Groundwater Quality in the Oil Sands Region: Determining the Geochemical Status Quo for Change Detection and Attribution Studies

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Introduction

Groundwater is required in Alberta to supply safe and secure drinking water for a growing population, to sustain healthy aquatic ecosystems, and for providing quality water for a growing economy. While considerable groundwater research has been conducted in Alberta by various organizations (e.g., Manchuk et al., 2021), a combined geochemical and hydrogeological approach to obtain an integrated understanding of aquifer extents, aquifer connectivity, as well as groundwater quality and contamination in Alberta's oil sands region has not been previously attempted. This knowledge is, however, essential for a wide variety of reasons including the following: 1) providing additional assistance with identifying safe zones for wastewater disposal; 2) identification of areas with groundwater-surface water interaction; 3) environmental impacts resulting from groundwater - surface water interaction; 4) assessing and accessing suitable groundwater supplies for economic development. Closing this knowledge gap is of vital importance.

Objective

The objective of this project was to investigate groundwater quality trends and anomalies in the oil sands region and to determine which natural and/or anthropogenic sources and processes are responsible for the observed water quality trends. This research established a current baseline against which potential future changes can be assessed. Within the funding cycle, the work investigated temporal trends in regional groundwater quality anomalies focussing on five previously identified areas in the oil sands region.

Methods

Five anomalous zones displaying unique groundwater geochemistry have been identified by Manchuk et al. (2021) and Birks et al. (2022) in the Oil Sand Region as shown in Figure 1. The groundwater quality data used for this report included samples collected from monitoring wells (GOWN) with data available from Alberta Environment and Protected Areas (AEPA), while a subset of GOWN samples was analyzed for geochemical composition at the University of Calgary. Additional samples from non-monitoring wells and associated chemical compositions were derived from publicly available sources such as the Alberta Water Well Information Database (AWWID), which provides groundwater geochemical data. Both GOWN and AWWID geochemical data were combined into one unified dataset (AGg dataset). An additional dataset called "AENV_2004" was also integrated, which contains geochemical information from non-monitoring wells with geological allocations in the Cold Lake area, which is publicly available via the Alberta Geological Survey (AGS).

Zones 1 and 5 are the areas with the highest density of groundwater samples available: over 400 groundwater samples in Zone 1, and over 4,000 groundwater samples in Zone 5, mainly from monitoring, domestic and industrial water wells. In contrast, in Zones 2, 3 and 4 less than 60 groundwater samples (Zone 2 = 18, Zone 3 = 9, Zone 4 = 25) were available for interpretation. All groundwater quality data for samples across the five different zones were subjected to a detailed QA/QC analysis that included an assessment of electroneutrality (< ± 10 %) to identify potential analytical errors or sampling handling problems, a well information verification to ensure that each groundwater sample is linked to a monitoring well with accurate coordinate assignments, and detailed depth and completion interval information, while ensuring only unique samples (e.g., not duplicates) were used for analysis of spatial and temporal trends in groundwater chemistry with the utilized geographic information systems. Only samples passing the QA/QC test were interpreted with the objective of determining the causes for anomalous groundwater chemistry.

The temporal analyses of select water quality parameters were performed using the Mann-Kendall Trend Test using the interface R, a non-parametric statistical method widely used to identify monotonic trends in environmental data such as groundwater constituent concentrations over time. This test is particularly advantageous for this study, because it does not require the assumption of a specific data distribution and it is insensitive to outliers, making it suitable for datasets that may not follow normal distribution patterns. The Mann-Kendall Trend Test was applied to select water quality parameters for each water well with multiple sampling dates enabling the detection of significant increasing or decreasing trends in concentrations of select groundwater quality parameters. A positive test statistic indicates an upward trend in concentrations, while a negative statistic suggests a downward concentration trend indicated by upward and downward arrows in Figure 4. It is important to note that the Mann-Kendall Trend Test is designed for analyzing a single variable at a time. Therefore, when dealing with multiple constituents, each constituent must be analyzed separately to accurately assess trends.

