Scientific Evaluation and Interpretation of Baseline Groundwater Well Testing Data Available for British Columbia

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Executive summary

Expansion of oil and gas activities into unconventional resource plays has been accompanied by some concerns about the current and future state of groundwater in Alberta and British Columbia. A key step in addressing this concern is characterizing current baseline groundwater conditions in a scientifically sound manner using methods that enable differentiation between natural variations in water and gas geochemistry from those caused by potential anthropogenic impacts. Such a project was recently completed for the province of Alberta. However, a similar assessment has not been conducted for shallow groundwater data in areas of hydrocarbon resource development in British Columbia.

Existing data on shallow groundwater geochemistry from various sources provide a unique opportunity for a comprehensive scientific assessment of baseline aqueous and gas geochemistry of groundwater in British Columbia in areas of past, current and future hydrocarbon resource development, against which future potential impacts, or the lack thereof, by hydrocarbon development can be scientifically documented. The **objective** of this project is to compile, evaluate and interpret all available baseline groundwater testing results on aqueous and gas geochemical compositions using data available for samples collected in British Columbia in its current and future hydrocarbon resource development areas.

The project commenced with a QA/QC data quality check (e.g. electroneutrality) to assess which results are acceptable for scientific evaluation (**milestone 1**; full report section 2). A total of 3585 groundwater samples passing the QA/QC test were identified from industrial, academic and public data sources for an in-depth evaluation and interpretation of baseline groundwater well testing data for the northeastern part of British Columbia and the northwestern part of Alberta overlying the Montney resource play. Subsequently a broad-scale characterization of water types was conducted (**milestone 2**; full report section 3). Multivariate statistical analysis was used to examine geochemical trends in groundwater samples and interpret relations between inorganic aqueous parameters for samples obtained from groundwater wells across the study area. Two multivariate methods were applied using SPSS software: principal component analysis (PCA) and cluster analysis (CA). These methods provide powerful grouping mechanisms and permit to establish a robust water sample classification approach that yield three major water types:

- Type 1 (45%): Geochemically evolved water characterized by a Na-HCO_3 water type with a low Ca/Na ratio and often associated with elevated residence times;
- Type 2 (16%): SO_4-rich water samples with elevated total dissolved solids (TDS) and either associated with a) an elevated Ca/Na ratio and shorter residence times, or b) a low Ca/Na ratio associated with elevated residence times;
- Type 3 (39%): Recently recharged water characterized by a Ca-Mg-HCO_3 water type.

Subsequently, the data evaluation focused on the occurrence, variability and source of methane in shallow groundwater (**milestone 3**; full report section 4). Of the 3585 groundwater samples with aqueous geochemistry parameters passing the QA/QC test, 297 samples (8%) had accurate gas composition analyses reported. Methane concentrations above the detection limit were observed in 223 of the 297 samples. The dissolved methane concentrations in the 223 groundwater samples varied from 0.0002 to >40 mg/L. More than 85% of the samples with detectable methane contents had concentrations < 1 mg/L. This indicates that the occurrence of elevated concentrations of methane in baseline groundwater samples in the study area is not widespread.

Aqueous geochemistry data were used to determine whether methane occurring in shallow groundwater was produced microbially in-situ by assessing the groundwater redox conditions as opposed to situations where methane transport from underlying stratigraphic units must be postulated (**milestone 4**, full report section 5). Where possible, the research team used the isotopic composition of methane in concert with other indicator parameters (e.g. ethane and propane concentrations, dryness parameter etc.) to differentiate potential cases of thermogenic gas transport (from deeper stratigraphic units) from occurrences of microbial oxidation of biogenic gas that may result in elevated carbon isotope ratios falsely suggesting the occurrence of thermogenic gas (**milestone 5**; full report section 6). 157 samples had sufficient methane to conduct carbon isotope fingerprinting to determine the origin and fate of methane in these groundwater samples. More than 70% of the 157 groundwater samples had a low average $\delta^{13}C_{CH4}$ value of -76.5 ‰ occurring in Na-HCO_3(-Cl) water types or Type 1 indicating that the methane had formed biogenically. More than 25% of the 157 samples had methane concentrations <0.05 mg/L and $\delta^{13}C_{CH4}$ > -55‰ occurring in rather oxidized groundwater environments (e.g. SO_4-rich and Ca-Mg-HCO_3 type samples or Types 2 and 3). This suggests that the elevated $\delta^{13}C$ values of methane in these samples have resulted from oxidation of biogenic methane. Only 4 of the 157 samples (<3 %) were characterized by methane concentrations > 1 mg/L and $\delta^{13}C_{CH4}$> -50 ‰. This may be an indication that this methane is of thermogenic origin.

The **key conclusions** of this study are therefore the following:

- The geochemical and isotopic patterns in baseline groundwater in North-Eastern British Columbia are very similar to those observed in baseline groundwater in North-Western Alberta;
- Methane detected in baseline groundwater in North-Eastern British Columbia has frequently low concentrations (<1 mg/L) and is almost always (>94%) of biogenic (e.g. natural) origin;
- Using a combination of chemical and isotopic techniques is a highly effective approach for assessing whether gas leakage from natural gas resource plays into shallow groundwater occurs in the study area, since natural gas in the Montney and Horn River Formations is of thermogenic origin and characterized by elevated and distinct carbon isotope ratios of methane, ethane and propane.

1. Introduction

Expansion of oil and gas activities into unconventional resource plays has been accompanied by some concerns about the current and future state of groundwater in Alberta and British Columbia. A key step in addressing this concern is characterizing current baseline groundwater conditions in a scientifically sound manner using methods that enable differentiation between natural variations in water and gas geochemistry from those caused by anthropogenic impacts. Such a project was recently completed for the province of Alberta. However, a similar assessment has not been conducted for shallow groundwater data in areas of hydrocarbon resource development in British Columbia.

Existing data on shallow groundwater geochemistry from various sources provide a unique opportunity for a comprehensive scientific assessment of baseline aqueous and gas geochemistry of groundwater in British Columbia in areas of past, current and future hydrocarbon resource development, against which future potential impacts, or the lack thereof, by hydrocarbon development can be scientifically documented. The **objective** of this project was to compile, evaluate and interpret all available baseline groundwater testing results on aqueous and gas geochemical compositions using data available for samples collected in British Columbia in its current and future hydrocarbon resource development areas.

The project commenced with a QA/QC data quality check (e.g. electroneutrality) to assess which results are acceptable for scientific evaluation (milestone 1; section 2). This was followed by a broad-scale characterization of water types (milestone 2; section 3). Subsequently, the data evaluation focused on the occurrence, variability and source of methane in shallow groundwater (milestone 3; section 4). Aqueous geochemistry data were used to determine whether methane occurring in shallow groundwater was produced microbially in-situ by assessing the groundwater redox conditions as opposed to situations where methane transport from underlying stratigraphic units must be postulated. Where possible, the research team used the isotopic compositions of methane and higher alkanes in concert with other indicator parameters (e.g. ethane and propane concentrations, dryness parameter etc.) to differentiate potential cases of thermogenic gas transport (from deeper stratigraphic units) from occurrences of microbial oxidation of biogenic gas that may result in elevated carbon isotope ratios falsely suggesting the occurrence of thermogenic gas (milestone 4, section 5).

The project yielded a thorough scientific assessment of baseline aqueous and gas geochemistry data for British Columbia groundwater in areas of past, current and future hydrocarbon resource development. The findings are described in the following section and the key results are summarized in the conclusion section at the end of this report.

2. Milestone 1: Groundwater data availability and QA/QC data quality determination

2.1 Inventory of industrial data

The project received geochemical analyses of 25 water samples from 5 different industrial sources that will be called sources A, B, C, D, E (Table 2.1). All the water samples have been collected from domestic wells located in the Peace River and Bulkley-Nechako regional districts (North Natural Resource area in NE BC). The Figure 1.1 presents the location where the groundwater samples were collected. For our evaluation of groundwater chemistry, only analyses were utilized that reported physico-chemical parameters as well as major dissolved constituents including Ca, Mg, Na, K, HCO_3, CO_3, Cl, and SO_4. Using these data, the ionic charge balance as a QA/QC criterium was calculated accepting samples with ionic charge balance values better than ±10%.

Table 2.1: Summary of the groundwater samples obtained from different industrial sources

Source	**n**	**Well charact.**	**Routine anal.-aq phase**	**Phys-chem param**	**Other param. including organic comp.**	**trace metals**	**gaseous comp.**	**Isotopic ratios**
Source A	7 samples 4 wells	Domestic Well	Yes	Yes	Yes	Yes	Yes (C_nH_{2n+2})	No
Source B	1 samples 1 well	Domestic Well	Yes	Yes	Yes	Yes		No
Source C	12 samples 8 wells	Domestic Well	Yes	Yes	Yes	Yes	Yes (C_nH_{2n+2})	No
Source D	3 samples 3 wells	Domestic Well	Yes	Yes	Yes	Yes	Yes (CH_4)	No
Source E	2 samples 2 wells	Domestic Well	Yes	Yes	Yes	Yes		No

All the industrial databases (100%) passed the QA/QC electroneutrality test for aqueous geochemistry.

2.2 Additional geochemical groundwater data sources in NEBC

The British Columbia Oil and Gas Commission (BCOGC) maintains a Water Portal and access to additional water quality monitoring data was realized through the Water Portal. The obtained data comes from different networks including the Provincial Groundwater Observation Well Network (PGOWN) and the Northern Health Authority. In collaboration with Simon Fraser University (SFU), additional aqueous and gaseous geochemical and isotopic data were made available for this project (Table 1.2) and were interpreted to complement the data set used in this study.

- Provincial Groundwater Observation Well Network in British Columbia (**PGOWN-BC**)

The Provincial Observation Wells Network was established in 1961. The network has > 150 active observation wells covering major groundwater areas of the province of British Columbia. We identified 7 **observation wells** belonging to the **PGOWN** that are located in the Peace River Region (Fig. 2.1). The water chemistry data are available through the Environmental Monitoring System (EMS) database, but no gas data are available. The groundwater well depth is not always reported. A total of **6 out of 7 groundwater samples (86%)** passed the ±10% QA/QC electroneutrality test.

Table 2.2: Summary of the water samples obtained from different additional sources

Source		**n**	**Well charact.**	**Routine anal.-aq phase**	**Phys-chem param**	**Other param. including organic comp.**	**Trace metals**	**Gaseous comp.**	**Isotopic ratios**
PGOWN (BC)	bulk	7 samples 7 wells	Monitoring Well	Yes	Yes	Yes	Yes		
	QAQC	6 samples 6 wells							
GOWN (AB)	bulk	30 samples 9 wells	Monitoring Well	Yes	Yes	Yes	Yes	Yes	Yes
	QAQC	29 samples 9 wells							
AHS (AB)	bulk	3083 samples 1418 wells*	Domestic Well	Yes	Yes				
	QAQC	3083 samples 1418 wells*							
Northern Health Authority	bulk	177 samples 46 wells	Domestic Well	Yes	Yes	Yes	Yes		
	QAQC	57 samples 32 wells							
SFU (NEBC)	bulk	381 samples +4 samples** =385 samples 255 wells 35 springs 4 lakes 4 ponds	Monitoring Well Spring Lake Pond	Yes	Yes	Yes	Yes	Yes	Yes
	QAQC	381 samples +4 samples = 385 samples 254 wells 35 springs 4 lakes 3 ponds							

* Groundwater wells are identified with distinct coordinates (limitation to the precision of the section with the ATS)

** 4 samples do not have any coordinates

- British-Columbian public data (**Northern Health Authority**)

Water quality data from the Northern Health Authority were available on the BC Water Portal. A total of 46 water wells were identified in the area of interest (Fig. 1). Water chemical data report major and minor ion concentrations and in some cases trace elements and for some private wells long-term records are available. Episodic analyses have been reported between 1980 and 2010 for a total of 177 groundwater samples. However, the chemical analyses compiled are not always complete and as a consequence only **57 out of 177 groundwater samples (32%)** passed the ±10% QA/QC electroneutrality test. No gas data are reported.

- Monitoring well data for NEBC contributed by **SFU**

Geochemical and isotopic data were compiled by Dr. Dirk Kirste from SFU for collaborative assessment and interpretation. The dataset contains 385 samples: based on the station name, 330 samples were collected from 255 monitoring wells; 47 samples were collected from 35 springs; 4 samples were collected from 4 lakes; and 4 samples were collected from 4 ponds. All samples were analyzed for concentrations of major and minor ions as well as gaseous composition and isotopic composition of dissolved constituents i.e. dissolved methane and sulfate. However, the groundwater well depth is not always reported. A total of **385 out of 385 water samples (100%)** passed the ±10% QAQC electroneutrality test.

The Montney formation extends beyond the British Columbia boundary into northwestern Alberta (Grande Prairie area). Hence groundwater data for samples obtained above the Montney formation in Alberta is highly valuable for extending the groundwater systems characterization and the establishment of environmental baseline data for this project.

- Albertan groundwater chemistry data (**AHS Alberta Health Service**) above the Montney play area extent

Water quality data have been compiled by AHS for samples from shallow groundwater wells and a subset of these groundwater wells are located above the Montney formation in the province of Alberta. A total of 3083 groundwater samples had chemical analyses with predominantly major ions reported. No gas data were analyzed. The ATS coordinate system does not permit to geo-locating the groundwater wells beyond the section from which the samples were collected. Many groundwater samples have thus similar coordinates. Figure 1 identifies 1418 data points with distinct coordinates in the Montney play area derived from the AHS database. All of the selected **3083 groundwater samples (100%)** passed the ±10% QA/QC electroneutrality test.

- Groundwater Observation Well Network in Alberta (**GOWN-AB**)

The Government of Alberta maintains a Groundwater Observation Well Network (GOWN) with more than 300 dedicated monitoring wells often completed with short screens in single formations. The Alberta GOWN is the only dataset that provides a description of the litho-stratigraphy of the sampled wells. Since 2006, a total of 30 groundwater samples were collected from 9 groundwater wells located above the Montney resource play in Alberta. These samples were analyzed for major and minor ion concentrations as well as gaseous composition and isotopic composition of dissolved constituents i.e. methane, sulfate, among others. The 9 groundwater wells are completed within the Wapiti or Grimshaw gravel aquifers and the water well depths vary from 12.6 to 109 m. A total of **29 out of 30 groundwater samples (97%)** passed the ±10% QA/QC electroneutrality test.

Hence, a total of 3585 groundwater samples passing the QA/QC test were identified for an in-depth evaluation and interpretation of baseline groundwater well testing data for the northeastern part of British Columbia and the northwestern part of Alberta overlying the Montney resource play.

