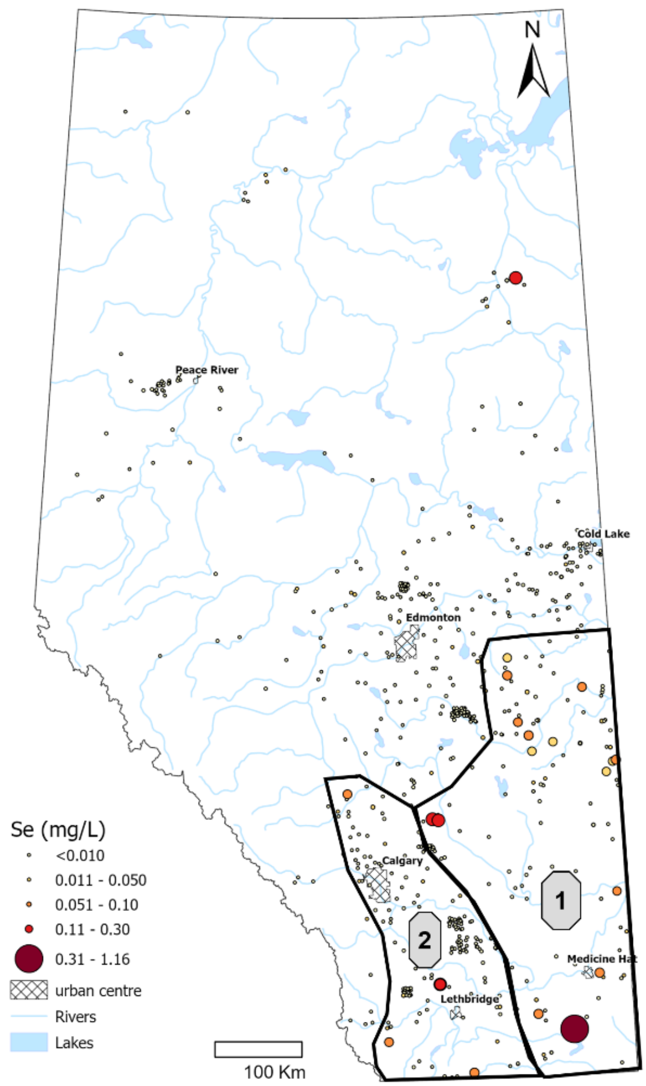


Figure 8: Spatial distribution of selenium concentrations in groundwater samples of Alberta.

Another focus of the project was to improve the understanding on the occurrence of methane, ethane and propane in shallow groundwater and its sources. Although concentrations and isotope compositions of dissolved or free gases such as methane, ethane and propane are rarely measured in routine groundwater quality surveys, a remarkable database of these parameters has been compiled in Alberta through targeted efforts associated the BWWT and GOWN sampling and measurement campaigns.

Methane was found in 1396 groundwater samples with concentrations in the free gas phase ranging from <1% to >95% (Figure 9b). Ethane was detected in 571 groundwater samples with concentrations in the free gas phase rarely exceeding 1% (Figure 9c). Propane was detected in only very few groundwater samples.

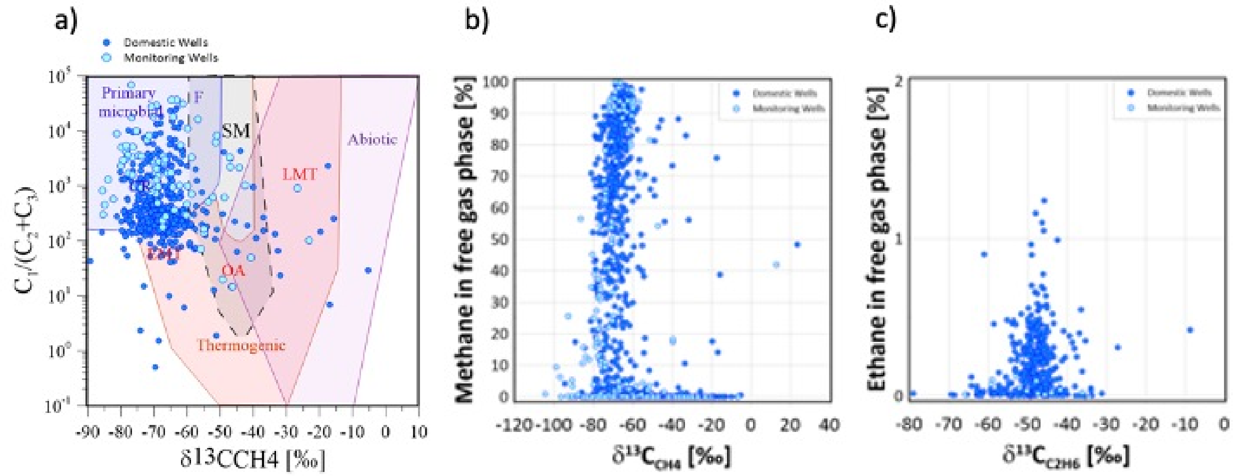


Figure 9: a) δ^{13}C values of methane versus gas dryness in free gases in groundwater obtained from domestic and monitoring wells. b) δ^{13}C values versus concentration of methane in free gas samples obtained from domestic and monitoring wells. c) δ^{13}C values versus concentration of ethane in free gas samples obtained from domestic and monitoring wells.

In Figure 9a, the δ^{13}C values of methane are plotted versus the dryness parameter (ratio of methane concentrations divided by the sum of higher alkanes) and shows the origin of methane based on Milkov and Etiope (2018). The majority of the samples plot towards the top left corner indicating a predominantly microbial origin of methane in shallow groundwater of Alberta, while some samples may also be consistent with an early maturity thermogenic gas signature. The finding of predominantly microbial methane is further confirmed by the average δ^{13}C value of methane shown in Figure 9b independent of methane concentrations. Elevated δ^{13}C values of methane are predominantly associated with very low methane concentrations (Figure 9b). This indicates the occurrence of partial methane oxidation which causes the enrichment of ^{13}C in the remaining methane. There are only very few cases of δ^{13}C values of methane ranging between -20 and -55 ‰ in concert with elevated methane concentrations, potentially indicating that the gas is of thermogenic origin.