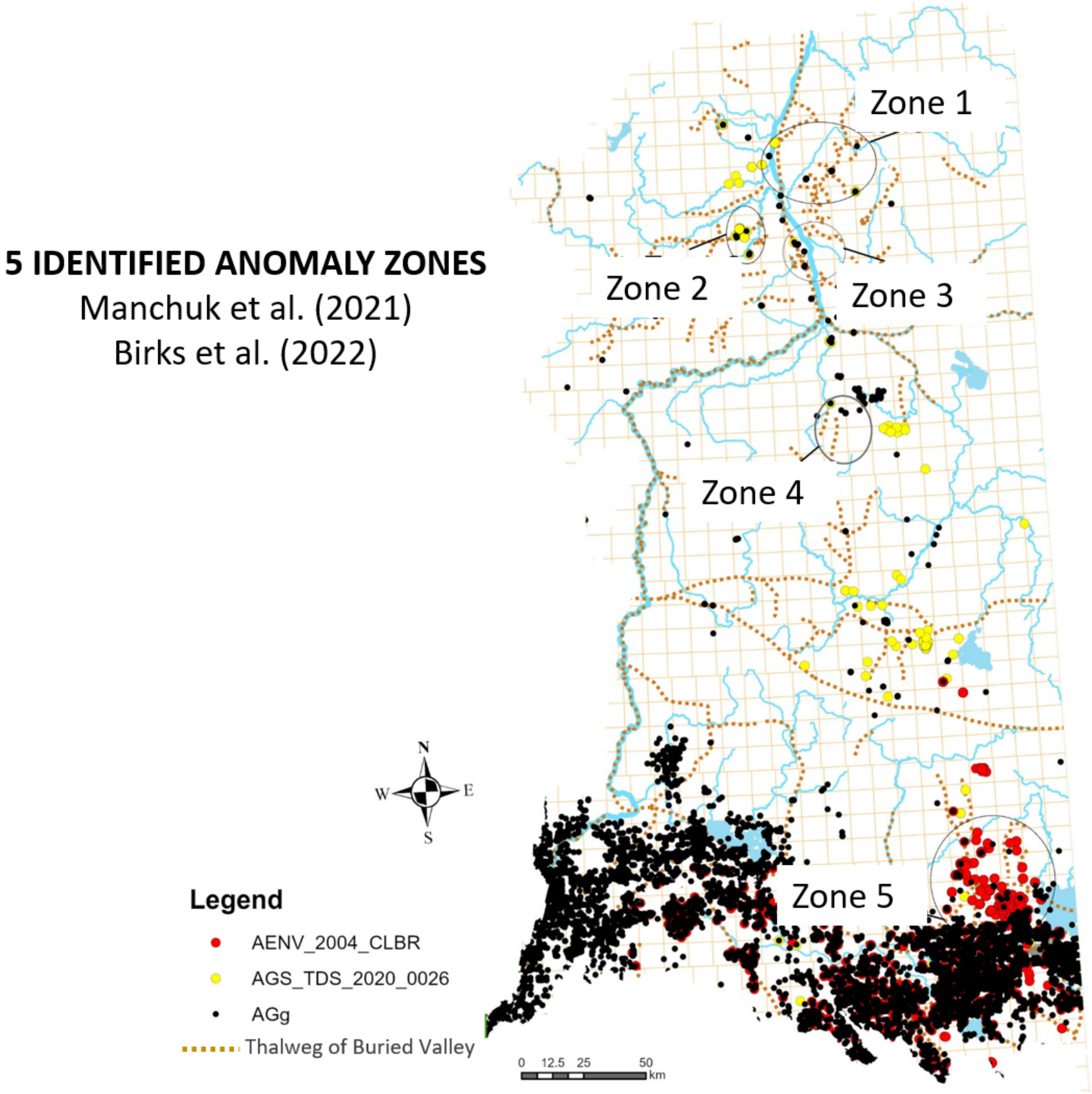


Figure 1: Five anomaly zones identified by Manchuk et al. (2021) and Birks et al. (2022) with the groundwater quality database compiled by the University of Calgary (AGg, black symbols) and publicly available groundwater quality data: AENV_2004, red colour symbol in the Cold Lake Beaver River (CLBR) and AGS_TDS (yellow colour symbol, Lemay et al. (2021)).Thalwegs of bedrock valleys are also shown in the map (Andriashek, 2018).

Groundwater level data for GOWN wells were obtained from the AEPA website and hydraulic data such as depth to static water level and digital elevation per station were available from AWWID and permitted the calculation of hydraulic heads. In all five zones, we have integrated hydro-geological context to better understand the geochemical composition of groundwater and anomalies specific to individual geological formations in a multi-step approach. A critical step was a literature search to determine the different boundaries of salt scarps in the underlying Paleozoic stratigraphic units. This also included the development of an approach to assign geological formations to all water wells that had a completion interval description without an assignment of the geological formation in which the well is completed. We used Petra® software to analyze available subsurface well data: water well depths, screen intervals and lithology logs, including geophysical logs where available. Geological allocations of water well completions were based on elevation of completed well screen intervals relative to previous Quaternary correlation work (Andriashek and Fenton, 1989), and where possible, new picks were allocated to screen intervals based on lithology log description and elevation of well screens (see *Figure 2*).