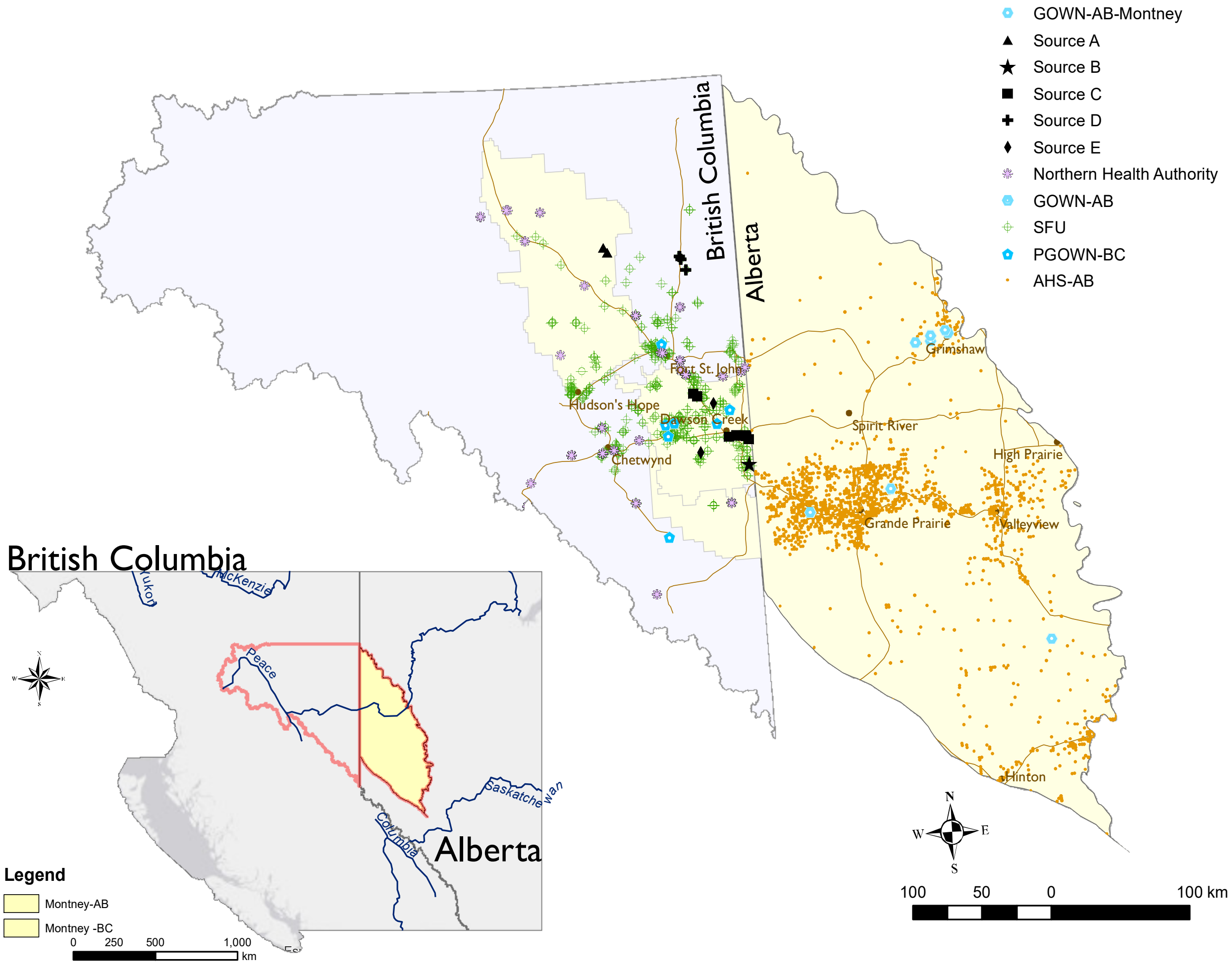


Figure 2.1: Inventory of groundwater wells located in the Montney resource play area for establishing an environmental baseline groundwater dataset (black symbols = A to E industrial data sources; colored symbols = additional public and academic data source).

2.3 Statistical analyses approaches

This abundance of data that have been compiled provides an opportunity to discover a wide range of geochemical processes that may have occurred. The use of data analysis and statistical methods combined with the use of geographical information system (GIS) present powerful means to study variables dependency and distribution, relationships between variables, and provide tool for geochemical process identification and for discovering geochemical patterns or making predictions.

Measures of skewness and kurtosis

Taking into consideration the normality assumption is important for drawing accurate and reliable conclusions regarding geochemical distribution and patterns. The skewness is a measure of lack of symmetry. A symmetrical distribution will have a skewness of 0. Kurtosis is a measure of whether the data are heavy-tailed or light-tailed relative to a normal distribution or indicates outliers. Histograms are an effective graphical technique for illustrating the skewness and kurtosis of a data set. Shapiro-Wilk tests were performed using SPSS to test the normality of the data and the significance value of less than 0.05 indicates that the data is not normal distributed.

Measures of associations between variables (bivariate analyses)

To measure the strength of association between two variables and the direction of the relationship, different bivariate analyses were performed: Pearson's r (parametric test), Kendall's τ and Spearman's ρ (non-parametric tests) coefficients were calculated using SPSS. The value of the correlation coefficient varies between -1 and +1.

Standardization of the data

Standardization the data is important preliminary step to eliminate the effect due to different dimensions of the variables. Standardization tends to inflate variables that display small variance and decrease the influence of variables with large variance.

Identification of geochemical patterns using multivariate analyses

When conducting geochemical pattern analysis, the most important issue is to choose the most appropriate pattern analysis technique. The most popular data reduction approaches are Cluster Analysis (CA) and Principal Component Analysis (PCA). Whereas cluster analysis separates samples into mutually exclusive groups based on the different inorganic variables, PCA separates variables into groups based on correlation between variables.

PCA is used to reduce variables with related relationships into a few comprehensive components. PCA is a special case of transforming the original data into a new coordinate system. Principal Component (PC) with eigenvalues >1 were retained and the retained factors were rotated via a Direct Oblimin method. The eigenvalues give the amount of the variation in the original data that is explained by the variation along the corresponding axis of the new coordinate system. The sum of the eigenvalues is thus equal to the total variation in the original variables. PCA was used to extract geochemical factors on the basis of their correlations.

Cluster Analysis (CA) creates patterns that are mutually exclusive as each water sample can belong to only one cluster. Multiple clustering algorithms exist. We use the K-means algorithm due to its widespread use as a non-hierarchical clustering method in literature. The primary purpose is to cluster water samples according to the properties of the variables. According to the Euclidean distance, clustering analysis divides water samples into a few groups, in which water samples in the same group have the most similar characteristic.

Multiple regression for understanding causes and for prediction

Multiple regression was used in SPSS to help with identifying relations between dependent variables (Y) and independent variables (X).

Re-sampling procedure: effect-size estimation

A re-sampling procedure was used whereby multiple sub-samples of the same size as the original samples are drawn randomly to provide data for empirical investigation of the variability of parameters estimates.

3. Milestone 2: Variation in geochemical signature and water-type distribution

3.1 General hydrochemical characteristics

The evaluation of hydrogeochemical processes that control the chemical composition of groundwater is required for water management purposes. The geochemistry of groundwater is partially a function of the composition of the infiltrating water and the mineral composition of the aquifer through which the water flows. Concentrations of major anions, cations and minor ions were analyzed and the water-type or hydrochemical facies was determined for each sample based on the predominant cation and anion concentrations. **A model has been developed permitting to attribute hydrochemical facies based on the relative abundance of ions for each water sample**. For example, water samples characterized by Na-HCO_3 hydrochemical facies have sodium as the dominant cation and bicarbonate as the dominant anion; a Ca-HCO_3 water type indicates that calcium is the dominant cation and HCO_3 is the dominant anion in solution. In addition, cation ratios can be used to further describe water types. An elevated Ca/Na ratio indicates the dominance of calcium in solution over sodium, and a low Ca/Na ratio indicates the predominance of sodium over calcium in solution. Detailed results for all relevant water types are summarized below for each data source, from the industrial sources to the additional sources.

We have developed a new tool called the PHO matrix that allows presenting in a quantitative fashion, large databases of water types combinations. The PHO matrix groups similar samples into bins and gives the number of samples per bin eliminating the problem of the dataset size. Matrix PHO reveals the different water-type combinations that were not visible in the Piper diagram for example.

3.1.1 Industrial sources

- Source A

For source A, the hydrogeochemical characteristics of the seven submitted water samples are summarized in Table 3.1. Five samples had a Na-HCO_3 and 2 samples a Na-HCO_3-SO_4 water type. The Na-HCO_3 samples were derived from the deeper wells (> 100 m) and have an average Ca/Na ratio of 0.08, sulfate concentrations <20 mg/L and average TDS of 631 mg/L. The Na-HCO_3-SO_4 samples were obtained from shallow wells (< 50 m), have sulfate contents > 400 mg/L, an average Ca/Na ratio of 0.3 and an average TDS content of 1020mg/L. All groundwater samples have negligible chloride concentrations.

Table 3.1: Hydrogeochemical characteristics of groundwater samples from source A.

	Ca/Na mass ratio	**Redox sensitive species {mg/L}**		**Completion interval**	**Salinity: TDS, Cl {mg/L}**	
		Mean	*SD*		*Mean*	*SD*
Na-HCO_3 (n=5 samples)	*0.08±0.02*	O_2 = n/a NO_3 =0.05 Fe =0.2 Mn = 0.02 SO_4=19.4 CH_4= 2.2	 0.05 0.008 11.24 3.8	*Deeper [115.8-140.2; 146.3-150.6]*	TDS =631 Cl=2.3	53.3 2.3
Na-HCO_3-SO_4 (n=2 samples)	*0.30±0.02*	O_2 = n/a NO_3<DL Fe = 0.2 Mn = 0.6 SO_4=405 CH_4<DL	 0.07 0.1 1.4	*Shallower [41.4-45.7]*	TDS=1020 Cl<DL	0

- Source B

For source B provided one water sample and the hydrogeochemical characteristic of the water sample is presented in Table 3.2. The groundwater sample collected from a shallow well (screen interval 21-30 m) has a $Na-HCO_3-SO_4$ water-type, a Ca/Na ratio of 0.3, a sulfate concentration of 1300 mg/L and a TDS content of 1,300 mg/L. The elevated dissolved oxygen concentration (8.1 mg/L) indicates an aerobic groundwater environment.

Table 3.2: Hydrogeochemical characteristics of groundwater samples from source B.

	Ca/Na mass ratio	**Redox sensitive species {mg/L}**	**Completion interval**	**Salinity TDS, Cl {mg/L}**
$Na-HCO_3-SO_4$	*0.3*	O_2= 8.05 NO_3 <DL Fe =0.8 Mn = 0.4 SO_4=1300 CH_4= n/a	*Shallower* *[21.34-30.48]*	TDS= 1300 Cl=15

- Source C

For source C, the hydrogeochemical characteristics of the 12 water samples are summarized in Table 3.3.

Table 3.3: Hydrogeochemical characteristics of groundwater samples from source C.

	Ca/Na mass ratio	**Redox sensitive species {mg/L}**		**Completion interval/ well depth {m}**	**Salinity TDS, Cl {mg/L}**	
		Mean	*SD*		*Mean*	*SD*
$Na-HCO_3$ *(n=1)*	*0.004*	O_2 = n/a NO_3 <DL Fe =0.43 Mn = 0.05 SO_4=80 $CH_{4=}$ n/a		*36.6*	TDS=1710 Cl=7	
$CaHCO_3Cl$ *(n=1)*	*4.3*	O_2 = n/a NO_3 =0.2 Fe =1.7 Mn = 0.07 SO_4=4.2 CH_4=n/a		*5.5*	TDS=162 Cl =43	
$CaMgHCO_3$ *(n=2)*	*8.7±0.09*	O_2 = n/a NO_3 <DL Fe =2 Mn = 0.15 SO_4=50 CH_4=0.005	 1.01 0.0 5.02 0.001	*n/a*	TDS=398 Cl=0.8	4.94 0.14
$CaMgNaSO_4$ *(n=2)*	*1.2±0.00*	O_2 = n/a NO_3 <DL Fe =0.15 Mn = 0.06 SO_4=256 CH_4 =0.004	 0.01 0.03 0 	*n/a*	TDS=400 Cl=13	1.4 0.7
$Na-HCO_3-SO_4$ *(n=6)*	*0.15±0.05*	O_2 = n/a NO_3 <DL Fe =1.12 Mn = 0.59 SO_4=1060 CH_4 <DL	 1.02 0.5 332 	*18.3 & 83.4*	TDS=2600 Cl=17	697 10

The following sequence of major water types was observed: Na-HCO_3-SO_4 (n=5) > Ca-Mg-Na-SO_4 (n=2) ≥ Ca-Mg-HCO_3 (n=2) > Na-SO_4 (n=1) = Na-HCO_3 (n=1) = Ca-HCO_3-Cl (n=1). Hence, the majority of samples (green highlights in Table 2.3) were characterized by elevated sulfate concentrations of at least 256 mg/L but frequently >1000 mg/L with Ca/Na ratios varying from 0.1 to 1.2. All samples of other water types have much lower sulfate concentrations of <80 mg/L and are distinguished by Ca/Na ratios > 4 for Ca-(Mg)-HCO_3-(Cl) waters and <0.1 for Na-HCO_3 samples. The groundwater samples have a wide range of TDS values from <200 to >2600 mg/L and a positive linear correlation has been identified between the TDS and sulfate concentrations (R-squared = 0.86).

- Source D

For source D, the hydrogeochemical characteristics of the three submitted water samples are summarized in Table 3.4. One sample has a Na-HCO_3 water type, a low sulfate concentration (3 mg/L) and a low Ca/Na ratio (< 0.1). The other two samples had water types dominated by sulfate (Na-HCO_3-SO_4, Na-SO_4) with average concentrations >1000 mg/L and Ca/Na ratios of 0.1 and 0.2, respectively. All groundwater samples have TDS values >1000 mg/L and Cl concentrations varying between 10 and 174 mg/L.

Table 3.4: Hydrogeochemical characteristics of groundwater samples from source D.

	Ca/Na mass ratio	**Redox sensitive species {mg/L}**	**Completion interval/ well depth {m}**	**Salinity TDS, Cl {mg/L}**
Na-HCO_3 *(n=1)*	*0.002*	O_2 =0.2 NO_3 =0.03 Fe =0.01 Mn =0.001 SO_4=3 CH_4= 11.9	*n/a*	*TDS=1060* *Cl=174*
Na-HCO_3-SO_4 *(n=1)*	*0.2*	O_2 =1.8 NO_3 =0.06 Fe = 0.24 Mn =2.92 SO_4=1650 CH_4 =0.005	*n/a*	*TDS=1427* *Cl=10*
Na-SO_4 *(n=1)*	*0.11*	O_2 =7.3 NO_3 =0.06 Fe = 0.44 Mn = 0.38 SO_4=1330 CH_4 =0.005	*495*	*TDS=2890* *Cl= 61*

- Source E

For source E, the hydrogeochemical characteristics of the two submitted water samples are summarized in Table 3.5. Both samples have water types dominated by calcium and sulfate (Ca-Mg-SO_4, Ca-SO_4). Both samples were obtained from shallow wells (<20 m) and are characterized by sulfate concentrations >1200 mg/L, elevated Ca/Na ratios of >2, and TDS values of circa 2500 mg/L.

- Summary of industry sample data

The majority of industrial samples (n=15) is characterized by a sulfate-rich water types (highlighted green in Tables 3.1-3.5) and TDS contents > 1500 mg/L. The second most dominant groundwater type (n=7) is

$Na\text{-}HCO_3$ (highlighted purple in Tables 2.1-2.5) with samples having low Ca/Na ratios and sulfate concentrations <80 mg/L.

Table 3.5: Hydrogeochemical characteristics of groundwater samples from source E.

	Ca/Na mass ratio	**Redox sensitive species mg/L**	**Completion interval**	**Salinity TDS, Cl {mg/L}**
$Ca\text{-}SO_4$ *(n=1)*	*2.5*	O_2 = n/a NO_3 <DL Fe <DL Mn = 0.6 SO_4=1720 CH_4= n/a	*16*	*TDS=2480* *Cl=6.4*
$Ca\text{-}Mg\text{-}SO_4$ *(n=1)*	*2*	O_2 = n/a NO_3 <DL Fe = 1.6 Mn = 0.6 SO_4=1460 CH_4 =n/a	*7*	*TDS=2550* *Cl=2.9*

Table 3.6: Hydrogeochemical characteristics of groundwater samples from PGOWN-BC.