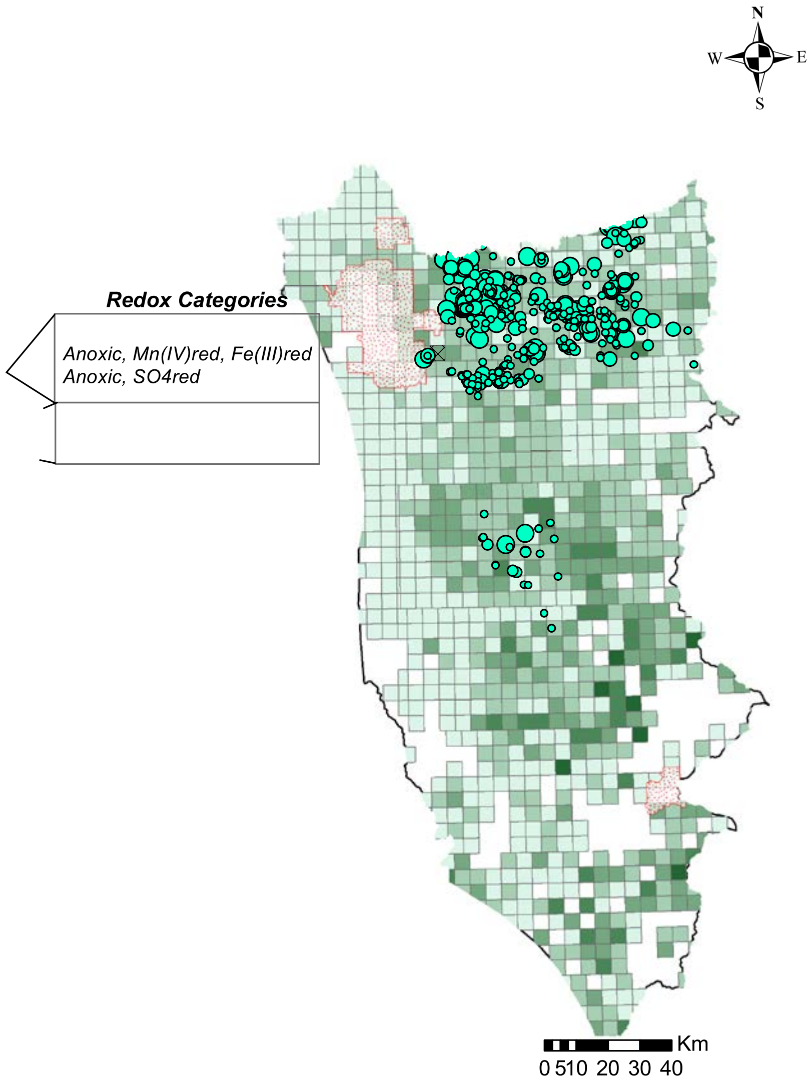


Figure 10: Distribution of methane concentrations in groundwater from monitoring (GOWN) and domestic wells (BWWT) and prediction of favorable versus non-favorable conditions for methane formation in groundwater in the CLC based on redox-sensitive parameters.

The formation of microbial methane requires highly reducing conditions in groundwater. The prediction of redox conditions in groundwater based on redox-sensitive species as shown in Figure 3 is therefore a suitable tool to predict whether conditions in aquifers may be suitable for the in-situ production of methane. Figure 10 summarizes the results of this approach with the lighter green colours indicating an increased likelihood of methane production. Also shown in Figure 10 are the measured concentrations of methane in groundwater obtained from domestic and monitoring wells revealing a very good agreement of the predicted and measured methane occurrences.

Task 3 focused on microorganisms living in groundwater. Groundwater microbes dynamically turn over oxygen, nitrate, sulfate, methane and other ions, as well as minerals such as pyrite, by oxidation and reduction reactions. Hence, microbial data as summarized in Figure 11 and discussed below can help understand sources and sinks of contaminants.

During the project, 208 GOWN samples were analysed using 16S rRNA gene amplicon sequencing (milestone 3.1). Geochemistry and microbial ecology showed consistent trends suggesting large-scale aerobic and anaerobic hydrogen, methane, nitrogen, and sulfur cycling carried out by diverse microbial communities. Older groundwaters, especially in organic carbon-rich strata, contained on average more bacteria (up to 1.4×10^7/mL) than younger groundwaters, challenging current global estimates of numbers of bacteria in groundwater. It should be noted that these numbers are conservative estimates capturing only the free-living cells from water samples, which cannot account for the substantial number of cells living in biofilms. Numbers of bacteria were higher in groundwater obtained from aquifers associated with coals and shales. Our results indicate that hydrogen was a major energy source driving bacterial growth and methane cycling in geochemically evolved groundwater. In many aquifers hydrogen consuming methane producers, including *Methanobacterium*, *Methanoregula* and *Methanospirillum*, showed high relative abundances consistent with in-situ microbial methane formation. Among the detected methane oxidizers were anaerobic methane oxidizing archaea that mainly use nitrate, as well as iron and manganese oxides, as electron acceptors for methane oxidation. Sulfate dependent methane oxidation was less prevalent. Hydrogen also facilitated bacterial sulfate reduction by *Desulforudis Desulfomicrobium* and diverse other sulfate and sulfur reducers and disproportionators. In some groundwaters, fermentative bacteria such as *Smithella* and *Syntrophus* might produce at least part of the hydrogen. Aerobic hydrogen-, methane-, and sulfur-oxidizing microbes such as *Hydrogenophaga*, *Methylobacter*, *Thiobacillus* and *Sulfuricurvum* were abundant in older groundwaters obtained from confined aquifers. Substantial concentrations of dissolved oxygen in older groundwaters explained the occurrence of these aerobic lifestyles in subsurface ecosystems at an unprecedented scale. *Methylotenera,* a denitrifying bacterium oxidizing methanol and other methylated compounds was the most abundant organism on average across all samples. The biomass produced by the diverse, coexisting autotrophs above apparently supported multitudes of archaeal and bacterial heterotrophs, including enigmatic nanoarchaea and Patescibacteria (also known as Candidate Phyla Radiation).

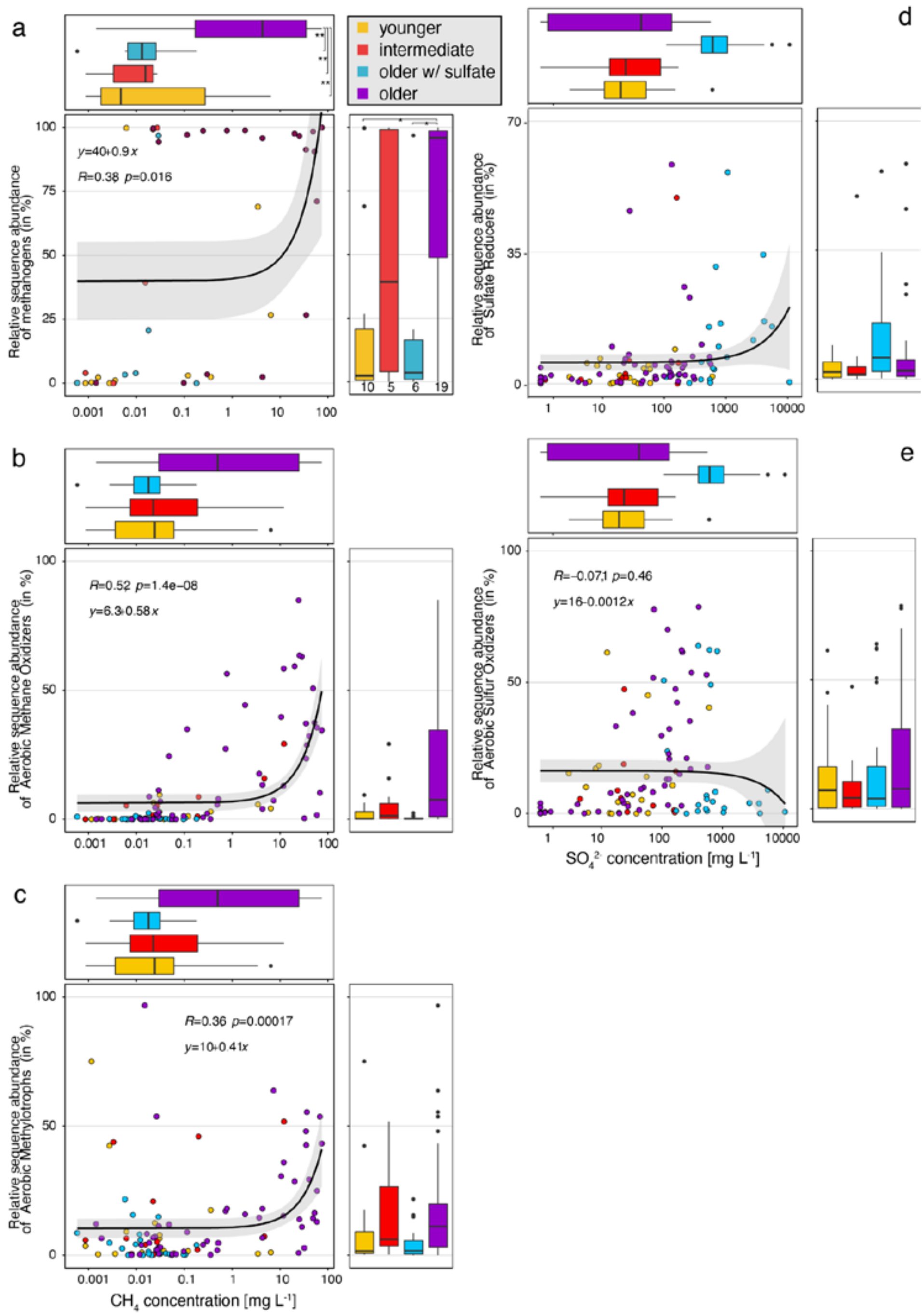


Figure 11: Left panel. Relative abundance of methane producers (methanogens), aerobic methane oxidizing (methanotrophs) and aerobic oxidizers of methylated compounds (methylotrophs) versus methane concentration. There was a significant positive correlation of these methane-cycling clades with the concentration of methane. **Right panel.** Relative abundance of sulfate reducers and sulfur oxidizers versus sulfate concentration. Sulfate reducers tended to be abundant in sulfate-rich waters, while sulfide oxidizers were most abundant in waters with intermediate sulfate concentrations. Concentrations on the x-axis are shown on pseudo-log10 scale, so as to include the samples in which the compound was

not detected (zero). Samples are color-coded by water types (younger, intermediate age, older with sulfate and older without sulfate).