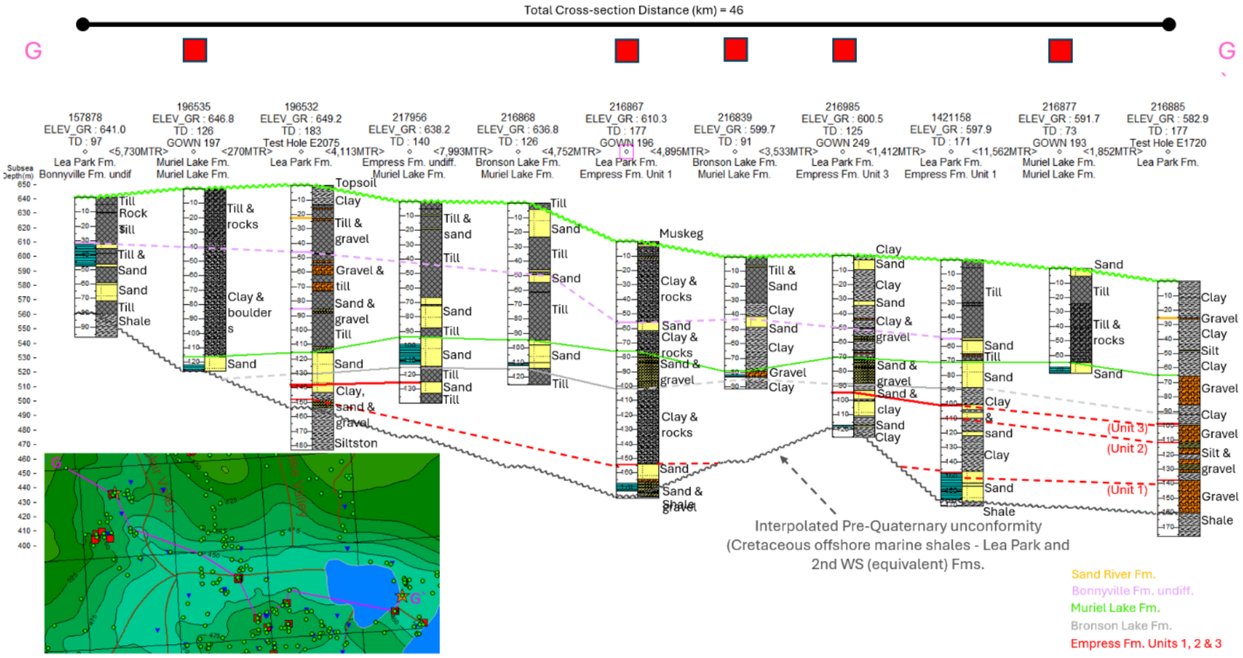


Figure 2: Example of a cross-section in Zone 5 (not to scale) that was used to assign Quaternary or Neogene geological units such as Sand River Fm., Bonnyville, Muriel and Empress Fm. for domestic well screens where only lithology logs were available. Cretaceous marine shales such as the Lea Park and Second White Specks Fm. represent the bedrock systems in this area. Bottom left of the figure shows the bedrock topography structure map shown for reference and geologic cross-section GG' through lithology logs and groundwater well locations. The bedrock topography varies from 525 m asl (dark green) to 450 m asl (light green to blue colors). The number at the top of each well is the Groundwater Information Centre Well ID.

Key Findings

Groundwater quality concentration ranges for Zones 1 and 5 are summarized in Table 1 separated for each hydro-stratigraphic zone where enough data were available. For Zones 2, 3 and 4, data availability was insufficient for inclusion in this table.

Table 1: Major ion concentrations range (minimum – maximum) per hydro-stratigraphic unit in Zones 1 and 5. *Abbreviations: ss = surficial sediments, McM = McMurray, CW = Clearwater, GC = Grand Centre, MC = Marie Creek, EL = Ethel Lake, BV = Bonnyville, ML = Muriel Lake, BL = Bronson Lake, EP = Empress Bed = Bedrock. DL = detection limit.*

n	Hydro-stratigraphic unit	Concentration range (minimum – maximum) per hydro-stratigraphic unit and per zone in mg/L							
		Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3-N
Zone 1 – data source (UofC)									
93	ss.	2.1 -210	0.5 - 141	125- 1375	2.1 – 114,5	0.5 - 320	0.5 - 660	239-2110	DL – 6.8
18	CW	2.5 - 44	0.01 – 3.2	198-700	2.5-118	3.5-200	0.89-103	423-1897	DL-39
230	McM	1.1 - 1397	0.1 - 318	2.8 – 111,250	0.3 - 493	0.6 – 172,000	0.7 – 44,431	105-2188	DL – 43.4
Zone 5 – data source (AENV_2004, AGS)									
333	GC	33 - 1800	10.5 - 688	1.9 -685	0.6 - 16	0.5 - 1460	0.2 - 313	184-4570	DL – 3.19
181	MC	31.7 - 180	0.5– 51.2	7.7 - 151	1.9 - 8	0.5 – 51.2	1.9 - 329	132 -807	DL – 7.9
173	EL	4.4 - 224	17 - 75	10.3 - 150	2.7 – 9.2	0.5 – 25.7	0.3 - 415	209 - 831	DL – 0.5
384	BV	9.9 - 171	14.7 - 55	13.1 - 254	2.8 – 11.9	0.5 – 59.6	0.2 - 518	349 - 896	DL – 2.4
713	ML	11 - 200	8 - 60	8 - 333	2.7 – 14.4	0.5 - 146	0.5 - 671	176-1060	DL – 1.1
919	EP fm	12.8 - 212	7 - 92	9.4 - 1820	1.7 - 145	0.5 - 2860	0.5 - 808	162 - 962	DL – 9.9
125	Bed fm.	9.5 - 320	13.3-111	63 - 6960	3.8 – 29.1	0.9 – 12,000	0.9 - 2900	71 - 763	DL – 0.6

Most of the water wells from which groundwater with quality data was available are completed in sediments above bedrock in Zone 5. For these wells, we assigned a refined Quaternary or Neogene period formation allocation (Marie Creek Fm., Ethel Lake Fm., Bonnyville Fm., Muriel Lake Fm., Empress units). In addition, geological features such as the presence of major buried valleys that could influence aquifers in quaternary deposits and sub-cropping bedrock geology were investigated and a bedrock topography structure map was created (see Figure 2). The depositional environments of the different formations across the five zones were considered to understand the potential influence of specific geochemical features on groundwater quality (see Figure 3). For instance, groundwater samples collected from water wells completed in marine sedimentary bedrock have an increased likelihood of being associated with higher salinity compared to groundwater samples obtained from non-marine formations. For example, in Zone 2 groundwater samples collected from water wells completed in the Waterways, Wabiskaw and Clearwater Formations have elevated TDS concentrations >3000 mg/L and Cl concentrations between 100 and 5000 mg/L consistent with an aquifer composed of marine depositional sedimentary units. The Alberta Environment Water Act defines saline groundwater as that containing greater than 4000 milligrams per litre (mg/L) total dissolved solids (TDS).