	Ca/Na mass ratio	**Redox sensitive species mg/L**	**Completion interval**	**Salinity parameters TDS, Cl {mg/L}**
$Ca\text{-}Mg\text{-}Na\text{-}HCO_3$ *(n=1)*	*0.8*	O_2 = n/a NO_3 =n/a Fe =0.8 Mn = 0.8 SO_4=25.4 CH_4= n/a	*n/a*	*TDS=392* *Cl=0.8*
$Ca\text{-}Mg\text{-}SO_4$ *(n=1)*	*1.6*	O_2 =8.5 NO_3 =0.03 Fe =1.84 Mn = 0.31 SO_4=847 CH_4 =0.005	*n/a*	*TDS=1900* *Cl=5*
$Na\text{-}SO_4$ *(n=1)*	*0.51*	O_2 = n/a NO_3 =0.002 Fe =0.01 Mn = 0.08 SO_4=2710 CH_4 = n/a	*n/a*	*TDS=4010* *Cl=3.2*
$Ca\text{-}Mg\text{-}Na\text{-}SO_4$ *(n=1)*	*0.63*	O_2 = n/a NO_3 =0.06 Fe =12.8 Mn = 0.15 SO_4=2160 CH_4 = n/a	*n/a*	*TDS=3710* *Cl= 10*
$Ca\text{-}Mg\text{-}HCO_3$ *(n=1)*	*3.11*	O_2 =2.1 NO_3 =0.002 Fe =0.003 Mn = 0.03 SO_4=94.9 CH_4 = n/a	*n/a*	*TDS=566* *Cl= 1.2*
$Ca\text{-}HCO_3$ *(n=1)*	*11.7*	O_2 = n/a NO_3 = n/a Fe =0.16 Mn = 0.04 SO_4= 15 CH_4 = n/a	*n/a*	*TDS=202* *Cl= 1.4*

3.1.2 Provincial Groundwater Observation Well Network in British Columbia

For samples from the Provincial Groundwater Water Observation Well Network in British Columbia **(PGOWN-BC)**, the hydrogeochemical characteristics of the 6 water samples that passed the electroneutrality QA/QC test are summarized in Table 3.6.

The six PGOWN groundwater samples have six different water-types: Ca-HCO_3, Ca-Mg-HCO_3, Ca-Mg-Na-HCO_3, Ca-Mg-SO_4, Na-SO_4, Ca-Mg-Na-SO_4. In the three samples with a hydrochemical facies dominated by SO_4 (highlighted in green), the concentrations of sulfate vary from 847 to 2710 mg/L, Ca/Na varies between 0.5 and 1.6, and TDS contents were >1900 mg/L. In the three groundwater samples showing HCO_3 dominated water types, concentrations of sulfate were <100 mg/L, Ca/Na varies between 0.8 and 11.7, and TDS contents were <600 mg/L.

3.1.3 Public data from the British Columbian Northern Health Authority

For the BC Northern Health Authority dataset, the hydrogeochemical characteristics of the 57 water samples are summarized in Table 3.7 (only major water types reported). The predominant water type is Ca-HCO_3 (n=34) with groundwater samples having an elevated average Ca/Na ratio of 10.1, a low average sulfate concentration of 35 mg/L and an average TDS content of 277 mg/L. The 2nd most dominant water type is Na-HCO_3 (n=13) groundwater samples having an average Ca/Na ratio of 0.1, an elevated average sulfate concentration of 105 mg/L, and an average TDS content of 891 mg/L. The remaining samples belong to the following water types: Ca-Na-HCO_3 (n= 4) > Ca-Mg-HCO_3 (n=2) ≥ Ca-Mg-Na-SO_4 (n=2) ≥ Ca-Mg-Na-HCO_3 (n=1) ≥ Ca-SO_4 (n=1).

Table 3.7: Hydrogeochemical characteristics of groundwater samples from the Northern Health Authority.

	Ca/Na mass ratio	**Redox sensitive species mg/L**		**Completion interval**	**Salinity parameters TDS, Cl {mg/L}**	
		Mean	*SD*		*Mean*	*SD*
Ca-HCO_3 (n=34)	*10.1±6.4*	*O_2 = n/a* *NO_3 =0.3* *Fe =0.5* *Mn = 12* *SO_4=34* *CH_4= n/a*	*0.5* *1.6* *7.0* *26*	*n/a*	*TDS=277* *Cl=10.1*	*131* *17.2*
Na-HCO_3 (n=13)	*0.1±0.1*	*O_2 = n/a* *NO_3 =0.8* *Fe = 0.3* *Mn = 11* *SO_4=105* *CH_4 = n/a*	*1.3* *0.3* *8.7* *80.3*	*n/a*	*TDS= 891* *Cl=26.9*	*257* *17.9*
Ca-Na-HCO_3 (n= 4)	*1.1±0.1*	*O_2 = n/a* *NO_3 =0.1* *Fe = 6.3* *Mn = 13.7* *SO_4=10* *CH_4 = n/a*	*1.6*	*n/a*	*TDS= 240* *Cl=56.5*	*22.1*

3.1.4 Monitoring well data for NEBC contributed by SFU

For monitoring well data for NEBC contributed by SFU, the hydrogeochemical characteristics of more than 300 water samples are summarized in Tables 3.8a and 3.8b (PHO matrix). The following water types were observed: Na-HCO_3 (n=91) > Ca-Mg-HCO_3 (n=72) > Ca-HCO_3 (n=52) > Na-HCO_3-SO_4 (n=29) > Ca-Mg-Na-HCO_3 (n=27) > Ca-Mg-Na-SO_4 (n=23) > Na-SO_4 (n=18) representing >80% of the 383 groundwater samples.

Table 3.8a: Main hydrogeochemical characteristics of groundwater samples from SFU.

	Ca/Na mass ratio	*Redox sensitive species mg/L*		*Completion interval*	*Salinity parameters TDS, Cl {mg/L}*	
		Mean	*SD*		*Mean*	*SD*
Na-HCO_3 (n=91 including 7 samples from springs)	*0.12±0.12*	O_2=1.3 N-NO_3 =0.5 Fe =1.04 Mn = 0.15 SO_4=186 CH_4= 3.46	*1.8* *1.4* *2.8* *0.3* *171* *7.4*	*n/a*	*TDS=1852* *Cl= 26.9*	*901* *54*
Ca-Mg-HCO_3 (n=72 including 6 samples from springs,1 sample from lake and 1 sample from pond)	*7.85±6.4*	O_2=2.6 N-NO_3 =0.29 Fe = 2.18 Mn = 0.27 SO_4=89.89 CH_4 = 0.09	*3.7* *1.82* *3.1* *0.39* *68* *0.59*	*n/a*	*TDS=888* *Cl=1.93*	*229* *6.8*
Ca-HCO_3 (n=52 including 8 samples from springs, 3 samples from lake and 1 sample from pond)	*10.4±8.5*	O_2=32 N-NO_3=0.88 Fe = 0.99 Mn = 0.15 SO_4=48.57 CH_4 = 0.03	*136* *5.7* *2.1* *0.51* *60.8* *0.11*	*n/a*	*TDS= 647* *Cl=15.27*	*275* *31*
Na-HCO_3-SO_4 (n=29 including 2 samples from springs)	*0.16±0.17*	O_2 =2.6 N-NO_3 =0.76 Fe = 0.93 Mn = 0.22 SO_4=874 CH_4 =0.34	*2.8* *3.9* *1.45* *0.47* *285* *1.25*	*n/a*	*TDS= 2929* *Cl=4.7*	*946* *2.5*
Ca-Mg-Na-HCO_3 (n=27 including 2 samples from springs)	*1.01±0.34*	O_2=3.09 N-NO_3 =0.31 Fe = 0.93 Mn = 0.49 SO_4=138 CH_4 =0.3	*2.78* *1.2* *1.9* *0.70* *96* *0.7*	*n/a*	*TDS= 1126* *Cl=3.19*	*337* *6.02*
Ca-Mg-Na-SO_4 (n=23 including 3 samples from springs)	*0.98±0.3*	O_2=5.1 N-NO_3 =0.27 Fe = 5.44 Mn = 0.67 SO_4=1550 CH_4 =0.02	*12.85* *1.6* *7.1* *0.9* *466* *0.07*	*n/a*	*TDS= 2929* *Cl=7.5*	*1124* *13.3*
Na-SO_4 (n=18 including 3 samples from springs)	*0.25±0.14*	O_2=1.4 N-NO_3 =0.33 Fe = 3.1 Mn = 0.86 SO_4=1479 CH_4 =0.02	*1.6* *1.4* *4.7* *1.76* *427* *0.03*	*n/a*	*TDS=3514* *Cl=21*	*1069* *74*

Table 3.8b: PHO matrix showing water types for water wells samples from the SFU database. The value in the box corresponds to the number of samples belonging to that specific water type (e.g. the number 52 first row and first column corresponds to 52 samples belonging to the Ca-HCO_3 water type).

	Ca	Mg	CaMg	CaMgK	CaMgNa	CaK	MgK	CaMgNaK	CaNa	MgNa	CaNaK	MgNaK	NaK	K	Na
HCO_3	52	1	72	1	27				2	2					91
CO_3															
HCO_3-CO_3															
HCO_3-CO_3-SO_4															
HCO_3-CO_3-Cl															
HCO_3-CO_3-NO_3															
HCO_3-SO_4	10	1	10		14				5	3					28
HCO_3-Cl	4								2						1
HCO_3-NO_3															
CO_3-SO_4															
CO_3-Cl															
CO_3-NO_3															
HCO_3-CO_3-SO_4-Cl															
HCO_3-CO_3-Cl-NO_3															
HCO_3-SO_4-Cl-NO_3															
SO_4-Cl															
SO_4-NO_3															
Cl-NO_3															
HCO_3-SO_4-Cl															
HCO_3-SO_4-NO3					1										
HCO_3-Cl-NO_3															
CO_3-SO_4-Cl															
CO_3-SO_4-NO_3															
CO_3-Cl-NO_3															
SO_4-Cl-NO_3															
SO_4	9		5		23				1	1					19
Cl															
NO_3															
HCO_3-CO_3-SO_4-Cl-NO_3															
Total	**385**														

The Na-HCO_3 samples have a low average Ca/Na ratio of 0.12, an average sulfate concentration of 186 mg/L and an average TDS content of 1552 mg/L. The Ca-HCO_3 and Ca-Mg-HCO_3 samples have average Ca/Na ratios >7.5, and average sulfate concentration <90 mg/L and average TDS contents of 888 and 647 mg/L respectively. The sulfate-rich water types have average Ca/Na ratios between 0.16 and 0.98, average sulfate concentrations > 850 mg/L and average TDS contents varying between 2929 and 3514 mg/L.

3.1.5 Albertan groundwater chemistry data from the Alberta Health Service public database

For monitoring well data from the Alberta Health Services (AHS) public database, the hydrogeochemical characteristics of more than 3083 water samples are summarized in Tables 3.9a (only major water types reported) 3.9b (PHO matrix). By far the most predominant water type is Na-HCO_3 (78%). Groundwater samples belonging to this water type have average Ca/Na ratios <0.1, an average sulfate concentration of 94 mg/L, and an average TDS concentration of 905 mg/L. In contrast, Ca-HCO_3 (6%) and CaNaHCO_3 (2%) samples have average Ca/Na ratios of 0.8 and 10.5, average sulfate concentrations of 34 and 74 mg/L, and TDS concentrations of 363 and 533 mg/L. Sulfate-dominated water types (Na-HCO_3-SO_4 (6%), Na-SO_4 (2%)) are characterized by a Ca/Na ratio near 0.1, average sulfate concentrations of 577 and 1392 mg/L, and TDS contents of 1527 and 2755 mg/L, respectively.

Table 3.9a: Hydrogeochemical characteristics of groundwater samples from AHS.

	Ca/Na mass ratio	**Redox sensitive species mg/L**		**Completion interval/ Well depth {m}**	**Salinity parameters TDS, Cl {mg/L}**	
		Mean	SD		Mean	SD
Na-HCO_3	0.04±0.07	O_2=n/a		58.9 ± 40.4	Cl= 9.2	14
(n=2414)		N-NO_3 =0.08	0.34		TDS=905	317
		Fe =0.24	0.77			
		Mn = n/a				
		SO_4=93.6	112			
		CH_4= n/a				
Ca-HCO_3	10.5±9.06	O_2=n/a		23.4 ± 22.5	Cl= 17.9	34.2
(n= 187)		N-NO_3 =0.86	2.58		TDS=363	160
		Fe =0.89	2.96			
		Mn = n/a				
		SO_4=34.3	48.4			
		CH_4= n/a				
Na-HCO_3-SO_4	0.10±0.12	O_2=n/a		41.4 ± 32.4	Cl= 5.55	14.6
(n=189)		N-NO_3 =0.95	1.36		TDS=1527	436
		Fe =0.5	42			
		Mn = n/a				
		SO_4=577	204			
		CH_4= n/a				
Ca-Na-HCO_3	0.92±0.27	O_2=n/a		39.3 ± 29.6	Cl= 8.09	27.0
(n= 38)		N-NO_3 =0.24	0.79		TDS=533	235
		Fe =0.91	1.68			
		Mn = n/a				
		SO_4=74.2	88.2			
		CH_4= n/a				
Na-SO_4	0.08±0.09	O_2=n/a		48. 2± 35.3	Cl= 33.1	94
(n=55)		N-NO_3 =0.28	0.65		TDS=2755	973
		Fe =0.96	2.25			
		Mn = n/a				
		SO_4=1392	542			
		CH_4= n/a				

Table 3.9b: PHO matrix showing water types for water wells samples from the AHS database. The value in the box corresponds to the number of samples belonging to that specific water type (e.g. the number 187 first row and first column corresponds to 187 samples belonging to the Ca-HCO_3 water type).

	Ca	**Mg**	**CaMg**	**CaMgK**	**CaMgNa**	**CaK**	**MgK**	**CaMgNaK**	**CaNa**	**MgNa**	**CaNaK**	**MgNaK**	**NaK**	**K**	**Na**
HCO_3	187	2	25		29				38				2	7	2414
CO_3										1					1
HCO_3-CO_3															
HCO_3-CO_3-SO_4															
HCO_3-CO_3-Cl															
HCO_3-CO_3-NO_3															
HCO_3-SO_4	18		10		13				17				1		189
HCO_3-Cl	10									1				1	12
HCO_3-NO_3															
CO_3-SO_4															1
CO_3-Cl															
CO_3-NO_3															
HCO_3-CO_3-SO_4-Cl															
HCO_3-CO_3-Cl-NO_3															
HCO_3-SO_4-Cl-NO_3															
SO_4-Cl															
SO_4-NO_3															
Cl-NO_3															
HCO_3-SO_4-Cl															
HCO_3-SO_4-NO3															
HCO_3-Cl-NO_3															
CO_3-SO_4-Cl															
CO_3-SO_4-NO_3															
CO_3-Cl-NO_3															
SO_4-Cl-NO_3															
SO_4	10	2	12		4				6	1					55
Cl	5								2						7
NO_3															
HCO_3-CO_3-SO_4-Cl-NO_3															
Total	**3083**														

3.1.6 Groundwater Observation Well Network in Alberta

For monitoring well data from the Alberta Groundwater Observation Well Network (GOWN-AB), the hydrogeochemical characteristics of 27 water samples are summarized in Table 3.10. By far the most predominant water type is Na-HCO_3 (78%). Groundwater samples belonging to this water type have an average Ca/Na ratio of 0.01, an average sulfate concentration of 357 mg/L, and an average TDS concentration of 1533 mg/L. In contrast, Ca-HCO_3 samples have an average Ca/Na ratio of 7.5, an average sulfate concentrations of 56 mg/L, and an average TDS concentration of 266 mg/L. Sulfate-dominated water types are characterized by a Ca/Na ratios between 0.02 and 6.2, average sulfate concentrations between 122 and 1026 mg/L, and TDS contents between 308 and 2596 mg/L. The groundwater samples collected from the deepest water wells have Na-HCO_3 water types and highest TDS values (Na-HCO_3-SO_4) are associated with the highest sulfate concentrations (Table 3.10).