In milestone 3.2, shotgun sequencing of all environmental DNA obtained from 25 groundwater wells yielded more than 846 medium to high quality complete genomes of groundwater bacteria. Genes encoded on these genomes confirmed the lifestyles of key bacteria described above. In addition, genes for production of oxygen from nitric oxide were abundant in some deeper samples, indicating that part of the oxygen found in deeper, older groundwaters was locally produced from nitrate in the subsurface. Oxygen isotope compositions supported this hypothesis. These findings suggest that old groundwaters sustain productive microbial communities and highlight an overlooked oxygen source in present and past subsurface ecosystems of Earth.

Milestone 3.3 addressed the identification of a microbial pathway for ethane production. In some groundwater samples, ethane was detected in low concentrations in the free gas phase of shallow groundwater with an average $\delta^{13}C$ value of ethane of -48 ‰ (Figure 9c). Metagenomes from samples with elevated ethane concentrations were analyzed for genes involved in ethane metabolism. Genes for methanogenesis were detected, including methyl-coenzyme M reductase (MCR) genes, one of which was similar to a MCR gene of Methanosarcina barkeri strain 227, which was previously shown to convert ethanol to ethane. No other genes involved in ethane production were found. Given that much more methane was detected than ethane (Figures 9b,c), co-production of a small amount of ethane by methanogens was the most plausible source for the ethane in the groundwater. Alternately, ethane found in some Alberta groundwater samples may also be associated with thermogenic gas or with radiolytic gas sources (Naumenko-Dezes et al., 2022). Further testing is required to conclusively identify the sources of ethane in Alberta groundwater.

Task 4 of this project achieved the first systematic sampling and reporting of radon in Alberta groundwater that we are aware of. Seventy-nine samples collected from 47 GOWN wells were analyzed for radon and compared to geochemical and isotopic analysis. Although radon is ubiquitous in groundwater, its concentrations are variable (Figure 12), ranging from a maximum value of 64.2 Bq/L (Mariana Lakes-1133 GOWN well) to a minimum of 0.2 Bq/L (Rosebud – 972). The median radon concentration is 8.9 Bq/L and the average is 13.0 Bq/L (standard deviation = 13.4).

Although there are few surveys of groundwater radon in Canada (Health Canada, 2009), the Alberta groundwater concentrations are substantially less than those found in Nova Scotia (e.g., concentrations ranging from 120 to 1400 Bq/L with an average of ~600 Bq/L in 16 Nova Scotia schools), and similar to those found in New Brunswick (mean 13.4 Bq/L, ranging from 0.2 to 39 Bq/L). There is no drinking water objective for radon since dissolved radon ingestion is not a significant pathway of concern. However, breathing in radon gas is a significant health concern, comprising the single largest exposure to radiation for Canadians. Since radon can partition out of water and contribute to airborne radon levels, Health Canada (2009) recommends that radon gas release from household water supplies be mitigated if water supply radon concentrations have an action level above 2000 Bq/L. Since groundwater radon concentrations observed in this project show action levels far below 2000 Bq/L, radon in groundwater pumped into residences and buildings does not pose a significant health hazard associated with Alberta groundwater sampled in this project.

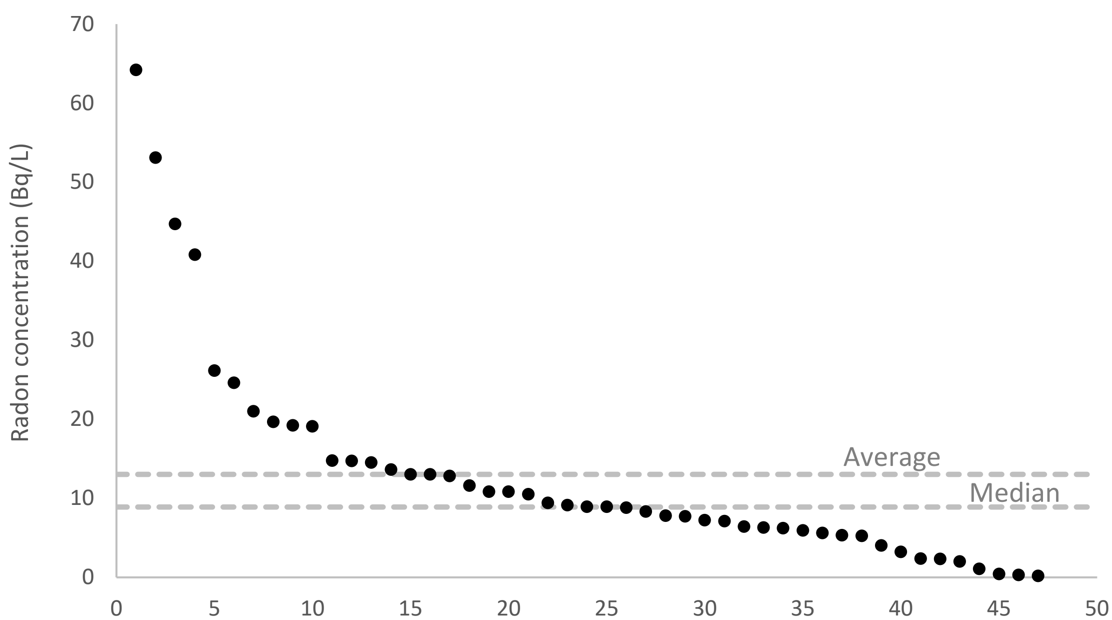


Figure 12: Radon concentrations (Bq/L) in groundwater samples collected from Alberta's Groundwater Observation Well Network, plotted in order of decreasing concentration. When more than one sample was analyzed from a given well, the average value is plotted.

Although radon concentrations are variable in Alberta groundwater, they do not show any strong correlations with groundwater geochemistry or the geologic units in which the monitoring wells are completed (Eldridge, 2022). Moderate correlations (nominally defined here as correlation coefficients between 0.40 and 0.65) were observed between radon concentrations and four parameters: total dissolved gas pressure (P_{TDG}), methane, sulfate (Figure 13), and uranium (not shown).

The correlations between radon and P_{TDG} and methane are negative (i.e., higher P_{TDG} and methane concentrations are observed in groundwater with low radon concentrations (Figure 13)). This is thought to be caused by stripping of radon by methane production. When microbial methane is formed and methane concentrations increase, the P_{TDG} similarly increases. Once the P_{TDG} reaches the point at which it exceeds the bubbling pressure, free phase gas bubbles will form. While the free phase gas will be mainly comprised of methane, other gases including radon will partition into the bubbles. When the bubbles grow to sufficiently large volumes, they are transported upwards under buoyancy and are progressively removed from the aquifer (Sebol et al., 2007). Thus, the negative correlation between these parameters and radon is thought to be a function of the stripping of both methane (as a 'carrier gas') and radon gases, and not because they have similar sources and/or geochemical relationships.