Formation name	Depositional environments	Salinity estimation	
Surficial Sediments	Non-marine	Low salinity	observed
Grand Rapids Fm.	Marine	High salinity	
Clearwater Fm.	Off-shore marine	High salinity	observed
Wabiskaw Fm.	Estuary to marine	High salinity	observed
McMurray Fm.	Fluvial to estuary	Moderate salinity	
Waterways	Marine Platform	High salinity	observed

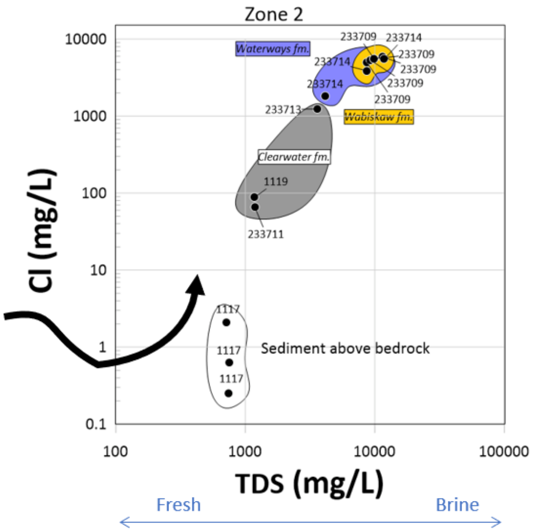


Figure 3: Groundwater salinity likelihood based on the depositional environments in Zone 2 displayed from the youngest (top) to the oldest units (bottom).

For all zones, temporal trends of select aqueous geochemistry parameters were investigated for water wells where groundwater samples were collected repeatedly. Trend detection involved analysis of time series of water quality parameters to determine if the concentrations of a specific parameter generally increase or decrease (referred to as monotonic) or remained constant over time (referred to as non-monotonic). We used Mann-Kendall Trend Tests to detect temporal trends in water quality parameters in groundwater from specific wells (Figure 4).

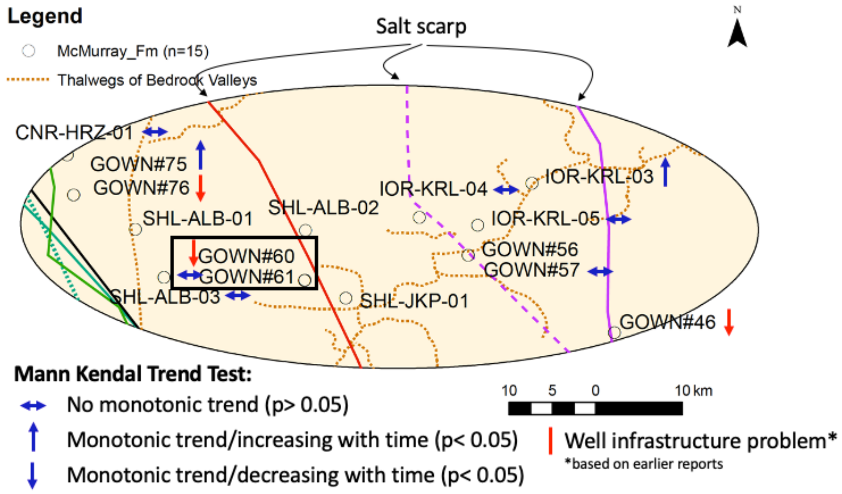
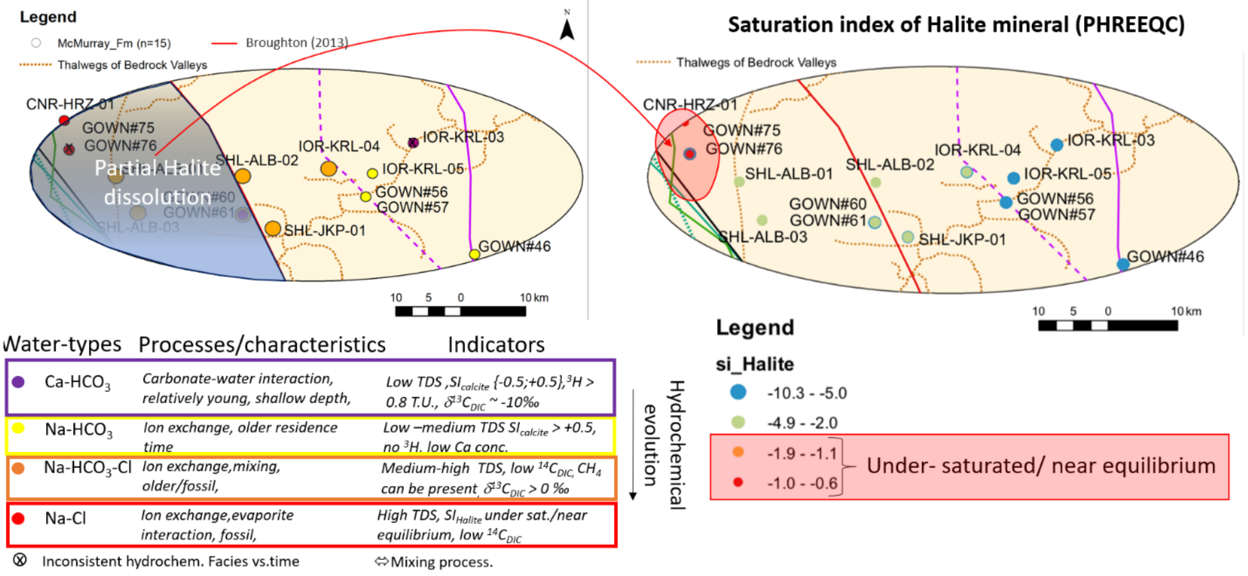