Table 3.10: Hydrogeochemical characteristics of groundwater samples from GOWN-AB

	Ca/Na mass ratio	**Redox sensitive species mg/L**		**Completion interval/ Well depth {m}**	**Salinity parameters TDS {mg/L} Cl {mg/L}**	
		Mean	*SD*		*Mean*	*SD*
Na-HCO_3 (n=10)	*0.01±0.003*	O_2=n/a N-NO_3 =0.05 Fe =0.09 Mn = 0.012 SO_4=357 CH_4= 0.57	 0.04 0.06 0.005 268 0.95	*40 to 109*	*TDS=1533* *Cl=4.55*	*589* *2.7*
Ca-Mg-HCO_3-SO_4 (n=7)	*6.19±1.5*	O_2=n/a N-NO_3 =0.59 Fe =0.79 Mn = 0.06 SO_4=122 CH_4=0.013	 0.39 0.41 0.04 15.4 0.009	*21 to 53*	*TDS= 308* *Cl=1.43*	*46* *1.69*
Ca-HCO_3 (n=5)	*7.47±1.5*	O_2=7.5 N-NO_3 =0.9 Fe =2.46 Mn = 0.01 SO_4=55.9 CH_4=0.001	 0.18 0.002 37.5 0.000	*12.6 to 21*	*TDS=266* *Cl=2.8*	*83* *0.84*
Na-HCO_3-SO_4 (n=3)	*0.02±0.0*	O_2=n/a N-NO_3 =0.05 Fe =2.36 Mn = 0.11 SO_4=1026 CH_4=0.017	 0.067 1.96 0.027 32 0.011	*42.7*	*TDS=2596* *Cl=2.5*	*83.8* *0.5*
Ca-HCO_3-SO_4 (n=2)	*6.98±0.44*	O_2=n/a N-NO_3 =0.56 Fe =0.93 Mn = 0.03 SO_4=141 CH_4=0.0007	 0.82 0.01 26.8 0.0005	*21 &53.2*	*TDS=354* *Cl=3.00*	*79* *1.41*

3.1.7 Summary of non-industry sample data

The majority of non-industry samples belong to the Na-HCO_3 water type with low average Ca/Na ratios <0.1, intermediate sulfate and TDS concentrations. The 2nd biggest group of water types is composed of sulfate-dominated groundwater samples that are characterized by the highest sulfate and TDS concentrations. The 3rd biggest group of water types is composed of Ca-HCO$_3$ and Ca-Na-HCO$_3$ samples that are characterized by the highest Ca/Na ratios, low sulfate and low TDS concentrations. Table 3.11 summarizes average concentrations for selected aqueous geochemistry parameters for all water types encountered in the data available for this project. Correlation analyses and principle component analysis (PCA) were performed with SPSS to examine trends and differences in inorganic parameters.

Table 3.11: Descriptive statistics of the different hydrochemical facies identified in the dataset.

		Ca/Na mass ratio		Well depth (m)		N-NO$_3$ (mg/L)		Fe (mg/L)		Mn (mg/L)		SO$_4$ (mg/L)		Cl (mg/L)		TDS (mg/L)		CH$_4$ (mg/L)	
	N	mean	*SD*	mean	*SD*	mean	*SD*	mean	*SD*	mean	*SD*	Mean	*SD*	mean	SD	mean	SD	mean	SD
Na-HCO$_3$	2535	0.04	*0.08*	59.2	*41.4*	0.12	*0.46*	0.28	*0.94*	1.08	*0.87*	97.7	*117*	10.0	*17.5*	939	*398*	3.13	*1.38*
Ca-HCO$_3$	279	10.4	*8.54*	23.2	*21.4*	1.16	*3.09*	0.88	*2.66*	3.31	*3.65*	37.3	*48.8*	16.2	*31.8*	404	*221*	0.032	*0.04*
Na-HCO$_3$-SO$_4$	230	0.11	*0.13*	42.6	*33.8*	0.47	*1.55*	0.59	*1.43*	0.35	*0.29*	637	*261*	5.63	*13.5*	1740	*735*	0.28	*0.33*
Ca-Mg-HCO$_3$	103	6.406	*5.86*	31.1	*18.1*	1.05	*1.98*	2.11	*3.56*	0.36	*0.81*	84.78	*69.7*	4.49	*12.4*	770	*281*	0.093	*0.40*
Na-SO$_4$	76	0.13	*0.13*	55.6	*63.7*	0.34	*0.66*	1.44	*3.08*	0.77	*0.89*	1430	*522.4*	29.98	*87.1*	2952	*1024*	0.023	*0.018*
Ca-Mg-Na-HCO$_3$	58	1.011	*0.31*	41.7	*23.9*	0.52	*0.83*	0.67	*1.42*	3.49	*11.3*	98.4	*102*	2.54	*4.45*	759	*443*	0.302	*0.44*
Ca-Na-HCO$_3$	44	0.930	*0.27*	39.8	*30.4*	0.23	*0.74*	1.10	*1.78*	4.76	*2.04*	74.0	*88.6*	12.29	*29.0*	560	*280*	0.009	*0.001*
Ca-Mg-Na-SO$_4$	32	0.977	*0.26*	55.6	*29.6*	2.16	*2.71*	4.48	*6.40*	8.06	*25.3*	1391	*559*	7.80	*11.3*	2603	*1*	0.025	*0.05*
Ca-HCO$_3$-SO$_4$	30	6.507	*3.16*	25.0	*18.8*	0.63	*0.60*	2.32	*4.29*	0.27	*0.46*	267	*121*	5.98	*14.6*	790	*358*	0.004	*0.002*
Ca-Mg-HCO$_3$-SO$_4$	27	6.208	*4.85*	30.6	*18.7*	0.76	*0.57*	0.41	*0.55*	0.06	*0.08*	301	*150*	18.12	*45.1*	929	*551*	0.011	*0.012*
Ca-Mg-Na-HCO$_3$-SO$_4$	27	1.02	*0.27*	27.5	*16.2*	1.44	*1.89*	0.79	*1.24*	0.64	*0.70*	507	*162*	10.65	*27.8*	1475	*515*	0.003	*0.003*
Ca-Na-HCO$_3$-SO$_4$	22	0.78	*0.28*	31.3	*24.1*	3.08	*6.66*	2.86	*3.08*	0.27	*0.14*	444	*131*	11.25	*18.6*	1253	*429*	0.031	*0.018*
Ca-SO$_4$	21	7.56	*6.03*	10.6	*14.4*	1.18	*2.40*	5.08	*13.6*	2.35	*2.20*	1004	*557*	6.77	*10.1*	1768	*875*	0.002	*0.002*

		Ca/Na mass ratio		**Well depth (m)**		**N-NO$_3$ (mg/L)**		**Fe (mg/L)**		**Mn (mg/L)**		**SO$_4$ (mg/L)**		**Cl (mg/L)**		**TDS (mg/L)**		**CH$_4$ (mg/L)**	
	N	mean	*SD*	mean	*SD*	mean	*SD*	mean	*SD*	mean	*SD*	Mean	*SD*	mean	SD	mean	SD	mean	SD
Ca-Mg-SO$_4$	19	4.48	*3.05*	25.5	*29.0*	1.86	*2.85*	1.64	*2.36*	0.23	*0.16*	1005	*612*	7.26	*12.0*	1815	*991*	0.005	*0.001*
Ca-HCO$_3$-Cl	15	4.11	*2.505*	21.8	*16.2*	2.69	*4.90*	0.60	*1.27*	0.61	*0.71*	50.4	*43.6*	168	*66.3*	725	*388*	0.011	*0.008*
Na-HCO$_3$-Cl	13	0.01	*0.009*	126	*77.2*	0.28	*0.70*	0.48	*1.34*	0.01	*0.00*	11.11	*23.7*	326.9	*4*	1188	*968*	40.9	*10.9*
Ca-Na-SO$_4$	7	0.995	*0.36*	24.2	*17.4*	0.08	*0.17*	3.72	*3.59*	0.28	*0.10*	942	*189*	5.27	*6.46*	1882	*527*	0.018	*0.006*
K-HCO$_3$	7	0.150	*0.19*	37.9	*24.0*	0.00	*0.00*	0.04	*0.05*			108	*154*	10.03	*14.4*	819	*665*		
Na-Cl	7	0.089	*0.11*	146	*93.3*	0.11	*0.19*	0.10	*0.07*			46.2	*76.7*	532	*172*	1265	*404*		
Ca-Cl	6	3.24	*1.87*	8.0	*5.11*	2.26	*3.73*	0.48	*0.44*	1.16	*0.43*	42.42	*41.9*	360	*132*	824	*303*	2.29	*0.85*

3.2 Data analysis: Measures of Central Tendency, Dispersion and Association of Two Variables

To test the relationships between the concentrations of dissolved constituents in the groundwater samples a number of statistical tests were conducted. The first steps in statistical data analysis are to verify the data features such as the central tendency and dependency of the variables.

3.2.1 Major ions distributions and normality tests

The descriptive statistics of major cation concentrations are detailed in Table 3.12. The mean and median values indicate the following sequence of cation concentrations: Na > Ca > Mg> K. A wide range of values of variance for the different cation concentrations was observed with the largest variance for Na and the smallest variance for K concentrations: Na > Ca > Mg> K (Table 3.12). Frequency histograms presented in Fig. 3.1 reveal an asymmetrical distribution shape for the four major cations. The majority (> 50%) of the groundwater samples have sodium concentrations <300 mg/L, calcium concentrations <20 mg/L, magnesium concentrations < 5 mg/L, and potassium concentrations < 2 mg/L. The positive skewness indexes (>1) in Table 3.12 indicate a long tail on the right side of the distribution (Fig. 3.1). The kurtosis index > 3 (Table 3.12) is an indicator that all concentration data have heavy tails and outliers. The Shapiro-Wilk was used and the sig. value is lower than 0.05, indicating that the data is not normal distributed; even after log-transformation of the data.

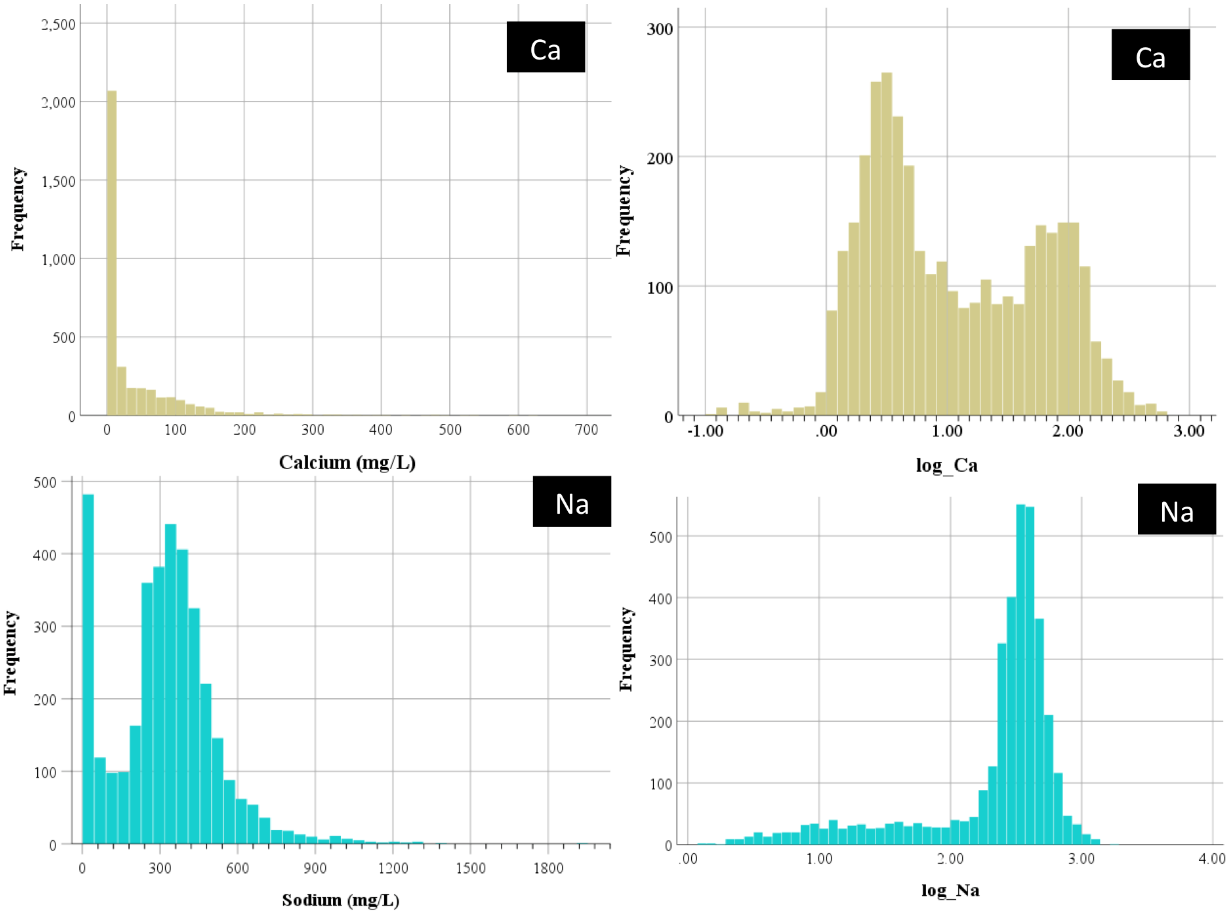


Figure 3.1: Frequency histograms for major cations without (left) and with (right) log transformation to test the normality.

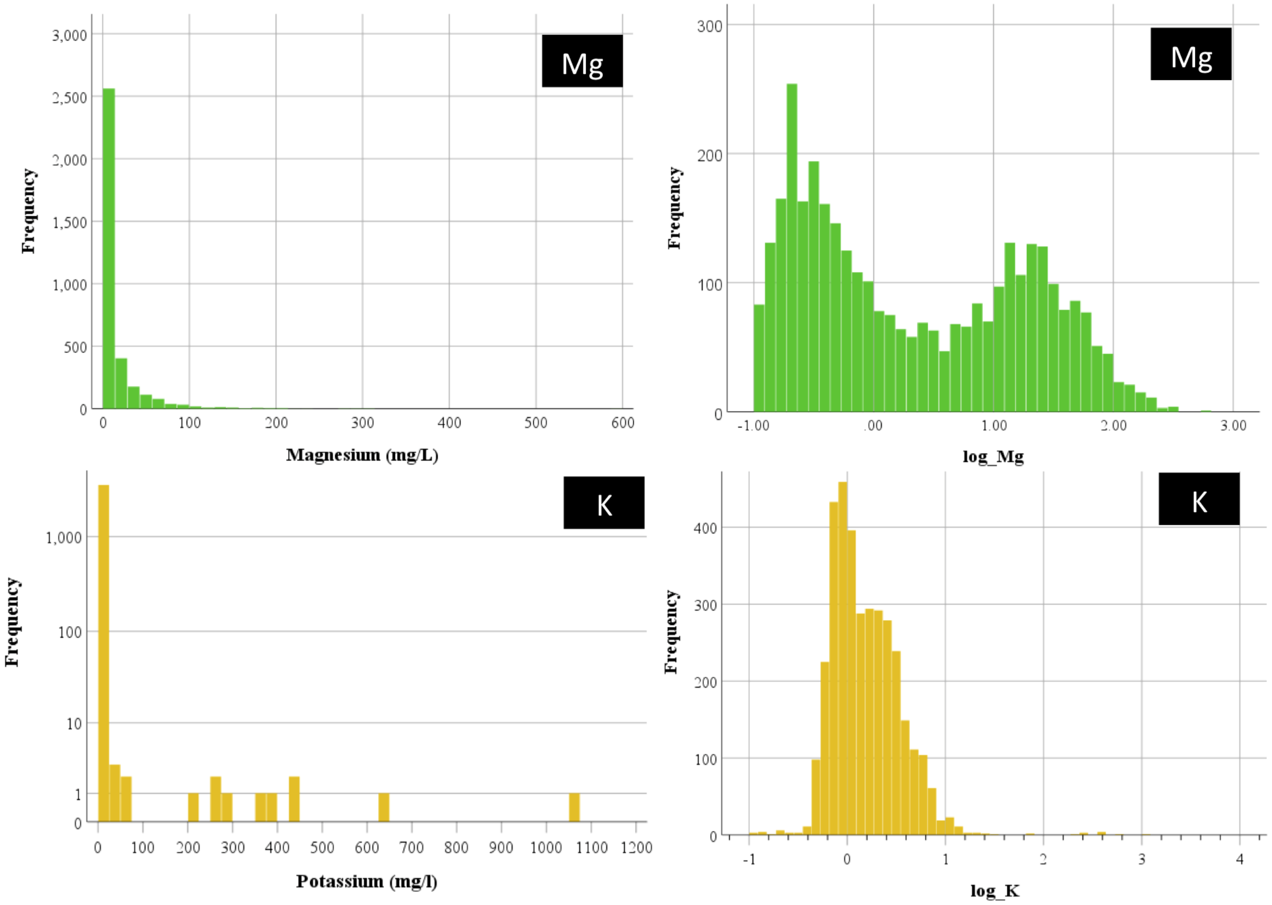


Figure 3.1: cont'd

Table 3.12: Descriptive statistics of major cation concentrations across the datasets