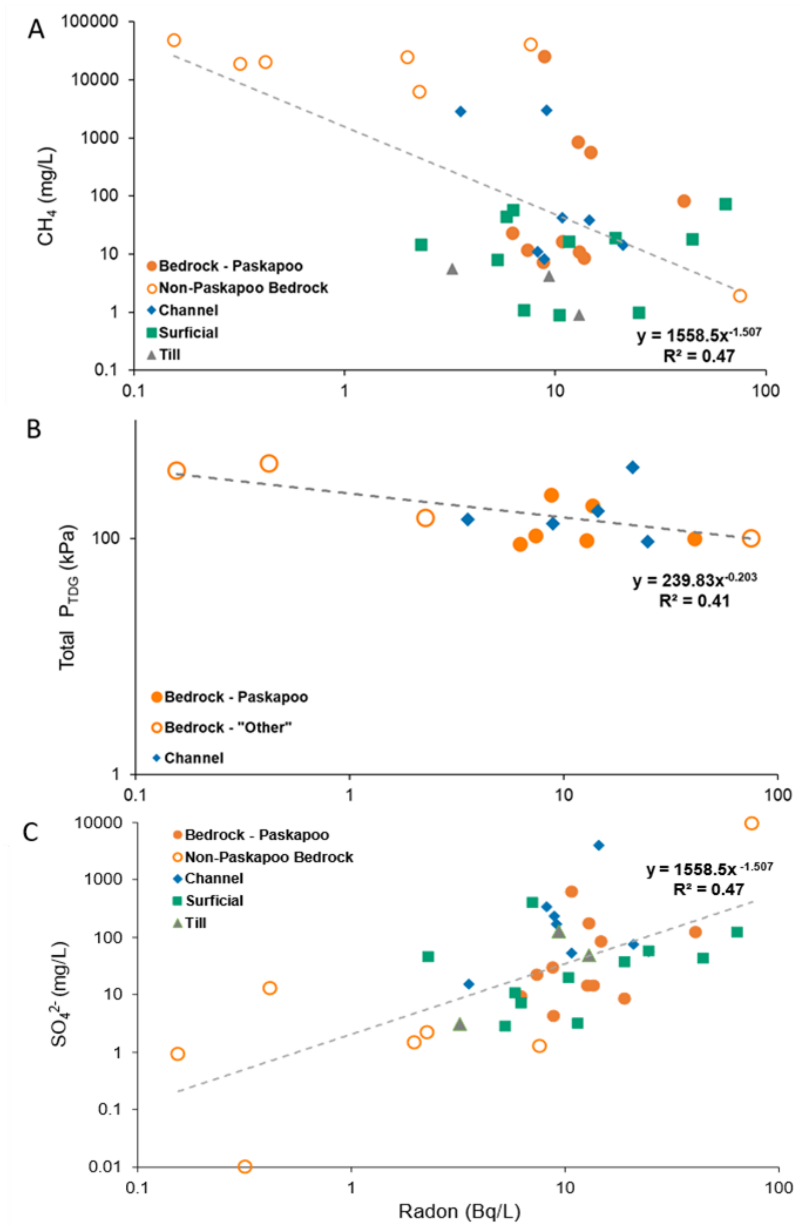


Figure 13. Cross plots showing correlations between radon concentrations in groundwater and A) methane concentrations (n=38), B) total (i.e., including P_{atm}) P_{TDG} (n=15), and C) sulfate concentrations (n=40).

The correlation between radon and sulfate (Figure 13c) appears to be a function of the correlation between radon and methane. In-situ methane production requires that bacterial sulfate reduction has occurred to generate suitable methanic redox conditions. Uranium has reduced solubility under reducing conditions and decreasing U concentrations are thought to reflect increased precipitation of uranium minerals under the highly reducing conditions in aquifers with elevated methane concentrations. Therefore, the moderate correlations between sulfate and uranium versus radon concentrations are both thought to be secondary correlations and are not reflective of shared sources and/or geochemical processes.

Elevated radon concentrations observed in groundwater were not clearly related to specific geologic formations (shown by different symbols in Figure 13), and no clear geogenic radon source was identified despite radon being ubiquitous in groundwater at varying but low concentrations.

Task 5 focused on the development of a 3D aquifer framework model for Alberta. Milestone 1 of task 5 (allocating geochemical data from unified geochemical database into the Geological Framework Model of Alberta [GFA], version 3) resulted in assigning geological model zones to each water quality sample based on either the well screen interval, or well depth if screen information was not available. The geological formation assignment of 200 GOWN wells was reviewed and we updated those wells without an assigned formation or where the formation was incorrect (48 of 200 wells). Updates to the GOWN well formation assignments were communicated to AEPA so official records can be updated.

The comparison of the GOWN well assignments with the GFA highlighted a bias in the model used to interpolate the provincial bedrock topography: it underestimated the depth of buried bedrock valleys. This finding, along with the low density of bedrock picks from well logs in southeastern Alberta, prompted an improvement of the bedrock topography model for milestones 2 and 3 of task 5 (integration of AGS hydrostratigraphic unit delineation into a 3D aquifer framework model, and delineation of 3D aquifer units based on hydrogeological characterization). A statistical natural language model, trained on geologists' picks of the top of bedrock, was used to automatically pick the top of bedrock from well logs, improving data density by 70% from circa 209,000 to approximately 350,000 tops throughout Alberta.

Milestones 2 and 3 of task 5 focused on the sediment above bedrock, because while the GFA differentiates between different bedrock aquifers, the sediments above bedrock were incompletely mapped across the province. A probabilistic machine learning approach was used to map the probability of encountering sand and/or gravel (i.e., favourable aquifer material) in 3D throughout Alberta using the updated bedrock topography as the model base. Figure 14 shows the probability of encountering sand and/or gravel just above bedrock, along with an outline of the extent of buried bedrock valleys. These basal sand and gravel units within buried valleys form important aquifers in Alberta. Analysis of the position, extent, and geological history of these units in task 5 resulted in an updated stratigraphic framework with which to map and formally name basal sand and gravel units in Alberta as part of the Empress Group.