Figure 4: Summary of Mann Kendall Trend Tests applied to individual parameters of groundwater chemistry for samples from monitoring wells completed in the McMurray Fm. in Zone 1. Data for samples collected between 1975 and 2024 provided insights into temporal variations in salinity proxy parameters such as sodium (Na), chloride (Cl), and sulfate (SO_4). The following significant monotonic trends were detected: GOWN # 60: monotonic trends (decreasing, Mann-Kendall Score S< 0, p-value < 0.05) for Na, Cl, but non-monotonic trend for SO_4 (p-value >0.05); GOWN # 75: monotonic trends (decreasing, Mann-Kendall Score S< 0, p-value < 0.05) for Na, Cl and SO_4; GOWN #76: monotonic trend (increasing, Mann-Kendall Score S> 0, p-value < 0.05) for SO_4, but non-monotonic trend for Na and Cl (p-value >0.05) and IOR-KRL-03: monotonic (increasing, Mann-Kendall Score S> 0, p-value < 0.05) for Cl, but non-monotonic for Na and SO_4 (p-value >0.05).

Over 300 temporal trend tests per major ion were performed for groundwater from wells in Zones 1 and 5 where a sufficient number of samples per water well were available for time series tests. In part due to highly discontinuous and variable analytical records for groundwater through time for selected wells, monotonic trends were detected only in few cases. In Zone 1 for instance, only 18% of the wells completed in the McMurray Fm. displayed increasing monotonic trends with respect to major ions, while 27% of the wells completed in the McMurray Fm. displayed decreasing monotonic trends for select major ions. Furthermore, the time series of only 16% of the parameters for samples collected from wells completed within the Muriel Lake Fm. displayed monotonic temporal trends. This indicates that for the majority of wells and groundwater parameters no consistent increasing or decreasing temporal changes in concentrations were identified.



Water-types	Processes/characteristics	Indicators
● $Ca\text{-}HCO_3$	*Carbonate-water interaction, relatively young, shallow depth,*	*Low TDS ,$SI_{calcite}$ {-0.5;+0.5},^3H > 0.8 T.U., $\delta^{13}C_{DIC}$ ~ -10‰*
● $Na\text{-}HCO_3$	*Ion exchange, older residence time*	*Low –medium TDS $SI_{calcite}$ > +0.5, no ^3H. low Ca conc.*
● $Na\text{-}HCO_3\text{-}Cl$	*Ion exchange,mixing, older/fossil,*	*Medium-high TDS, low $^{14}C_{DIC}$, CH_4 can be present, $\delta^{13}C_{DIC}$ > 0 ‰*
● $Na\text{-}Cl$	*Ion exchange,evaporite interaction, fossil,*	*High TDS, SI_{Halite} under sat./near equilibrium, low $^{14}C_{DIC}$*

⊗ Inconsistent hydrochem. Facies vs.time

⇔Mixing process.

Figure 5: Hydro-chemical facies and respective geochemical properties for groundwater samples collected in the McMurray formation in Zone 1. All saturation index (SI) calculations were conducted with PHREEQC. Salt scarp extent and boundaries have been digitalized for this study from various sources including Broughton (2013, red color line), Walker et al. (2017, purple color line), Schneider and Grobe (2013, dotted purple color line), Meijer Drees (1994, black line), Wightman et al. (1995, blue color line) and Hauck et al. (2017, green color line).

In all five zones, we determined the hydro-chemical facies (e.g., water type) for the groundwater samples obtained from specific geological units and performed geochemical speciation using PHREEQC to reveal the dominant geochemical processes in each geological formation for which groundwater data were available. Figure 5 shows significant geochemical variability in the groundwater samples within the McMurray Fm. in Zone 1. The groundwater varies from Ca-rich ($Ca\text{-}HCO_3$) low TDS waters in the east to Na-rich (Na-Cl, $Na\text{-}HCO_3\text{-}Cl$) high TDS waters in the west (Figure 5). This distribution of different water types suggests an influence of salt dissolution in the subsurface in the western portions of Zone 1, which is further supported by saturation index calculation of halite (Figure 5) and consistent with the salt scarp demarcations shown in Figure 4.