		Calcium	**Sodium**	**Magnesium**	**Potassium**
Unit		mg/L	mg/L	mg/L	mg/L
Mean		37.5	321	14.2	3.31
Median		7.82	327	1.37	1.35
Std. Deviation		62.2	200	30.8	26.2
Variance		3,866	40,135	950	686
Skewness		3.27	0.77	5.5	27.5
Kurtosis		15.8	2.74	54.6	915
Minimum		0.11	1.23	0.10	0.10
Maximum		615	1913	591	1061
Shapiro-Wilk test	Raw	<0.005	<0.005	<0.005	<0.005
	Log	<0.005	<0.005	<0.005	<0.005

The descriptive statistics of major anion concentrations are detailed in Table 3.13. The mean and median values indicate the following sequence of anion concentrations: $HCO_3 > SO_4 > Cl$. A wide range of values of variance for the different anion concentrations was observed with the largest variance for SO_4 and the smallest variance for Cl, with HCO_3 concentrations displaying an intermediate value. Frequency histograms presented in Fig. 3.2 reveal an asymmetrical distribution shape for sulfate and chloride. Over 50% of the groundwater samples have chloride concentrations < 8 mg/L and sulfate concentrations <135 mg/L. The positive skewness indexes (>1) shown in Table 3.13 indicate a long tail on the right side of the distribution (Fig. 3.2). The kurtosis index > 3 (Table 3.13) is an indicator that sulfate and chloride concentration data have heavy tails and outliers. Bicarbonate concentrations display a more symmetrical distribution than the other major anions, with a heavy tail on the right hand (Fig. 3.2). None of the major anions pass the normality tests of Shapiro-Wilk p-value < 0.05.

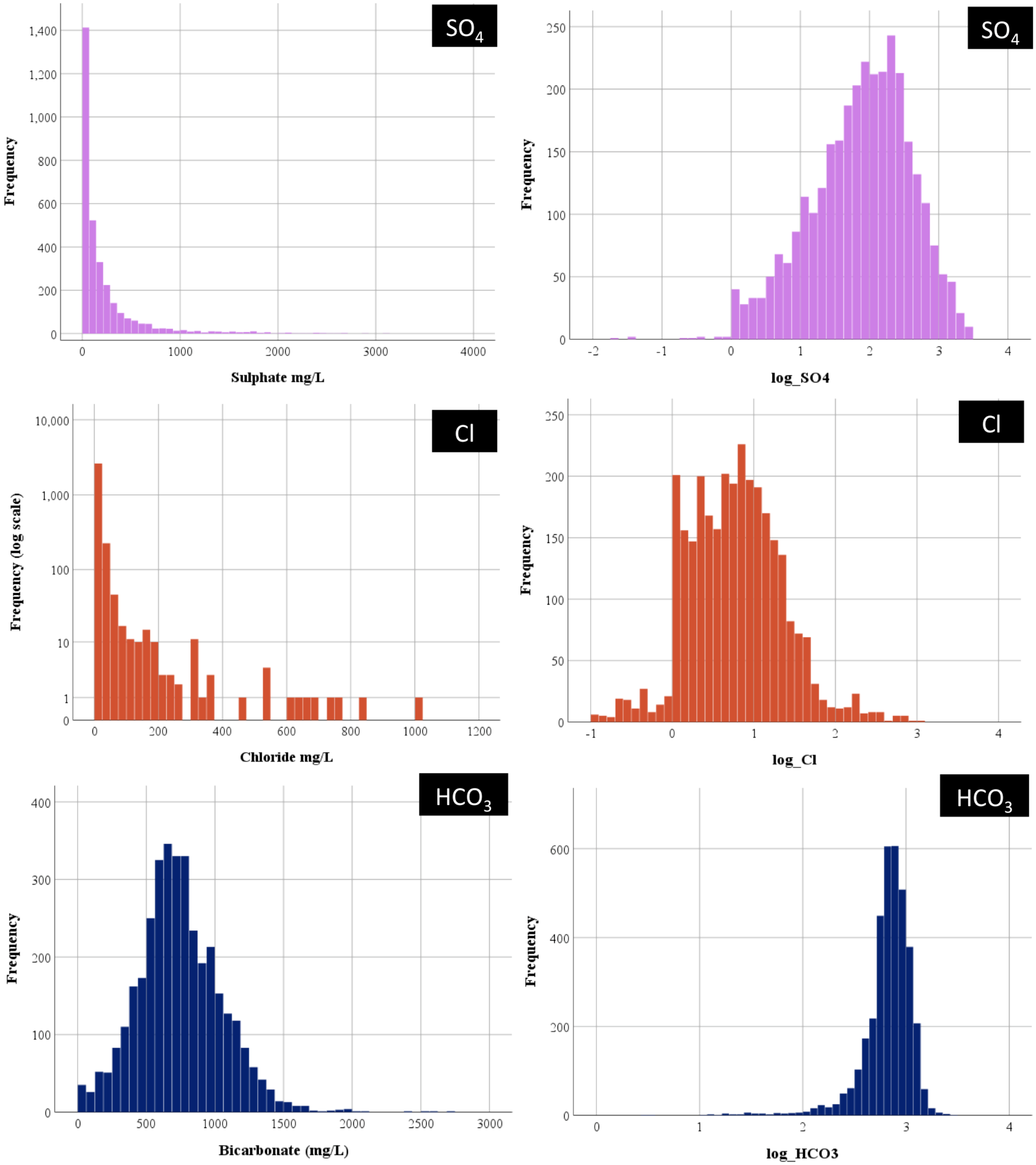


Figure 3.2: Frequency histograms for major anions without (left) and with (right) log transformation to test the normality.

Table 3.13: Descriptive statistics of major anion concentrations across the datasets

		Sulfate	**Bicarbonate**	**Chloride**
Unit		mg/L	mg/L	mg/L
Mean		215	743.8	17.4
Median		90.5	718.9	5.90
Std. Deviation		347.5	307.8	54.3
Variance		120,691	94,788	2,944
Skewness		3.40	0.56	9.5
Kurtosis		14.6	1.68	115
Minimum		0.02	3.00	0.10
Maximum		3114	2706	1000
Shapiro-Wilk test	Raw	<0.005	<0.005	<0.005
	Log	<0.005	<0.005	<0.005

3.2.2 Association of Two Variables

Correlation analysis indicates a statistical relation between variables and thus can help to reveal the physical, chemical and biogeochemical reactions that have established the observed water chemistry. The Pearson correlation coefficient, Kendall's τ coefficient and Spearman ρ coefficient were calculated using SPSS and the results are summarized in Table 3.14.

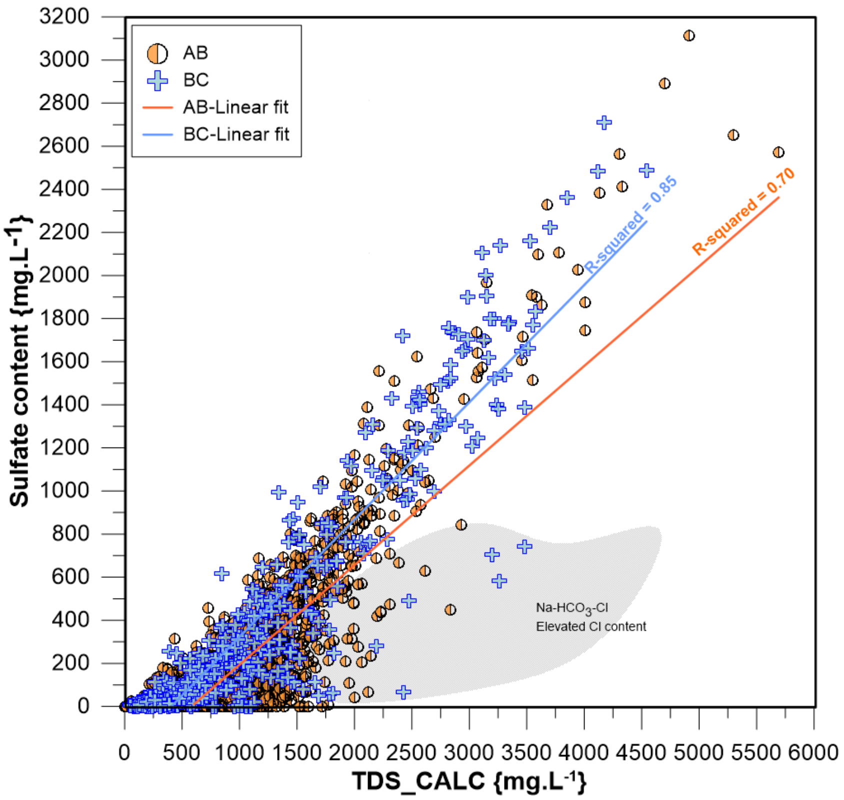


Figure 3.3: Sulfate versus TDS concentrations in the groundwater samples from Alberta (AB) and British Columbia (BC). An excellent positive correlation with R-squared of 0.70 for AB and 0.85 for BC water samples was observed.

Table 3.14: Pearson, Kendall, Spearman correlation of physicochemical parameters

	method	Ca	Fe	Na	Cl	SO_4	Mg	K	F	HCO_3	pH	TDS
Ca	r	1.00										
	τ*	1.00										
	ρ*	1.00										
Fe	r	.412	1.00									
	τ*	.289	1.00									
	ρ*	.408	1.00									
Na	r	-.299	-.111	1.00								
	τ*	-.111	-.066	1.00								
	ρ*	-.247	-.099	1.00								
Cl	r	.046	.012	-.003	1.00							
	τ*	-.026	.012	.063	1.00							
	ρ*	-.038	.017	.087	1.00							
SO_4	r	.550	.251	.469	-.080	1.00						
	τ*	.244	.111	.294	-.177	1.00						
	ρ*	.347	.162	.413	-.257	1.00						
Mg	r	.839	.383	-.198	.022	.590	1.00					
	τ*	.811	.285	-.153	-.017	.228	1.00					
	ρ*	.950	.403	-.292	-.026	.329	1.00					
K	r	.020	.016	-.058	.029	.046	.030	1.00				
	τ*	.672	.264	.037	.013	.305	.665	1.00				
	ρ*	.824	.375	-.021	.016	.440	.838	1.00				
F	r	-.300	-.108	.082	.036	-.176	-.222	-.051	1.00			
	τ*	-.461	-.144	.140	.107	-.176	-.457	-.402	1.00			
	ρ*	-.622	-.207	.228	.150	-.245	-.625	-.550	1.00			
HCO_3	r	-.227	-.073	.789	.018	.147	-.123	0.00	.079	1.00		
	τ*	-.074	-.017	.685	.126	.168	-.118	.063	.164	1.00		
	ρ*	-.156	-.026	.856	.172	.241	-.211	.059	.252	1.00		
pH	r	-.651	-.279	.292	-.054	-.316	-.585	-.047	.354	.183	1.00	
	τ*	-.638	-.248	.144	-.011	-.174	-.632	-.566	.383	.069	1.00	
	ρ*	-.814	-.351	.260	-.015	-.254	-.817	-.741	.551	.134	1.00	
TDS	r	.328	.158	.785	.009	.874	.401	.060	-.119	.591	-.138	1.00
	τ*	.149	.056	.715	.016	.536	.107	.272	-.011	.608	-.084	1.00
	ρ*	.150	.081	.837	.024	.710	.104	.339	.002	.762	-.080	1.00

r	Pearson correlation (parametric) – strength and direction of a linear relationships between two variables
τ*	Kendall rank correlation (non-parametric) – strength of dependence between two variables
ρ*	Spearman rank correlation (non-parametric) – degree of association between two variables

The different bivariate coefficients from non-parametric and parametric tests summarized in Table 3.14 reveal that TDS content is strongly correlated with SO_4 concentrations. This is further evidenced by Fig. 2.3, which displays an excellent positive correlation between TDS and sulfate concentrations with R-squared of 0.70 for groundwater samples from Alberta and 0.85 for groundwater samples from British Columbia.

Physical and (bio-)geochemical reactions releasing these ions along the groundwater flow path are of key importance in controlling the aqueous geochemistry of the investigated groundwater samples. Correlations analysis of major ion concentrations (Table 3.14) revealed expected process-based relationships between the following parameters:

- Strong positive correlation between Na and DIC (r, τ, $\rho > 0.7$, $p<0.05$);
- Strong positive correlation between Mg and Ca (r, τ, $\rho > 0.8$; $p<0.05$);
- SO_4 has a moderate positive correlation with Ca (r, τ, $\rho > 0.5$, $p<0.05$), Na (r, τ, $\rho > 0.4$, $p<0.05$), Mg (r, τ, $\rho > 0.5$. $p<0.05$), DIC (r, τ, $\rho > 00.2$, $p<0.05$);
- Moderate negative correlation between Ca and Mg and Na (r, τ, $\rho >-0.3$, $p<0.05$).

Concentrations of K, Cl, and F have weak correlations with most of the other parameters and do not seem to have a significant influence on the water chemistry of the majority of the investigated groundwater samples.

Figure 3.4 (left) further investigates the relationship between major anion concentrations and displays a strong negative correlation between SO_4 concentrations versus the HCO_3+Cl/SO_4 ratio (R-squared = 0.9) all groundwater samples. This indicates that there are at least two distinct groups of groundwater samples controlled by different processes: a) one that results in elevated bicarbonate but low sulfate concentrations, and b) another process that results in high sulfate concentrations and much lower bicarbonate and chloride concentrations.

Figure 3.4 (right) further investigates the relationship between major cation concentrations and shows that the ratio Ca/Na is strongly positively correlated to (Ca+Mg+K)/Na (R-squared = 0.9) in all groundwater samples. In agreement with the correlation analyses shown in Table 3.14, such strong correlation indicates a very small influence of variations in Mg and K concentrations on the chemistry of water samples with only few exceptions.