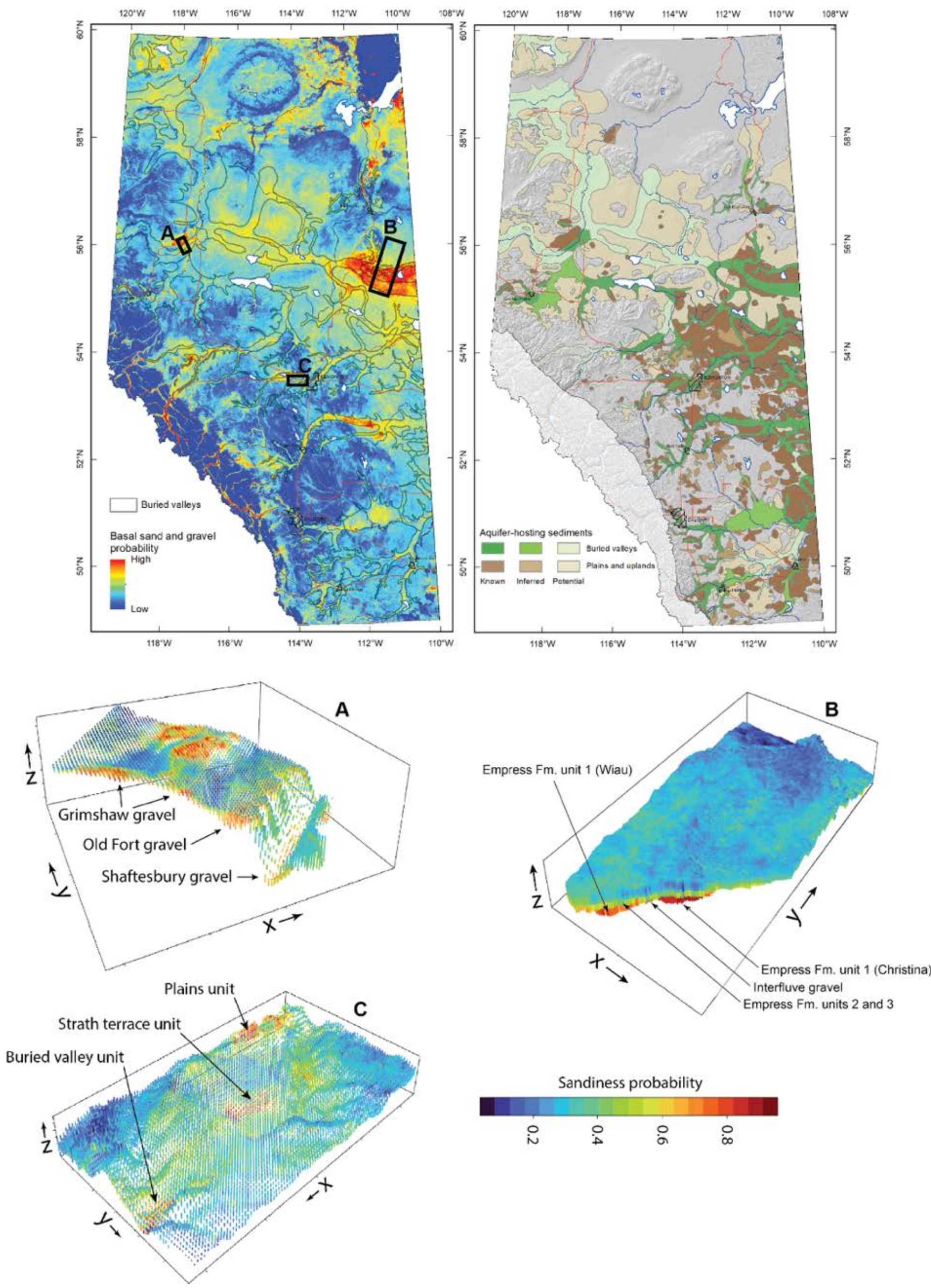


Figure 14: Modelled basal sand and gravel probability (upper left) showing potential accumulation of sand and gravel at the base of many buried valleys. Insets A, B, and C show the 3D

distribution of the sand and gravel probability in the Grimshaw, South Athabasca Oilsands, and Edmonton areas, respectively. The aquifer-hosting sediments above bedrock map (upper right) shows where sediments are known, inferred, or have the potential to contain aquifers based on the occurrence of sand and gravel and presence of water supply wells.

The 3D model of sandiness in the sediments above bedrock was also used in developing a 2D map of the distribution of aquifer-hosting sediments above bedrock (Figure 14). This provincial-scale map shows where sediments are known, inferred, or have the potential to contain aquifers. Evidence of permeable aquifer material is based on the occurrence of sand and gravel deposits and the distribution of water supply wells completed above bedrock (indicative of groundwater production from sediments above bedrock). Results of task 5 were also used in tasks 2 and 6 to investigate the occurrence, mobilization, and fate of sulfate and fluoride in groundwater of Alberta.

Task 6 comprised the development of a unifying model of occurrence, sources, and potential fate of groundwater contaminants in aquifers throughout Alberta. Using the information obtained by analysis of GOWN samples (including metagenomics, among others) and by evaluation of BWWT, AH, AGI and AWWID data, the research team determined the most likely sources of selected groundwater contaminants including methane, ethane, nitrate, manganese, arsenic, iron, sulfate, selenium, fluoride and radon (milestone #6) as described above. This revealed zones of groundwater vulnerability for selected contaminants that are of concern if groundwater is used, or is planned to be used in the future, for drinking water purposes by humans or livestock.

Project specific metrics and deliverables

The performance metrics that were targeted for this project during proposal submission are outlined below, followed by a statement outlining the achievements after the completion of this 3-year project.

Proposed: 80,000 samples compiled and QA/QC-ed to generate a unified dataset.
Achieved: 131,491 high-quality groundwater samples compiled and QA/QC-ed to generate a unified dataset (task 1) and interpretation of the observed trends for various groundwater constituents and contaminants (task 2).

Proposed: 360 samples analyzed for metagenomics including 180 existing samples.
Achieved: 208 newly obtained GOWN samples were analyzed using 16S rRNA gene amplicon sequencing (task 3).

Proposed: 60 samples analyzed for radon contents.
Achieved: 79 samples collected from 47 GOWN wells were analyzed for radon and compared to geochemical and isotopic analyses (task 4).

Proposed: The construction of a 3D aquifer framework model with groundwater samples allocated from the unified geochemical database.
Achieved: Completed 3 digital AGS publication of 3D aquifer framework model:

- Digital datasets of 3D sandiness above bedrock modelling (in press)
- Interactive web map of sandiness above bedrock model (in prep)
- Distribution of aquifer-hosting sediments above bedrock map and digital dataset (published)

Proposed: The production of 5 aquifer-specific groundwater quality maps.
Achieved: Digital map product (shapefile format) of the spatial distribution (by quarter township) of 15 chemical parameters (Ca, Mg, Na, K, NO_3, SO_4, Cl, HCO_3, CO_3, F, Fe, Mn, TDS, alkalinity, and hardness) for 12 geological/aquifer units. This is the equivalent of 180 individual maps.

Proposed: 4 highly qualified personnel trained.
Achieved: 5 highly qualified personnel were trained.

Proposed: 6 conference presentations given and 6 manuscripts to be published.
Achieved: 6 conference abstracts, 7 journal manuscripts submitted or in preparation as outlined in subsequent sections of this report.

KEY LEARNINGS

Several key learnings emerged from this project that include the following:

There is astonishingly detailed information available on the quality of groundwater in Alberta based on the availability of 131,491 QA/QC'ed groundwater samples with > 10 million groundwater quality parameters. This project has amalgamated this information into a unified dataset that reveals the spatial distribution of groundwater quality parameters across Alberta. This has provided an improved understanding of the occurrence, the origin, and the fate of select groundwater constituents and contaminants in shallow groundwater of Alberta.

Groundwater in Alberta systematically evolves from freshly recharged, low TDS, Ca-Mg-HCO_3 water types towards more geochemically evolved Na-HCO_3 type waters in some cases associated with elevated sulfate concentrations, often resulting in elevated TDS contents. However, only 1% of the groundwater samples were found to be saline with TDS contents > 4,000 mg/L. High concentrations of TDS and sulfate can also be found in groundwater recharged through sulfide-rich tills and shallow bedrock since the last continental glaciation.

Evaluation of geochemical parameters in combination with microbiological techniques revealed that redox reactions are a key driver in controlling water quality in Alberta's aquifers. The successful assignment of redox zones in the context of hydrogeological frameworks is of critical importance for understanding the occurrence, the sources and the fate of select groundwater contaminants.

Only 3.2% of the groundwater samples analyzed for nitrate (n=2,442) had nitrate-N concentrations above the Health Canada drinking water limit of 10 mg/L. Circa 66% of the samples (n=49,184) had negligible nitrate concentrations (e.g. below the analysis detection limit). This indicates that either nitrate never entered the aquifer or, in the case of aquifers with anoxic redox environments, previously occurring nitrate is not stable and has been removed via denitrification.

For manganese (Mn), 2,217 samples exceeded the Health Canada drinking water limit of 0.12 mg/L, while for arsenic (As) the maximum allowable concentration (MAC) of 0.01 mg/L was exceeded in 443 samples. Elevated Mn and As concentrations were mainly observed in shallow aquifers in sediments above bedrock that were characterized by post-oxic redox conditions.

The concentration of sulfate in Alberta groundwater is highly variable with 22% of the samples exceeding 500 mg/L. Oxidation of sulfide minerals in tills and shallow bedrock was identified as the predominant source of sulfate in groundwater. In aquifers with sulfidic redox environments sulfate is removed via bacterial sulfate reduction.

It was also found that a considerable number of groundwater samples in Alberta have elevated fluoride (F) concentrations of > 1.5 mg/L. Hotspots of elevated F were always associated with groundwater having low Ca concentrations and Na-dominated water types.