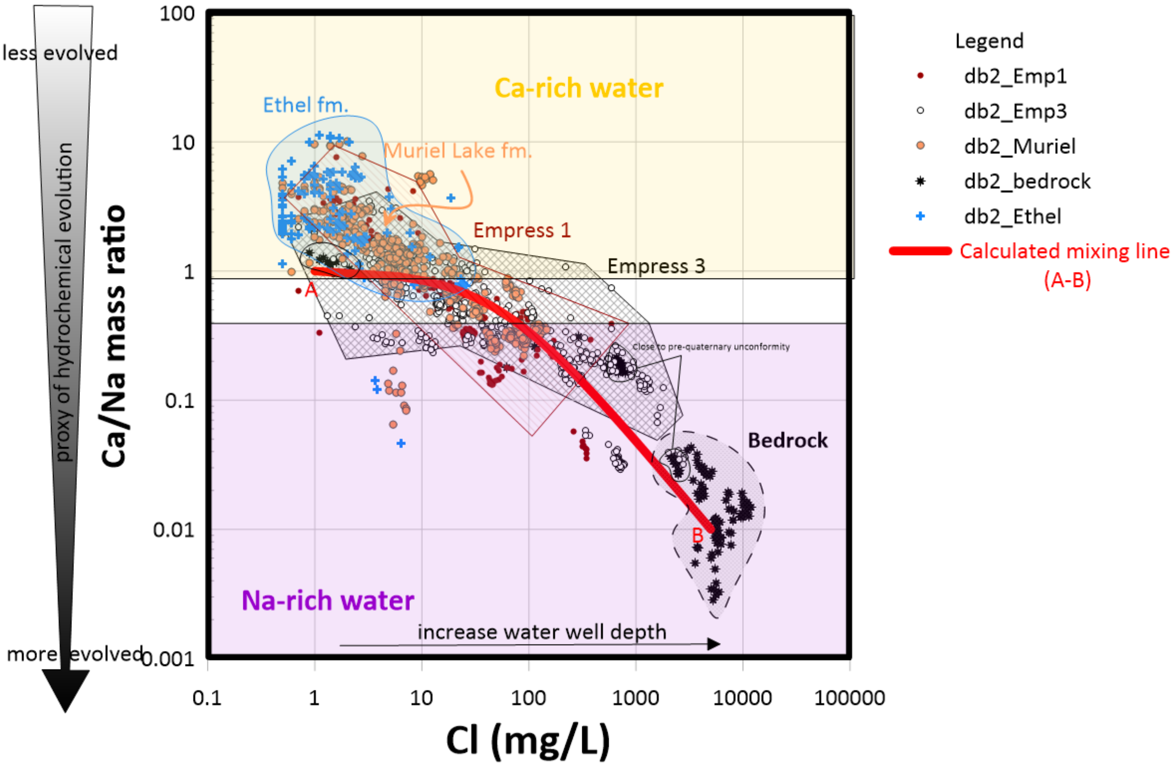


Figure 6: Overview of geochemical patterns in groundwater for different geological formations in Zone 5 based on samples from the Alberta Geological Survey database (AENV_2004). Groundwater samples from select surficial formations are indicated by different colors in Zone 5 such as Ethel Lake, Muriel Lake, Empress formations. Data ranges of select groundwater quality variables from Grand Centre, Marie Creek, Bonnyville formations are summarized in Table 1.

Zone 5 was identified as another area with remarkable variability in the geochemistry of groundwater and we conducted a detailed investigation of the causes of this variability. In Zone 5, water well screen intervals are predominantly associated with various hydro-stratigraphic units in quaternary formations (see Figure 2). Figure 6 shows a plot of Ca/Na ratios versus Cl concentrations for groundwater from the extended database containing over 4000 samples for Zone 5. The Figure displays a clear and systematic trend of groundwater samples with low Cl concentrations and high Ca/Na ratios in samples from the Ethel Fm., towards samples with markedly increasing chloride concentrations associated with decreasing Ca/Na ratios in parts of the Muriel Lake Fm. and the Empress 1 and Empress 3 Fms. (Figure 6). Such a trend could be caused by admixture of increasing proportions of a saline water source with chloride concentrations >1000 mg/L and a Ca/Na ratio <0.1 as shown in Figure 6 by the red line. Figure 2 and cross-section GG' reveal that the underlying bedrock in Zone 5 is composed of the Cretaceous

Lea Park and Second White Specks Fm. which are dominated by marine shales. The geochemistry of formation waters of these bedrock formations is characterized by Cl concentrations > 1000 mg/L and a Ca/Na ratio <0.1. Therefore, we hypothesize that saline fluids from Cretaceous bedrock units influence to various extents the geochemistry of groundwater in surficial sediments, causing the significant geochemical variability in groundwaters as displayed in Figure 6. We tested whether mixing processes between Ca-rich freshwater from aquifers in surficial sediment formations and Na-rich saline water from the Cretaceous bedrock units (e.g., Lea Park, Second White Specks Fm.) can explain the observed trends shown in Figure 6 using Cl concentrations as a conservative tracer. We found that less than 6% of water from bedrock formations would be required to increase the salinity of the groundwater present in the surficial formations. Therefore, we conclude that admixture of saline water is a key factor in water quality degradation of groundwater in Zones 1 and 5 of the study area. The question of whether the admixture of saline water is predominantly caused by natural factors, for instance associated with water pressure variations associated with glacial cycles, or whether anthropogenic causes play a partial role cannot be answered based on geochemical analyses alone.