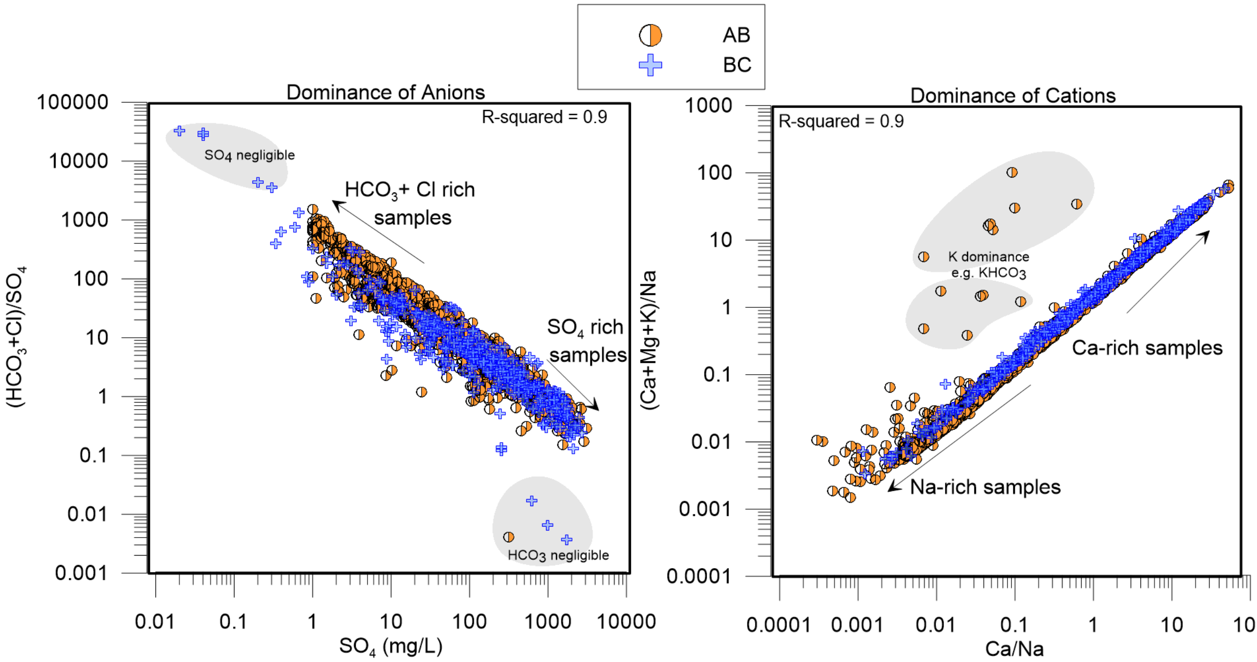


Figure 3.4: Evaluating the distribution of anions (left) and cations (right) with different parameters within the water samples.

The descriptive statistics have shown a wide range of variances and dimensions among the variables and bivariate analyses have permitted to examine strong and weak correlations between inorganic parameters/variables. Knowledge of the variable distribution and relative magnitudes of variables are critical for performing further statistical analyses. The use of multivariate analyses described in the next section will permit to assess classification of the water samples based on geochemical patterns.

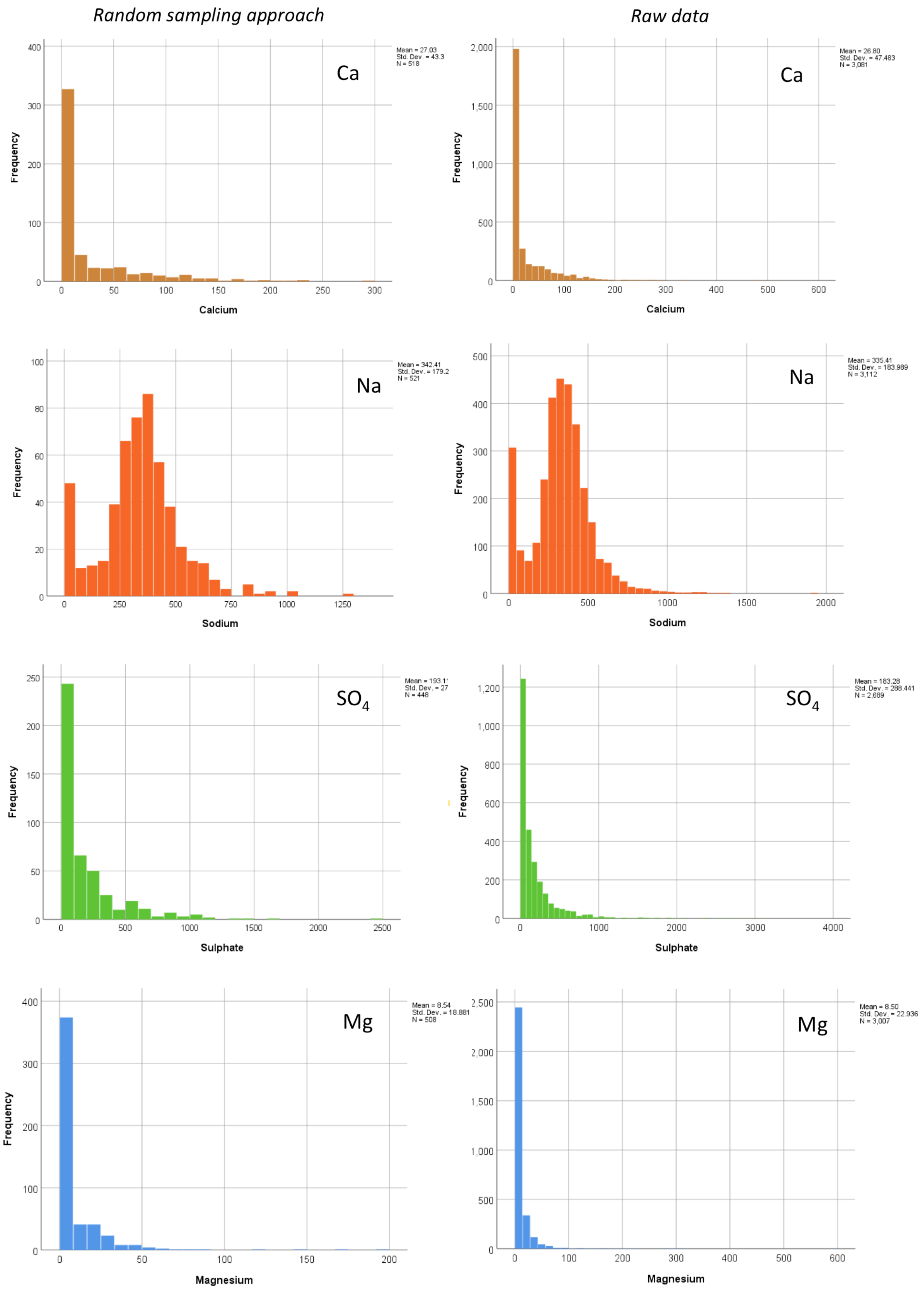
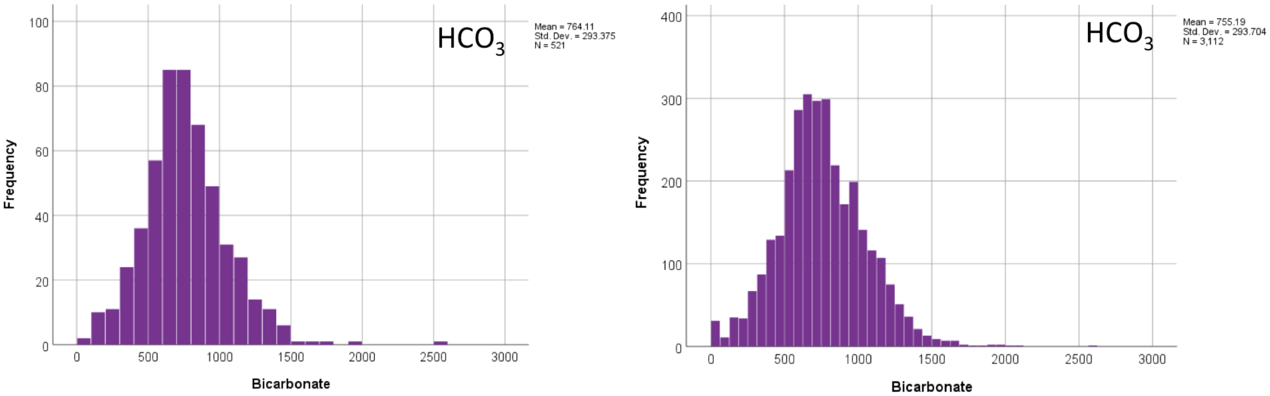


Figure 3.5: Comparison of the distribution of major ions for the Alberta dataset (left) after random sampling technique (right) the initial raw data.



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3.3 Geochemical patterns using multivariate analyses

3.3.1 Handling imbalanced datasets

There is an imbalance in the Alberta (n= 2679) versus British Columbia (n= 468) datasets. Such bias could influence many algorithms outcomes and thus bias potential patterns. The objective of this section is to reduce the datasets imbalance by a resampling technique. A random sampling was performed with SPSS to form a subsampling in which a number of distinct samples are selected randomly from the total samples from Alberta dataset in a way that each sample has equal chance to be selected. A subset (17%) of Albertan samples was selected to balance the datasets across Alberta and British-Columbia. The distribution of the subset for the Alberta dataset is presented in Fig. 3.5 that shows that the random sampling technique was well representative of the initial raw data. The subset data of the Alberta dataset is constituted of 521 samples randomly selected.

The metadata that compiles both balanced Alberta and British Columbia geochemical datasets is characteristic of n_{total} = 989 samples that will be used to perform multivariate analyses.

3.3.2 Data analysis using principal component analysis (PCA): grouping variables

One concern regarding the application of the PCA is the robustness of such analysis in the presence of normality violation and outliers. As previously described during the univariate normality test, variables are highly skewed and kurtokic. Violation of univariate normality increases the likelihood that multivariate normality has been violated. PCA consists of eigenvalue decomposition of the covariance matrix of Gaussian distributed random variables and obtaining uncorrelated linear combinations of these variables stating with the highest variance to the lowest. If the multivariate normality assumption does not hold, one consequence would be that the components are guaranteed to be uncorrelated but not independent (non-unique). The adverse effects of non-normality will generally be small if sample sizes are large. For all these reasons, PCA has been used here first, as an exploratory analysis, to reduce the dimensionality of hydrochemical data e.g. Na, Ca, Mg, Fe, K, pH, HCO_3, SO_4, Cl, F. PCA using Direct Oblimin rotation with Kaiser normalization has resulted in the extraction of three main principal components which identifies the factors influencing each principal components for the physic-chemical parameters.

Two factors explain most of the information (68.3%) in the dataset. The Cl variable was discarded because of too weak an influence on the water sample chemistry and impacting the Kaiser-Meyer-Olkin (KMO) value (<0.2). After discarding Cl variables, the KMO value was >0.5 indicating that the samples were suitable for PCA analyses. The number of components to keep in PCA was determined based on the Kaiser criterion for which only the components with eigenvalues greater that one are retained. The eigenvalues of the first two factors are: 3.44 and 2.02. Table 3.15 presents the determined initial principal component and its eigenvalues and percentage of variance contributed in each principal component.

Table 3.15: Total Variance explained - PCA analysis

	Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings^a
Component	Total	% of Variance	Cumulative %	Total
1	3.439	38.210	38.210	3.328
2	2.024	22.485	60.695	2.283

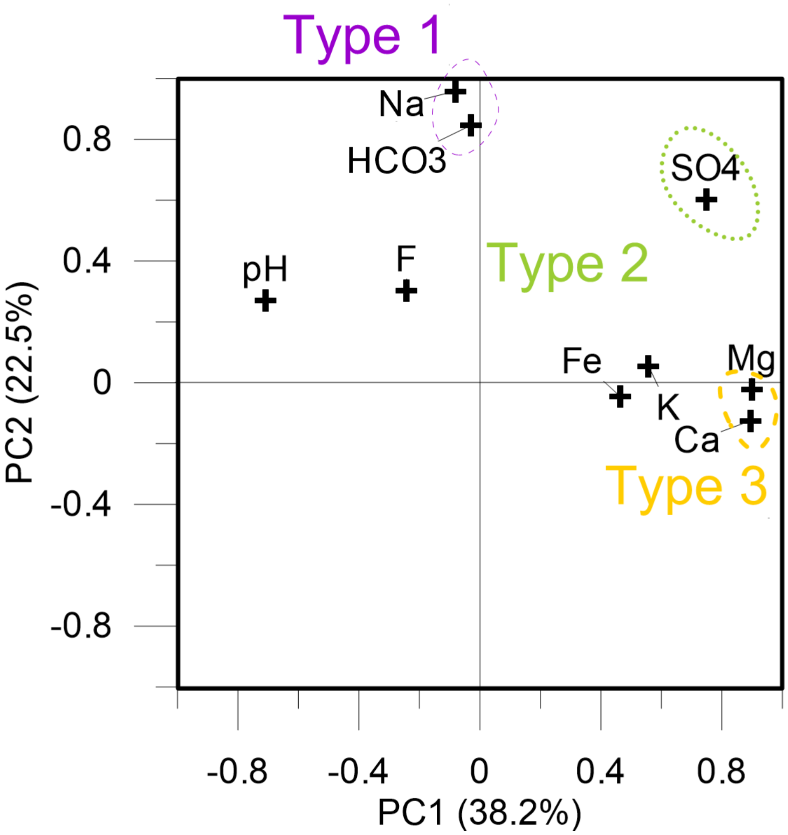

Figure 3.6: Components plot in rotated space

Table 3.16 shows the rotated component matrix of the main physico-chemical parameters. Component 1 explains 38.2% of total variance and shows a strong positive loading for Ca, Mg (>0.9), moderate loadings for Fe, and SO_4 (<0.7). Factor or component 2 explained 22.5% of the total variance with strong positive factor scores for Na and DIC (>0.8) and moderate loading for SO_4 (<0.5). The components plot in rotated space is presented in Fig. 3.6.

At least three groups are identified containing 1) Na and DIC 2) SO_4 and 3) Ca Mg variables as suggested by correlation analyses. This grouping pattern shows the strength of the mutual relation among the hydrochemical variables.

Table 3.16: Component matrix of the main physic-chemical parameters (absolute values greater than 0.6 are in bold)

	PC1	PC2
Ca	**.894**	-.125
Mg	**.899**	-.022
pH	**-.708**	.271
SO_4	**.748**	**.603**
Fe	.464	-.045
Na	-.081	**.959**
HCO_3	-.029	**.847**
K	.557	.056
F	-.242	.303

A cluster analysis of the water chemistry data without treatment would lead to the repeated use of variable data, causing the geochemical information represented by the weighted water data to be used, resulting in distortion of the calculated cluster results. The correlation analyses and the principal component analysis were used to process the data permitting to define new and not too strongly correlated variables for the cluster analyses.

3.3.3 Cluster analysis (CA): grouping observations

After standardization of the variables to have equal variance, a cluster analysis was performed using the k-means algorithm. A cluster refers to a collection of data points aggregated together because of certain similarities. This is based on geometric similarities which gives a measure of the Euclidean distance from each record to the cluster center or centroids and from each cluster to the others (Table 3.17). A series of steps were taken to select the most suitable number of clusters (k) for the analysis. First, several runs were conducted with a varying number of clusters. For each run, cluster proximities for each cluster center were examined and the number of iterations per each cluster was increased to ensure minimum error in cluster membership and that the model had converged to a solution.

Geochemical patterns derived by cluster analysis using inorganic variables were compared. We use standardized Na, Ca and SO_4 variables; HCO_3, Mg variables were not taking into account because of the strong correlation with Na and Ca respectively. K and Cl were discarded because of the weak influence they have on the water samples chemistry.

Table 3.17: Description of the four final cluster centers

	Cluster 1	Cluster 2	Cluster 3	Cluster 4
Standard_Ca	-.60662	.39821	2.83830	-.09980
Standard_Na	.40212	-.95716	.17428	2.19407
Standard_SO_4	-.35113	-.34266	2.54431	1.61399

A total of four clusters were found to best represent geochemical patterns (Table 3.17). One-way ANOVA with post-hoc test and Krustal-Wallis non-parametric test were performed to validate the cluster analysis and to hunt for significant differences between the points in the clusters. The results show statistically significant differences (p-value <0.005) for all variables among the different clusters. A summary of the cluster profiles is presented in Table 3.17.