Due to the often highly reducing conditions in some aquifers of Alberta, methane was detected in 1396 groundwater samples. Stable isotope analyses revealed that methane is predominantly of microbial origin. Radon was also found to be ubiquitous in groundwater obtained from 47 GOWN wells with comparatively low concentrations of <65 Bq/L and is therefore not considered a significant health risk.

Microbiological analyses on samples obtained from GOWN wells revealed that older groundwaters especially from coal and shale containing aquifers contained surprisingly high numbers of bacteria sustaining productive microbial communities that are actively involved in cycling of oxygen, nitrate, sulfate and methane among others. Hydrogen was identified as a major energy source driving bacterial growth and cycling of methane in aquifers, while aquifer-internal formation of oxygen from nitric oxide was also revealed by metagenomic analyses.

The information compiled in this project was used to further advance the development of a 3D aquifer framework model for Alberta. This has resulted in an improved differentiation between different bedrock aquifers and aquifer-hosting sediments above bedrock including an updated stratigraphic framework for basal sand and gravel units that are part of the Empress group. A high probability of sandiness correlates with a high probability of permeable material favourable for aquifers and hence important recharge areas, but also highly susceptible areas to contamination from surface. The aquifer-hosting sediment map incorporates this new predictive modelling to provide provincial coverage of the occurrence of aquifers above bedrock, which can be used in regional groundwater planning and management.

Broader impacts of the key learnings to users of groundwater in Alberta include a province-wide and systematic understanding of the quality of groundwater including its salinity, the water type, and the redox state of the groundwater. Salinity, water type and redox conditions are the key factors controlling the occurrence and fate of many groundwater constituents and contaminants including nitrate, manganese, arsenic, fluoride, sulfate and methane. Knowledge of Alberta's current groundwater quality offer the following benefits for various stakeholders:

- Developing more efficient decision-making processes in AEPA and Government of Alberta (GoA) related to groundwater supply and protection. Resources needed to support the Water Act and Environmental Protection and Enhancement Act applications could be maximized.
- Targeting groundwater monitoring network expansion by AEPA and reducing the number of costly new well installations, water quality sampling, and analyses required to report on the current state of groundwater quality across the province.
- Maximizing use of existing data sources and provincial monitoring networks to reduce/optimize the cost of new data acquisition and to support best management practices, policies and directives that support groundwater protection.
- More consistent and effective reporting of environmental conditions of groundwater quality and quantity by GoA and AER.
- Watershed Planning and Advisory Councils (WPACS) can be empowered to play a key role in connecting local stakeholders to support healthy waters and watershed management.
- Sustainable expansion of agriculture and natural resource development and enhanced monitoring infrastructure where commercial opportunity and new investment is occurring.

OUTCOMES AND IMPACTS

Project Outcomes and Impacts: By combining water quality information from five large data sources into a unified water quality database, with 131,491 groundwater samples, the research team has gained unprecedented insights into the spatial distribution of groundwater quality parameters in Alberta. This enabled the research team, for the first time to identify regional, spatial, and depth-related trends in current water types, redox conditions, and groundwater salinity variations, and explore natural and anthropogenic causes that impact groundwater quality. To our best knowledge, no other research team or government agency has a comparable data source that describes the current status of groundwater quality across the province in such a comprehensive fashion.

The **program specific metrics** were achieved as follows:

131,491 high-quality groundwater samples were compiled and QA/QC-ed to generate a unified dataset (task 1) and interpretation of the observed trends for various groundwater constituents and contaminants on a province-wide scale (task 2).

208 newly obtained GOWN samples were analyzed using 16S rRNA gene amplicon sequencing (task 3).

79 samples collected from 47 GOWN wells were analyzed for radon and compared to geochemical and isotopic analysis (task 4).

Three digital AGS publications of 3D aquifer framework models were completed:

- Digital datasets of 3D sandiness above bedrock modelling (in press)
- Interactive web map of sandiness above bedrock model (in prep)
- Distribution of aquifer-hosting sediments above bedrock map and digital dataset (published)

Map products produced in this project include:

- AGS-published map of the distribution of aquifer-hosting sediments above bedrock as a PDF and digital data (shapefile format).
  - Hartman, G.M.D., Pawley, S.M., Liggett, J.E., Atkinson, N. and Utting, D.J. (2023): Distribution of aquifer-hosting sediments above bedrock in Alberta; Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Map 632, scale 1:3 000 000. https://ags.aer.ca/publication/map-632
  - Hartman, G.M.D., Pawley, S.M., Liggett, J.E., Atkinson, N. and Utting, D.J. (2022): Distribution of aquifer-hosting sediments above bedrock in Alberta (GIS data, polygon features); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2022-0031. https://ags.aer.ca/publication/dig-2022-0031
- AGS-published digital data (shapefile format) of the spatial distribution of 15 chemical parameters (Ca, Mg, Na, K, NO_3, SO_4, Cl, HCO_3, CO_3, F, Fe, Mn, TDS, alkalinity, and hardness) for 12 geological units.
  - Thistle, S., Humez, P., Pooley, K.E. and Liggett, J.E. (2022): Statistical summary and distribution of groundwater quality parameters by quarter township from selected Alberta geological units (GIS data, polygon features); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2022-0032. https://ags.aer.ca/publication/dig-2022-0032
- Map-figures for presentations and reports, for example, the figures in this report.
- 5 highly qualified personnel were trained.

Project outputs include the following:

Journal articles

Hartman, G.M.D., Pawley, S.M., Utting, D.J., Atkinson, N. and Liggett, J.E. (submitted): The Empress Group in Alberta, Canada. Submitted to Canadian Journal of Earth Sciences, Dec. 2022.

Ruff et al. (in revisions): Hydrogen and dark oxygen drive microbial productivity in diverse groundwater ecosystems. – Nature Communication, in review.

Liggett, J.E., Humez, P., Pooley, K.E., Atkinson, N., Thistle, S., and Mayer, B. (in preparation): Controls on regional sulfate distribution and dynamics in shallow groundwater in the northern Prairies.

Eldridge E., Mayer B., Humez P., McClain C.N., Goodarzi A., Ryan M.C. (in prep): Radon, water well use, and groundwater geochemistry in Alberta, Canada.

Plata et al. (in preparation): Occurrence and geochemical controls of Mn, As, and Fe in groundwater of Alberta, Canada.

Thistle et al. (in preparation): Potential geogenic sources and hydrogeological dynamics controlling the occurrence and distribution of elevated fluoride in groundwater in Alberta.

Humez et al. (in preparation): The occurrence, source and fate of nitrate in groundwater of Alberta.

Conference proceedings

Liggett, J.E., Humez, P., Pooley, K.E., Atkinson, N., Thistle, S. and Mayer, B. (submitted): Controls on regional sulfate distribution in groundwater resources in Alberta; Submitted to IAH-CNC GeoSaskatoon 2023. Saskatoon, SK, October 1-4, 2023.

Hartman, G.M.D., Pawley, S.M., Utting, D.J., Atkinson, N. and Liggett, J.E. (submitted): The Empress Group in Alberta, Canada. Submitted to GeoConvention, Calgary, AB. May 15-17, 2023.

Plata I, Humez P, Ligget J, McClain CN, Mayer B (2022) Assessment of the occurrence and geochemical controls of Mn concentrations in groundwater of Alberta, Canada. GeoHalifax2022.

Plata I, Humez P, McClain CN, Mayer B (2022) The distribution of As, Fe and Mn in groundwater of Alberta, Canada Goldschmidt Conference.

Ruff SE, Humez P, Hrabe de Angelis I, Nightingale M, Cho S, Connors L, Kuloyo OO, Seltzer A, Wankel S, McClain CN, Mayer B, Strous M (2022) productive and diverse microbial communities in ancient groundwaters are fueled by hydrogen, sulfur, methane, and oxygen. 18th International Symposium on Microbial Ecology.

Eldridge EL, McClain CN, Humez P, Mayer B, Ryan C (2021) A preliminary assessment of geochemical and geologic controls on radon in Alberta groundwater. GeoNiagara2021.