To further investigate the causes of salinity variations in groundwater, we used water level fluctuation data when available to explore potential hydraulic connectivity, or lack thereof, between water wells. Figure 7A shows water levels continuously measured in 5 monitoring wells located in Zone 5. Four of the monitoring wells are completed in the Muriel Lake Fm. (#193, #195, #200 and #250), while one well is completed in the underlying Empress Fm. (#196). Figure 7A shows several episodes of decreasing water levels in the water wells completed in the Muriel Lake Fm. happening at similar time intervals. These low water levels in the Muriel Lake Fm. occur at the same time when a significant decrease in the water table by > 50 meters occurred in the Empress Fm. (well #250) as shown in Figure 7. This indicates that there is hydraulic communication between different groundwater systems in Zone 5 and it appears that the marked decreases of groundwater levels in the Empress Fm. caused more nuanced groundwater table decreases in the Muriel Lake Fm. at the same time. Similar observations were made in Zone 1. Figure 7B shows continuous water levels measured in two nested monitoring wells (#61 and #62). Water well #61 is completed in the McMurray Fm. and #62 is completed in Devonian bedrock. Although completed in different geologic units, the water level variations in both wells are similar. Since 2001, the water level of both wells has continuously decreased with time. This suggests a hydraulic connectivity between the two aquifer units. This finding is further supported by similar isotope fingerprints (δ^2H_{H2O} = -171‰; $\delta^{18}O_{H2O}$ = -22.2‰ for #61 and δ^2H_{H2O} = -171‰; $\delta^{18}O_{H2O}$ = -22.0‰ for #62 both sampled in 2019).

Continuous water level recordings for monitoring wells permitted to identify hydraulic connectivity and sensitivity of the groundwater systems over multiple geological formations to a hydraulic stress response at a local scale (Figure 7).

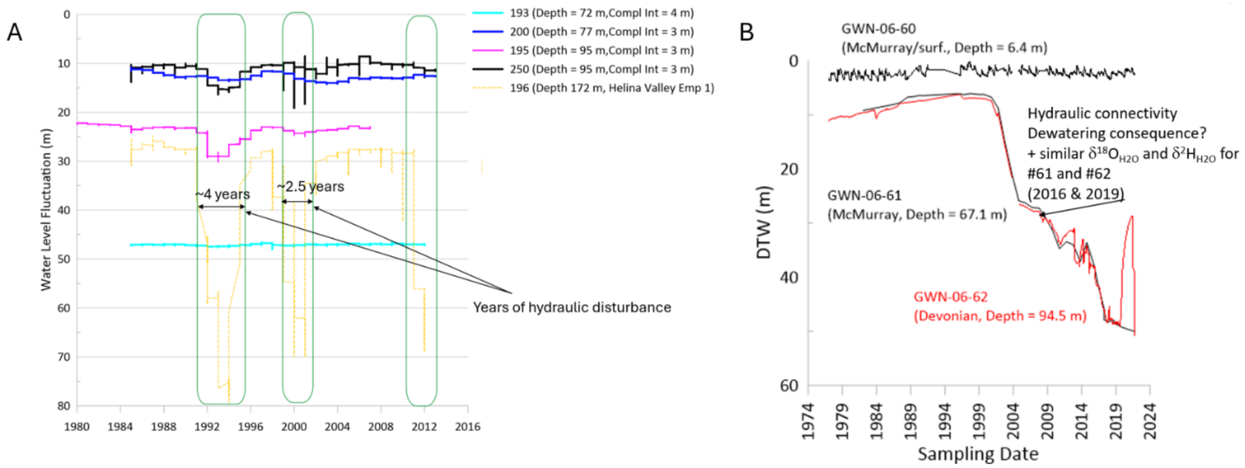


Figure 7: Static water level fluctuation with time in nested monitoring wells at a local scale, demonstrating hydraulic connectivity and sensitivity across formations over hydraulic stress A) in Zone 5 B) in Zone 1 (DTW= depth to water).

It is recommended that future research uses hydraulic head data based on elevations of wellheads and static water levels of domestic wells to further investigate potential hydraulic connectivity and direction of flow systems (horizontal, downward, upward) in the different formations at a larger scale. Some of this work has already commenced for Zone 1. Figure 8 shows that groundwater in the McMurray Fm. and in Devonian strata have similar hydraulic heads suggesting potential mixing between the two units. Such pressure-elevation plot and the hydraulic communication between water in the McMurray Fm. and Devonian strata further highlight the preliminary observations made in Figure 7B in the nested wells at local scale. The vertical connectivity between the marine Devonian and overlying non-marine formations shown at larger scale in Zone 1 (e.g., Cowie et al., 2015) is a potential mechanism that can explain trends towards higher TDS and salinity in McMurray Fm. groundwater samples as observed in Figure 5.