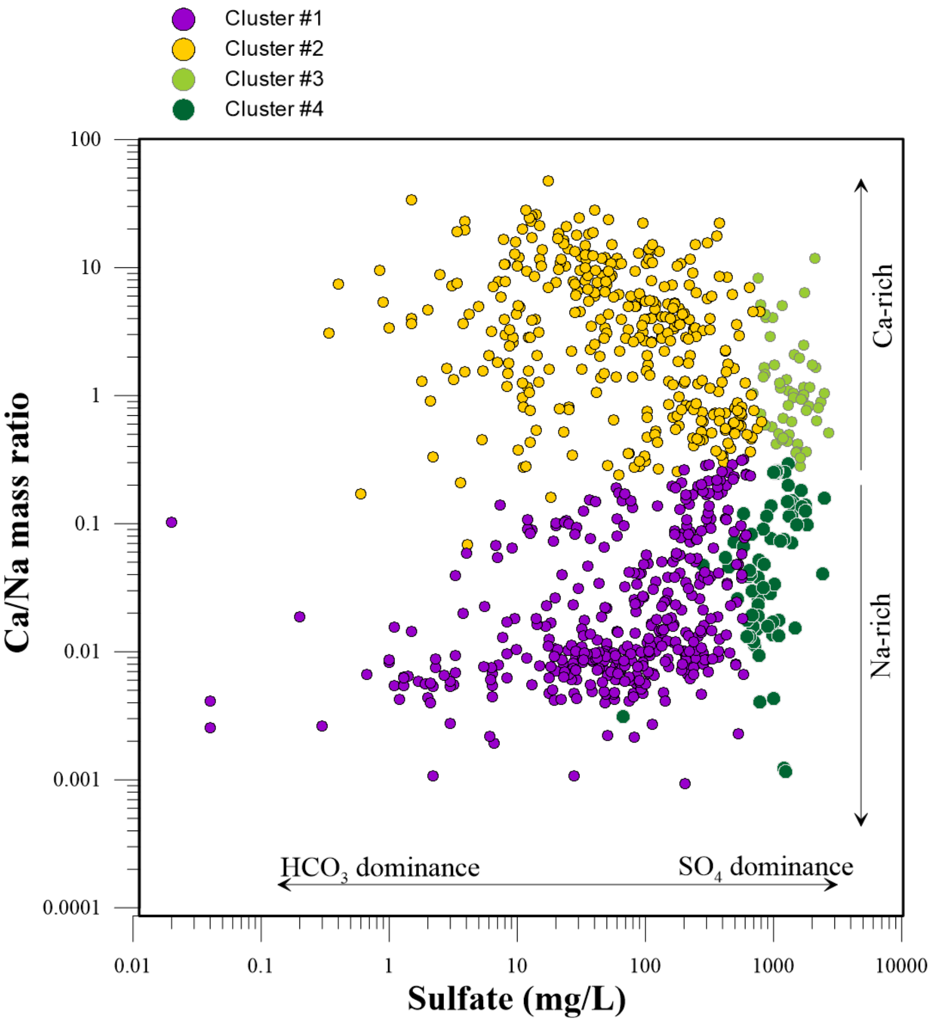

Figure 3.7: Binary plot of the four different clusters from the balanced datasets (n=915)

An illustration of the different clusters is presented in Fig. 3.7. The Ca-rich water samples from clusters 2 and 3 have systematically a high Ca/Na mass ratio > 0.2 (minimum value) and Na-rich water samples represented in clusters 1 and 4 have a low Ca/Na mass ratio <0.2 (maximum value). Where sulfate is dominant anion in clusters 1 and 2, concentrations in average are > 900 mg/L. Both PCA and cluster analyses have been performed on the raw datasets (n=3147) and similar clusters have been obtained (Fig. 3.8).

Each cluster is further described below:

- ***Cluster 1****: water dominated by sodium, bicarbonate*

The geochemical profile is described in Table 3.18. In average the samples have elevated concentrations of Na >380 mg/L, HCO_3 >850 mg/L and low Ca/Na mass ratio. The SO_4 concentration is in average > 140 mg/L and TDS content is in average >1000 mg/L.

While linking Clusters and hydrochemical facies determined in the section 3.1, it is found that 93% of the samples belonging to Cluster 1 are describing Na-HCO_3. The remaining water samples are described by Na-HCO_3-SO_4 (6.8%) >Na-Cl and Na-HCO_3-Cl (0.2%) hydrochemical facies.

- ***Cluster 2**: water dominated by calcium, bicarbonate*

The geochemical profile is described in Table 3.18. The SO_4 concentration is similar to cluster 1 and in average > 140 mg/L. In average the samples are characterized elevated concentration of calcium >95 mg/L that mainly permits to differentiate cluster 2 from cluster 1; resulting in elevated average Ca/Na mass ratio > 5. Bicarbonate and TDS content are in average >470 mg/L and <850 mg/L respectively.
While linking Clusters and hydrochemical facies determined in the section 3.1, it is found that Ca-(Mg)-HCO_3 represents > 55% of the water samples. The following sequence in term of major hydrochemical facies occurrence is: Ca-Mg-Na-HCO_3 (9%), Na-HCO_3 (9%) > Ca-Mg-Na-HCO_3-SO_4 (4%) Ca-HCO_3-SO_4 (4%) Ca-Mg-HCO_3-SO_4 (4%) > CaNa-HCO_3 (3%) and Ca-Na-HCO_3-SO_4 (3%) > Na-HCO_3-SO_4 (2%).

- ***Cluster 3**: water dominated by calcium, sulfate*

The geochemical profile is described in Table 3.18. This cluster is marked by elevated concentrations of calcium > 290 mg/L and sodium > 300 mg/L. The Ca/Na mass ratio is >1, the very high concentration of sulfate >1400 mg/L is the main parameter that differentiates the Cluster 3 from cluster 1. The TDS content is thus very highly >2000 mg/L.
While linking clusters and hydrochemical facies determined in the section 3.1, it is found that 43% of samples are described by Ca-Mg-Na-SO_4 hydrochemical facies. The following sequence of major hydrochemical occurrence is found: Ca-SO_4 (15%) > Na-SO_4 (13%) > Ca-Mg-SO_4 (12%) > Ca-Mg-Na-HCO_3-SO_4 (5%) > Ca-Na-SO_4 (3.3%), Na-HCO_3-SO_4 (3.3%), Mg-Na-HCO_3-SO_4 (3.3%).

- ***Cluster 4**: water dominated by sodium, sulfate*

The geochemical profile is described in Table 3.18. This Cluster is characterized by elevated concentrations of Na > 790 mg/L and very high sulfate concentration > 1000 mg/L participating the elevated TDS content >2900 mg/L. The Ca/Na ratio is <0.07 which permits to differentiate from Cluster 3.
While linking Clusters and hydrochemical facies determined in the section 3.1, it is found that 58% of samples are describing by Na-HCO_3-SO_4 hydrochemical facies. The following sequence of major hydrochemical occurrence is found: Na-SO_4 (27%) > Na-HCO_3 (14%) > Na-HCO_3-Cl (1%).

The statistical analyses permitted to cluster the water samples based on the geochemical patterns. Each of the Clusters is marked by dominant hydrochemical facies. This indicates that the distinct hydrochemical water types revealed in section 3.1 are a good choice to describe the water chemistries. A water-type classification is now proposed and discussed.

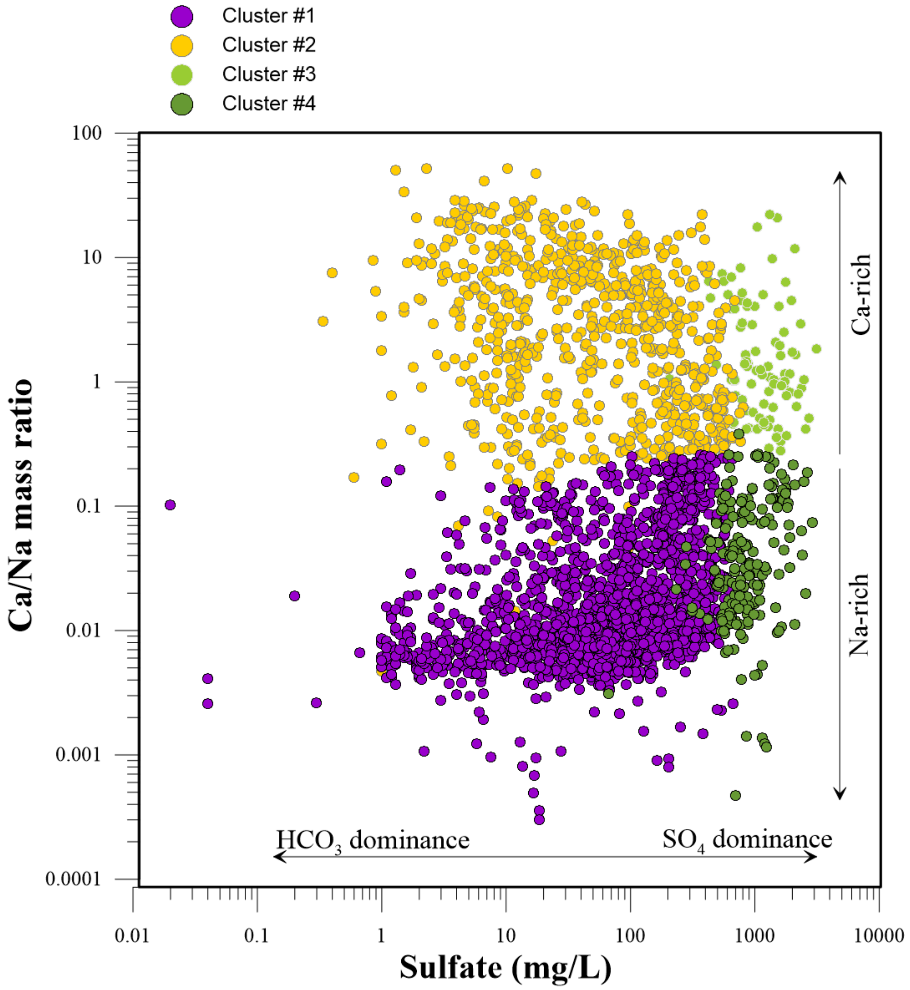

Figure 3.8: Binary plot of the four different clusters for the raw datasets (n= 3147)

Table 3.18: Geochemical profiles in the four clusters

	Cluster 1		**Cluster 2**		**Cluster 3**		**Cluster 4**	
	n=417		n=364		n=60		n=74	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Ca	15.46	21.84	98.11	44.79	298.81	101.44	57.15	50.28
Fe	0.29	0.76	1.55	3.18	3.69	5.23	0.87	2.57
Na	380.95	110.89	64.88	77.92	327.97	179.23	797.63	186.60
Cl	16.81	45.57	16.11	40.94	9.24	25.42	29.70	103.57
SO_4	141.54	150.21	145.31	173.78	1432.28	471.17	1017.55	442.31
TDS	1114.93	463.17	834.20	476.28	2878.72	950.64	2992.69	958.23
HCO_3	857.78	270.89	472.58	219.01	680.62	240.22	1151.78	456.57
Mg	5.83	11.36	41.38	26.58	134.65	49.35	35.12	46.43
K	1.70	1.35	3.60	4.36	6.99	2.77	3.86	2.10
F	0.91	0.84	0.36	0.31	0.92	0.75	0.58	0.44
Ca/Na	0.04	0.06	5.66	6.42	1.66	2.06	0.08	0.07

3.3.4 Additional hydrochemical characteristics of the clusters

Groundwater age dating and water isotopes

Additional hydrochemical parameters have been provided from some datasets such as groundwater residence time proxies. Groundwater residence time can be defined as the period of time elapsed since the infiltration of water. Radioactive environmental isotopes, in particular ^{14}C and ^{3}H have proved useful tools for determining groundwater residence times (Vogel et al., 1974; Wigley, 1975). ^{14}C of Dissolved Inorganic Carbon (^{14}C-DIC) and tritium (^{3}H) have been provided by SFU dataset.

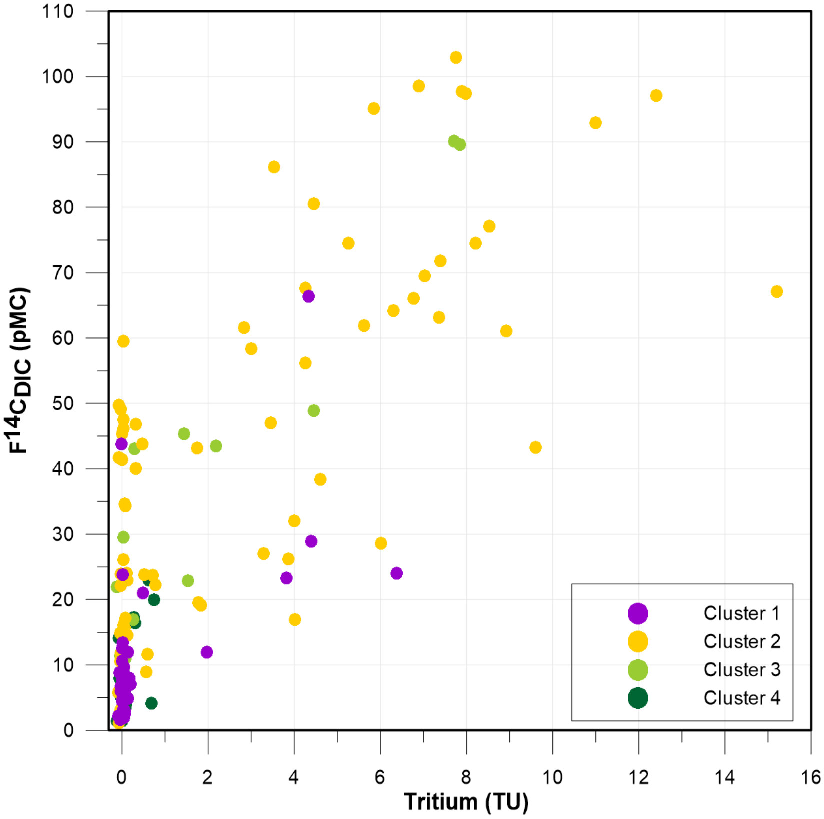

Figure 3.9: ^{14}C (pMC percent of Modern Carbon) versus tritium (Tritium Unit) in groundwater samples compiled form SFU dataset indicating predominance of older groundwater in Clusters 1, 3 and 4 and freshly recharged water belonging to Cluster 2.

Produced in the atmosphere by the interaction of nitrogen with cosmic rays, ^{14}C has a half-life of 5730 years and can be used to trace groundwater with residence times up to 30-40 ka. ^{14}C dating of groundwater requires identifying hydrochemical reactions that could alter the ^{14}C of the DIC in addition to the rate of radioactive decay.

With a shorter half-life (12.33 years) ^{3}H can be used to date groundwater residence times (<40 years). Because groundwater tritium concentrations reflect atmospheric tritium levels when the water was last in contact with the atmosphere, tritium can be used to date groundwater recharge.

The ^{14}C activities are expressed as pMC (percent modern carbon) and ^{3}H activities are expressed in tritium units (TU).