Reports

AGS report on derivation of 3D aquifer framework model – revised and complete

- Sandiness above bedrock modelling documentation found in numerous products including digital dataset metadata, interactive web map (non-technical methods), GitHub publication of code (technical methods), journal article on the Empress Group in Alberta.
- Methods for aquifer-hosting sediments above bedrock map included in map description and digital dataset metadata.

Digital data

Pawley, S.M. (in press): Sandiness above bedrock model (GIS data, ACSII format); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2023-XXXX.

Pawley, S.M. (in prep): Web application for sandiness above bedrock model (Interactive map and app); Alberta Energy Regulator / Alberta Geological Survey.

Pawley, S.M. (planned): Machine learning model code for sandiness above bedrock; Code published on GitHub.

BENEFITS

Economic benefits associated with commercial opportunities and new investments are reliant on sufficient quantity and quality of water. Knowledge of Alberta's current groundwater quality allows the Government of Alberta (GoA) and its various departments to make more efficient decisions related to groundwater supply and protection. Resources needed to support the Water Act and Environmental Protection and Enhancement Act applications can be maximized. Furthermore, water quality sampling and analyses required to report on the current state of groundwater quality across the province can be optimized using the information obtained from this project reducing the number of costly new well installations. By maximizing the use of existing data sources, provincial monitoring networks can optimize the cost of new data acquisition and better support best management practices, policies and directives that support groundwater protection.

From an **environmental perspective**, the research conducted in this project focused on assessing the occurrence of groundwater quality impacts in Alberta thereby directly supporting several key actions within **Water for Life**. In particular, for 1) identifying priority water contaminants as outlined for safe, secure drinking water as well as irrigation and livestock water; and 2) advancing water quality programs aimed at source protection information and planning. The assessment of groundwater quality and vulnerability to non-point-source contamination addresses the challenge of ensuring that Albertans have access to reliable, high-quality water supplies during a period of increasing dependency on water resources across all sectors.

Beneficial social impacts are achieved since the inhabitants of Alberta have the desire to understand whether drinking water sources, including groundwater, are “safe”. The comprehensive information on groundwater geochemical composition in Alberta obtained through this project has resulted in new insights into the quality and safety of groundwater across the province. Hence, the conducted research provides value for rural areas and indigenous communities as they plan for future water demand increases, and for drinking water supply systems to comply with the health-based guidelines for water quality.

Training highly qualified and skilled personnel (HQSP) was a key component of the research. The project supported the positions of several graduate students, postdoctoral fellows and research associates. Thereby, the project contributed to the creation and retention of several jobs and made major contributions to the development of highly qualified personnel (HQP). These HQP benefited from working in a multidisciplinary team to achieve the project goals. HQP with multidisciplinary skillsets are highly sought after within industry, academia, and governments.

RECOMMENDATIONS AND NEXT STEPS

Throughout the last decade and especially through this project, significant progress has been made with a province-wide investigation of groundwater quality and an initial assessment of sources and sinks of groundwater constituents and contaminants. In collaboration with AEPA, shallow groundwater from the GOWN network has been repeatedly sampled. Analysis of a wide range of groundwater quality parameters, supplemented by free and dissolved gas data, stable isotope compositions, and microbiological and metagenomic data has resulted in a world-class groundwater data set based on repeated sampling of ~200 wells. In addition, the applicant’s research team has amalgamated a unified water quality dataset using archived water quality data from five sources (Alberta Health, Baseline Water Well Testing, GOWN, Alberta Water Well Information Database, and Alberta Agriculture and Irrigation) that has enabled unprecedented insights into the spatial distribution of groundwater quality parameters in Alberta. However there has not yet been a regional assessment of historical change of shallow (<50m) groundwater quality nor an analysis of how such potential temporal trends in some groundwater quality parameters relate to land use changes throughout the last decades. Furthermore, climate change is expected to have significant impacts on hydrological systems in Alberta in the next few decades. Current models predict earlier snowmelts, longer summer droughts, significant variations in groundwater recharge rates, and extended and record-low baseflow conditions in rivers and creeks throughout fall and winter. While there is some literature on climate change predictions for surface water flows in various parts of the world including Western Canada, detailed reports on impacts on groundwater quantity and quality are scarce.

Given the connection of groundwater to land use, climate, and surface water, groundwater quality cannot be studied or managed in isolation without consideration of broader impacts and cumulative effects. Hence, an investigation of past changes and expected future trends in Alberta's groundwater quality due to land use changes, climate change, and water management scenarios is timely. Hence, a follow-up investigation is proposed to study temporal trends in select groundwater contaminants, the indicators that track these changes, whether changes have resulted from human activities, and which indicators in shallow groundwater (<50m) serve as early warnings for future changes to deeper (>100m) high-quality groundwater sources. To advance integrated approaches to water management in Alberta it is imperative to explore connections between historical trends in groundwater quality, land use, and surface water quality. This will help identify future threats potentially impacting this essential resource.

KNOWLEDGE DISSEMINATION

AEPA and AGS have made significant investments in the Provincial Groundwater Inventory Program for over 10 years with the primary purpose to apply science, knowledge, and regulatory/policy tools to regulate and manage groundwater allocation and protection in the context of sustainable resource development. The new knowledge gained about Alberta's groundwater quality enables the development of science-based policies, regional plans, environmental management frameworks, and risk-based decision tools through the direct involvement of AEPA and AER/AGS. Through advanced 3D mapping, visualization and the ability to communicate 3D variations in water quality related to Alberta's aquifer framework, geoscientists and regulators have unparalleled products for decision making and testing outcomes of current and future water protection initiatives. The outcomes of this project are a better understanding of the groundwater quality characteristics of Alberta's groundwater and its vulnerability with respect to selected contaminants. This information can now be used by AEPA Resource Stewardship Division to directly inform the design and potential expansion of Alberta's ambient groundwater monitoring, evaluation and reporting program, filling key information gaps identified as part of this project.

The project team intends to write plain-language fact sheets and intends to present results to Watershed Planning and Advisory Councils (WPACs). WPACs are well connected to end-users such as local municipalities, watershed stewardship groups, agricultural and hydrocarbon industry groups, indigenous communities and academic and governmental institutions. In collaboration with WPACs we plan to ensure awareness of the project and its findings among local stakeholders.

One map and two digital datasets have been published by the AGS in collaboration with research team members and are currently publicly available on the AGS website:

1. Hartman, G.M.D., Pawley, S.M., Liggett, J.E., Atkinson, N. and Utting, D.J. (2023): Distribution of aquifer-hosting sediments above bedrock in Alberta; Alberta Energy Regulator / Alberta

Geological Survey, AER/AGS Map 632, scale 1:3 000 000. https://ags.aer.ca/publication/map-632

2. Hartman, G.M.D., Pawley, S.M., Liggett, J.E., Atkinson, N. and Utting, D.J. (2022): Distribution of aquifer-hosting sediments above bedrock in Alberta (GIS data, polygon features); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2022-0031. https://ags.aer.ca/publication/dig-2022-0031

3. Thistle, S., Humez, P., Pooley, K.E. and Liggett, J.E. (2022): Statistical summary and distribution of groundwater quality parameters by quarter township from selected Alberta geological units (GIS data, polygon features); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2022-0032. https://ags.aer.ca/publication/dig-2022-0032

In addition, knowledge dissemination occurs through conference presentations and scientific publications to be submitted in 2023, including the following:

Journal articles

Hartman, G.M.D., Pawley, S.M., Utting, D.J., Atkinson, N. and Liggett, J.E. (submitted): The Empress Group in Alberta, Canada. Submitted to Canadian Journal of Earth Sciences, Dec. 2022.

Ruff et al. (in revisions): Hydrogen and dark oxygen drive microbial productivity in diverse groundwater ecosystems. – Nature Communication, in review.

Eldridge E., Mayer B., Humez P., McClain C.N., Goodarzi A., Ryan M.C. (in prep): Radon, water well use, and groundwater geochemistry in Alberta, Canada.