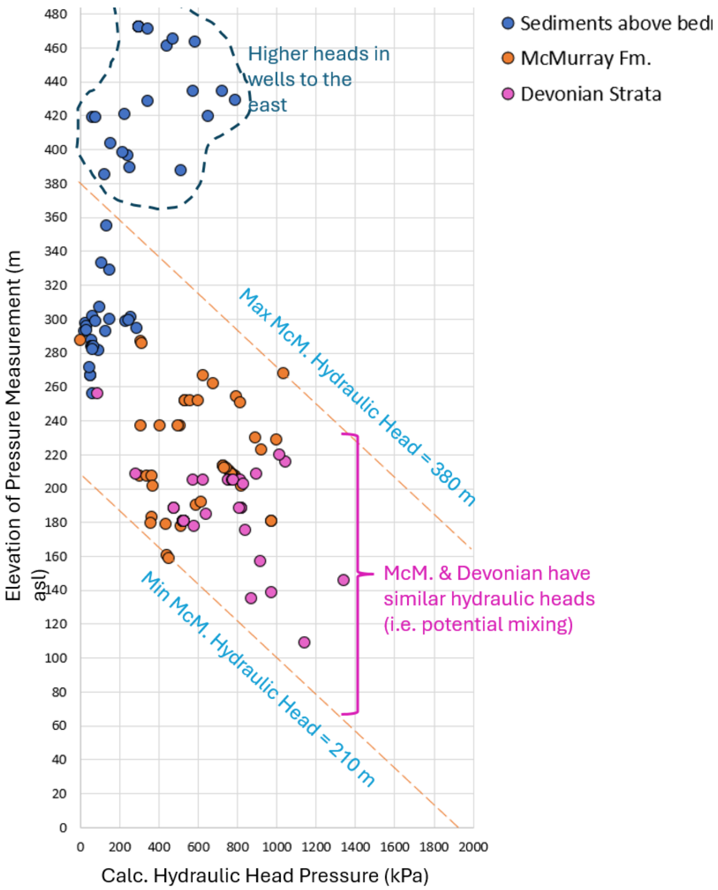


Figure 8: Pressure-elevation profile for Zone 1 that shows at larger scale that hydraulic heads of groundwater in the McMurray and Devonian strata are similar, indicating a connectivity between the two formations with different depositional environments (marine versus non marine) that can influence the geochemistry of groundwater samples in the McMurray formation.

Conclusions

Both Zones 1 and 5 have high-density groundwater quality data that enabled a detailed investigation of variations in groundwater geochemistry in dependence of the geological formations from which groundwater was obtained. In both zones, the geochemical variability of groundwater within and across formations was found to be significant with 2-3 orders of magnitude difference in terms of TDS and salinity thereby confirming previously detected groundwater quality trends and anomalies in these two zones. Low salinity groundwater with low Cl concentrations and high Ca/Na ratios were detected in samples from the Ethel Fm., whereas higher salinity groundwater with markedly increasing chloride concentrations associated with decreasing Ca/Na ratios were detected in samples from the Muriel Lake and the Empress 1 and Empress 3 Fms. In Zones 1 and 5, admixture of saline water was identified as a key factor in water quality degradation of groundwater. In both zones, vertical hydraulic connectivity between different formations and their sensitivity to hydraulic stress response have been detected making the definition of baseline groundwater quality in these areas challenging. For the majority of wells, no consistent increasing or decreasing temporal changes in most water quality parameters (e.g., major ions, etc.) were detected.

The question of whether the admixture of saline water is predominantly caused by natural factors, for instance associated with water pressure variations associated with glacial cycles, or whether anthropogenic causes play a partial role cannot be answered based on geochemical analyses alone. Therefore, it is recommended that future work uses hydraulic head data based on elevations of wellheads and static water levels of domestic wells to further investigate potential hydraulic connectivity and direction of flow systems (horizontal, downward, upward) in the different formations at a larger scale. This can be most effectively accomplished in a collaboration with the Alberta Geological Survey (AGS) since they have already begun reviewing data for the Cretaceous, Neogene and Quaternary. This collaboration will also enhance the use of a refined and consistent geological model for the study area.

In zones 2, 3 and 4 less than 60 groundwater samples were available for interpretation preventing a detailed assessment of groundwater quality trends and anomalies in these three zones. The proposed expansion of the groundwater quality information with samples from the Water Use Reporting System (WURS) and the Groundwater Management Framework (GWMF) for 2024-25 will enable the research team to investigate the question of temporal and/or regional anomalous trends in more detail.

Future Work

It is recommended that the here proposed hypotheses of the causes of water quality variations in the oil sands regions are further tested by the addition and inclusion of additional data, for example from the Water Use Reporting System (WURS), among others. Expanding the currently existing data set will open the doors for a more in-depth and more regionally extensive assessment of groundwater quality trends and their causes in collaboration with the Alberta Geological Survey, industry partners, and others. This expanded data base would improve the ability to (1) perform Mann-Kendall tests across multiple wells facilitating comprehensive trend analysis and (2) test the extent of hydrogeological connectivity amongst different aquifers and formations. The addition of isotope data, where available, is also recommended for future research.

Deliverables include:
Attachment 1: a progress report task list;
Attachment 2: a final report on trends in regional groundwater quality anomalies focussing on 5 previously identified areas in the oil sands region and associated data sets;
Attachment 3: A Powerpoint presentation summarizing the key findings;
Attachment 4: An excel spreadsheet containing all relevant geochemical data.

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