Liggett, J.E., Humez, P., Pooley, K.E., Atkinson, N., Thistle, S., and Mayer, B. (in preparation): Controls on regional sulfate distribution and dynamics in shallow groundwater in the northern Prairies.

Plata et al. (in preparation): Occurrence and geochemical controls of Mn, As, and Fe in groundwater of Alberta, Canada.

Thistle et al. (in preparation): Potential geogenic sources and hydrogeological dynamics controlling the occurrence and distribution of elevated fluoride in groundwater in Alberta.

Humez et al. (in preparation): The occurrence, source and fate of nitrate in groundwater of Alberta.

Conference proceedings

Liggett, J.E., Humez, P., Pooley, K.E., Atkinson, N., Thistle, S. and Mayer, B. (submitted): Controls on regional sulfate distribution in groundwater resources in Alberta; Submitted to IAH-CNC GeoSaskatoon 2023. Saskatoon, SK, October 1-4, 2023.

Hartman, G.M.D., Pawley, S.M., Utting, D.J., Atkinson, N. and Liggett, J.E. (submitted): The Empress Group in Alberta, Canada. Submitted to GeoConvention, Calgary, AB. May 15-17, 2023.

Plata I, Humez P, Ligget J, McClain CN, Mayer B (2022) Assessment of the occurrence and geochemical controls of Mn concentrations in groundwater of Alberta, Canada. GeoHalifax2022.

Plata I, Humez P, McClain CN, Mayer B (2022) The distribution of As, Fe and Mn in groundwater of Alberta, Canada Goldschmidt Conference.

Ruff SE, Humez P, Hrabe de Angelis I, Nightingale M, Cho S, Connors L, Kuloyo OO, Seltzer A, Wankel S, McClain CN, Mayer B, Strous M (2022) productive and diverse microbial communities in ancient groundwaters are fueled by hydrogen, sulfur, methane, and oxygen. 18th International Symposium on Microbial Ecology.

Eldridge EL, McClain CN, Humez P, Mayer B, Ryan C (2021) A preliminary assessment of geochemical and geologic controls on radon in Alberta groundwater. GeoNiagara2021.

Digital data

Pawley, S.M. (in press): Sandiness above bedrock model (GIS data, ACSII format); Alberta Energy Regulator / Alberta Geological Survey, AER/AGS Digital Data 2023-XXXX.

Pawley, S.M. (in prep): Web application for sandiness above bedrock model (Interactive map and app); Alberta Energy Regulator / Alberta Geological Survey.

Pawley, S.M. (planned): Machine learning model code for sandiness above bedrock; Code published on GitHub.

CONCLUSIONS

The **objective** of this project was to determine the occurrence of key contaminants in groundwater throughout Alberta and to assess groundwater quality in a 3D aquifer framework. Where possible it was also attempted to understand the origin and potential fate of selected contaminants including methane, ethane, propane, nitrate, manganese, iron, sulfate, selenium, fluoride and radon.

There is astonishingly detailed information available on the quality of groundwater in Alberta based on the availability of 131,491 QA/QC'ed groundwater samples with > 10 million groundwater quality parameters. This project has amalgamated this information into a unified dataset that reveals the spatial distribution of groundwater quality parameters across Alberta.

This has provided an improved understanding of the occurrence, the origin, and the fate of select groundwater constituents and contaminants in shallow groundwater of Alberta.

Circa 65% of the groundwater samples have total dissolved solids (TDS) concentrations <1000 mg/L while 34% of the samples have TDS concentrations between 1,000 and 4,000 mg/L, and only 1% of the samples are saline (e.g., TDS >4,000 mg/L). A high proportion of groundwater samples were found to have mildly to highly reducing redox conditions ranging from post-oxic to sulfidic and methanic conditions. Consequently, circa 80% of the groundwater samples had negligible nitrate concentrations, while only 3% of the samples exceed 10 mg/L nitrate-N.

For manganese (Mn), 2,217 samples exceeded the maximum acceptable concentration (MAC) for drinking water of 0.12 mg/L, while arsenic (As) concentrations exceeded the MAC of 0.01 mg/L in 443 samples. Elevated Mn and As concentrations were mainly observed in shallow aquifers in sediments above bedrock characterized by post-oxic redox conditions.

The concentration of sulfate in Alberta groundwater is highly variable with 22% of the samples exceeding the aesthetic objective (AO) for drinking water of 500 mg/L. Oxidation of sulfide minerals in tills and shallow bedrock was identified as the predominant source of sulfate in groundwater. It was also found that a considerable number of groundwater samples in Alberta have fluoride (F) concentrations above the MAC of 1.5 mg/L. Hotspots of elevated F were always associated with groundwater having low Ca concentrations and Na-dominated water types. Only 25 samples exceeded the MAC for selenium (Se) of 0.05 mg/L.

Due to the often highly reducing conditions in some aquifers of Alberta, methane was detected in 1396 groundwater samples. Stable isotope analyses revealed that methane is predominantly of microbial origin. Radon was also found to be ubiquitous in groundwater obtained from 47 provincial groundwater observation well network (GOWN) wells but with comparatively low concentrations <65 Bq/L and is therefore not considered a significant health risk.

Microbiological analyses on samples obtained from GOWN wells revealed that older groundwaters, especially those from aquifers containing coal and shale, had surprisingly high numbers of bacteria sustaining productive microbial communities that are actively involved in cycling of oxygen, nitrate, sulfate and methane among others. Hydrogen was identified as a major energy source driving bacterial growth and cycling of methane in aquifers, while aquifer-internal formation of oxygen from nitric oxide was also revealed by metagenomic analyses.

The information compiled in this project was used to further advance the development of a 3D aquifer framework model for Alberta. This has resulted in an improved differentiation between different bedrock aquifers and aquifer-hosting sediments above bedrock including an updated stratigraphic framework for basal sand and gravel units that are part of the Empress group.

Outcomes of this project include an unprecedented knowledge of the spatial distribution of groundwater quality parameters across Alberta and an improved understanding of the province-wide occurrence, origin and fate of select groundwater contaminants having health implications for humans, livestock and ecosystems.

Key learnings are that there is astonishingly detailed information available on the quality of groundwater in Alberta based on the availability of 131,491 QA/QC'ed groundwater samples. This project has amalgamated this information into a unified dataset that reveals the spatial distribution of groundwater quality parameters across Alberta. This has provided an improved understanding of the occurrence, the origin and the fate of select groundwater constituents and contaminants in shallow groundwater of Alberta.

Broader benefits of the key learnings to users of groundwater in Alberta include a province-wide and systematic understanding of the quality of groundwater including its salinity, the water type, and the redox state of the groundwater. Salinity, water type and redox conditions are the key factors controlling the occurrence and fate of many groundwater constituents and contaminants including nitrate, manganese, arsenic, fluoride, sulfate and methane.

Next steps: The conducted research has enabled unprecedented insights into the spatial distribution of groundwater quality parameters in Alberta. However there has not yet been a regional assessment of historical change of shallow (<50m) groundwater quality nor an analysis of how such potential temporal trends in some groundwater quality parameters relate to land use changes throughout the last decades. Furthermore, climate change is expected to have significant impacts on hydrological systems in Alberta in the next few decades.

Given the connection of groundwater to land use, climate, and surface water, groundwater quality cannot be studied or managed in isolation without consideration of broader impacts and cumulative effects. Hence, an investigation of past changes and expected future trends in Alberta's groundwater quality due to land use changes, climate change, and water management scenarios is timely. Hence, a follow-up investigation is proposed to study temporal trends in select groundwater contaminants, the indicators that track these changes, whether changes have resulted from human activities, and which indicators in shallow groundwater (<50m) serve as early warnings for future changes to deeper (>100m) high-quality groundwater sources. To advance integrated approaches to water management in Alberta it is imperative to explore connections between historical trends in groundwater quality, land use, and surface water quality. This will help identify future threats potentially impacting this essential resource.

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