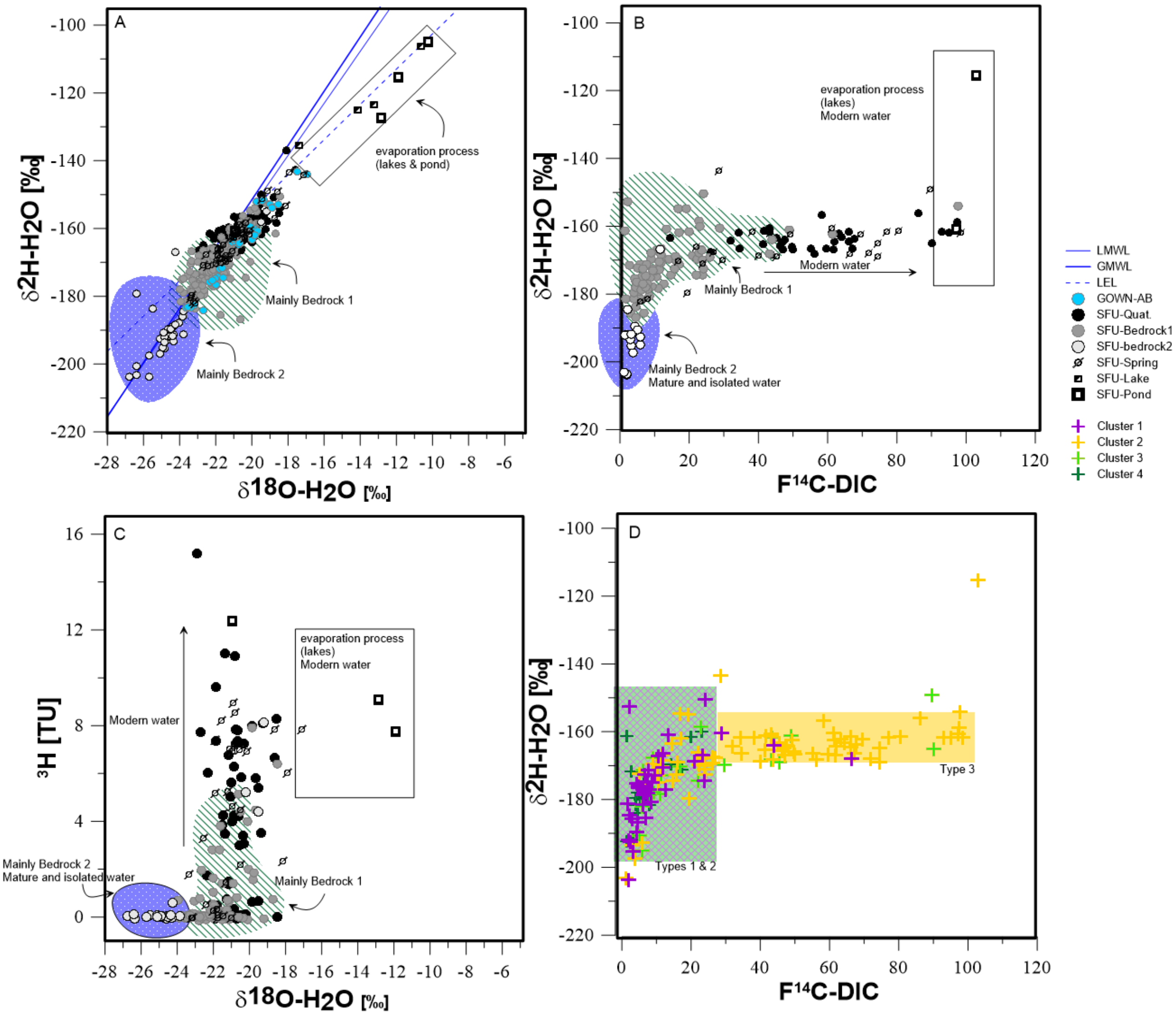

Figure 3.10: (A) ^{2}H vs. ^{18}O values in the water samples compiled from SFU and GOWN-AB. GMWL= Global Meteoric Water Line (Craig, 1981), LMWL= Local Meteoric Water Line (Wassenaar, et al., 2011) (B) F^{14}C$_{DIC}$ vs. ^{2}H of water samples (C) ^{3}H vs. ^{18}O values of water samples and (D) F^{14}C$_{DIC}$ vs. ^{2}H and clusters.

The datasets compiled from SFU and GOWN-AB report δ^{2}H-H$_2$O and δ^{18}O-H$_2$O values and, for SFU dataset only, age dating information e.g. ^{3}H and ^{14}C-DIC (Figs. 3.9 and 3.10). The δ^{18}O and δ^{2}H values of groundwater varied from -28 to -10 ‰ and from -200 to -110 ‰ respectively for SFU dataset and from -24‰ to -17‰, and from -180 to -140 ‰ respectively for GOWN-AB. The δ^{18}O and δ^{2}H values of groundwater are plotting close to the Global Meteoric Water Line (Craig, 1961) and Local Meteoric Water Line (LMWL, Wassenaar et al., 2011) indicating that water was derived from precipitation and local recharge. Deviations from meteoric water lines are associated with evaporation processes from ponds and lake water samples collected by SFU (Fig. 3.10a). The SFU dataset reports different geologic characteristic from where the water samples were collected.

The groundwater samples collected from wells completed in quaternary sediments (black symbols for SFU dataset, Fig. 3.10) seem to have been influenced by local recharge and have young groundwater ages (F^{14}C$_{DIC}$ > 50 pMC, >2 TU) than the samples collected from wells completed in bedrock formations. Most of the samples from Quaternary formations are associated with Cluster 2 (Ca-Mg-HCO_3) which contains samples with a component of young (less than 50 years) groundwater on the basis of tritium >1 TU. Cluster 2 indicates thus freshly recharged groundwater that has interacted with carbonate minerals (Fig. 3.9, Fig.3.10d) with typical $\delta^{13}C_{DIC}$ values varying from -15‰ to -10 ‰ (Fig. 3.11).

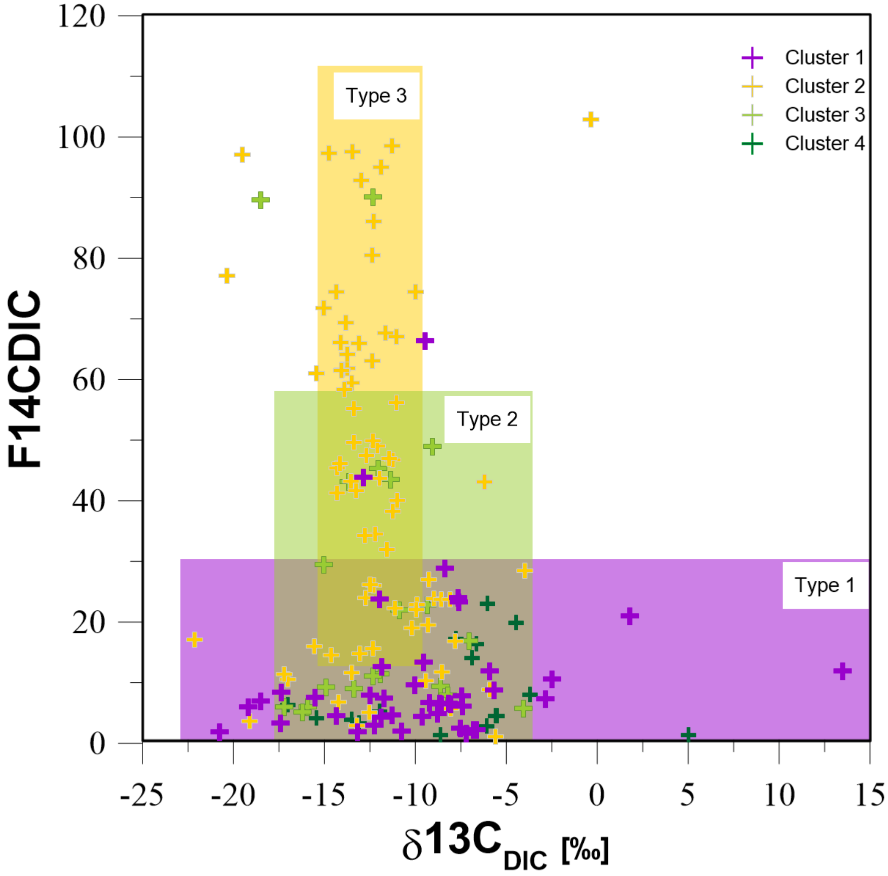

Figure 3.11: δ^{13}CDIC vs. $^{14}C_{DIC}$ in the different water types from the SFU dataset

The SFU dataset differentiated two different bedrock types called bedrock #1 and bedrock #2. We have no further information on the geological characteristics that differentiate bedrock #1 and bedrock #2.

Groundwater samples from bedrock #2 have lower hydrogen and oxygen isotope ratios, similar to average recharge during Pleistocene glaciation when temperatures were cooler (Martini et al., 1998). In addition, Figs. 3.10 b and 3.10c show that groundwater samples obtained from wells completed in bedrock #2 reflect a distinct group of more mature groundwater systems compared to those from bedrock #1 or from groundwater samples belonging to wells completed in quaternary sediments. Most of the samples from bedrock #2 are associated with Cluster 1 and samples from bedrock #1 with Clusters 1, 3 and 4. Relatively lower δ^{18}O, δD, $^{14}C_{DIC}$ and tritium values for Cluster 1 (mainly Na-HCO_3) and Cluster 4 mean that these groundwaters recharged during the last glaciation period (>10,000 yrs) and have longer mean residence times. In addition, the occurrence of ^{1}H and ^{16}O enriched H_2O in some groundwater samples indicate that bedrock formations have not been flushed by modern or postglacial recharge. Samples in cluster 3 represent a mixture of old and young groundwater (Fig. 3.10).

Occurrence of fluoride and bromide in groundwater

Fluoride has been commonly reported in groundwater from all datasets. The concentration of fluoride in water samples varies from 0.1 mg/L to 6.8 mg/L with mean and median values of 0.9 mg/L and 0.5 mg/L respectively. Water samples characterized with Na-HCO_3 in the Cluster 1 have the highest concentrations of fluoride where the Ca/Na ratios and sulfate concentrations are the lowest (Fig. 3.12). The lowest concentrations of fluoride are found in water samples belonging to the Cluster 1 (mainly Ca-Mg-HCO_3 types) associated with short residence times (Fig. 3.12). Fluoride-rich groundwater seems to occur in conditions with high Na, HCO_3 concentrations, moderate TDS and with relatively long residence time (Cluster 1).

When reported, the bromide concentration varies in the water samples from 0.001 to 2.45 mg/L. We used the ratio between chloride and bromide (Cl/Br) to characterize the groundwater samples. As shown in Fig. 3.13, the majority of the groundwater samples had Cl concentrations <20 mg/L and a Cl/Br < 100. Only 6 samples were characterized by Cl concentrations > 20 mg/L and Cl/Br > 100.

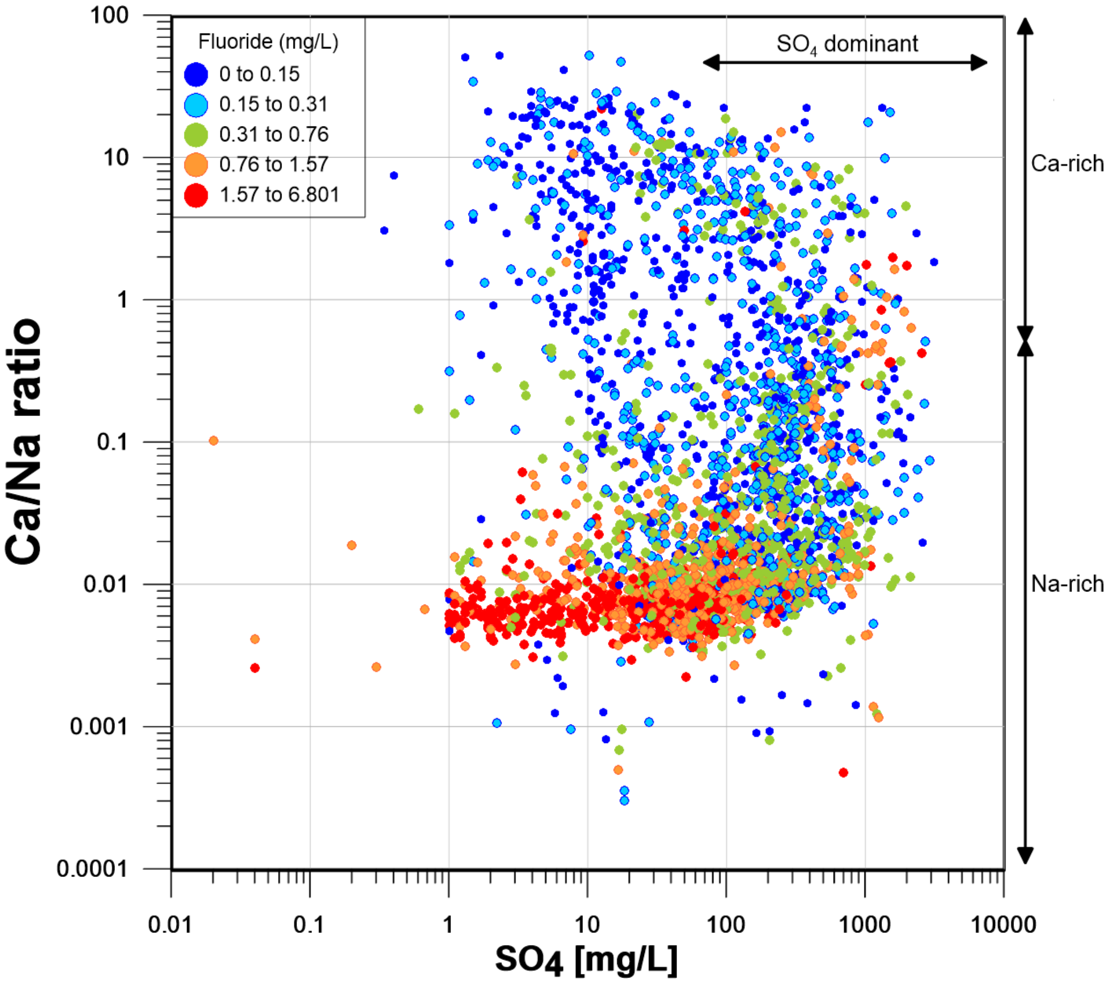

Figure 3.12: Distribution of fluoride concentration across the datasets.

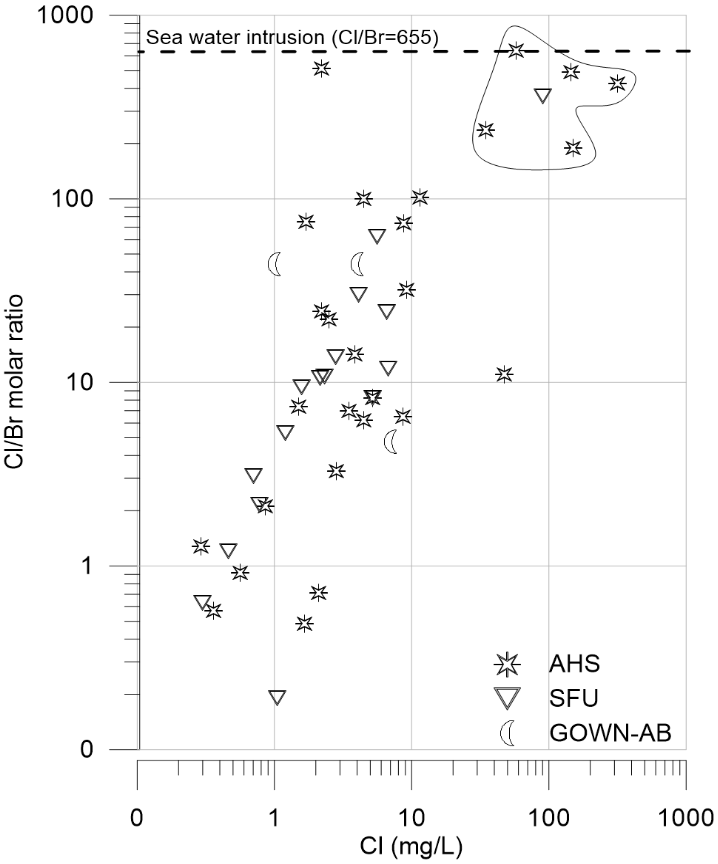

Figure 3.13: Plot of Cl/Br ratio versus chloride concentration

3.4 Geochemical/statistical classification of groundwater samples

By compiling hydrochemical facies, multivariate statistics, and additional geochemical and isotopic parameters we developed a water classification that describes the geochemical patterns observed in groundwater (see Fig. 2.14). These observed geochemical patterns are mainly derived from the geochemical processes such as ion-exchange, redox processes, and water-rock-interaction with carbonates, sulfates, sulfides, and silicates within the aquifers.

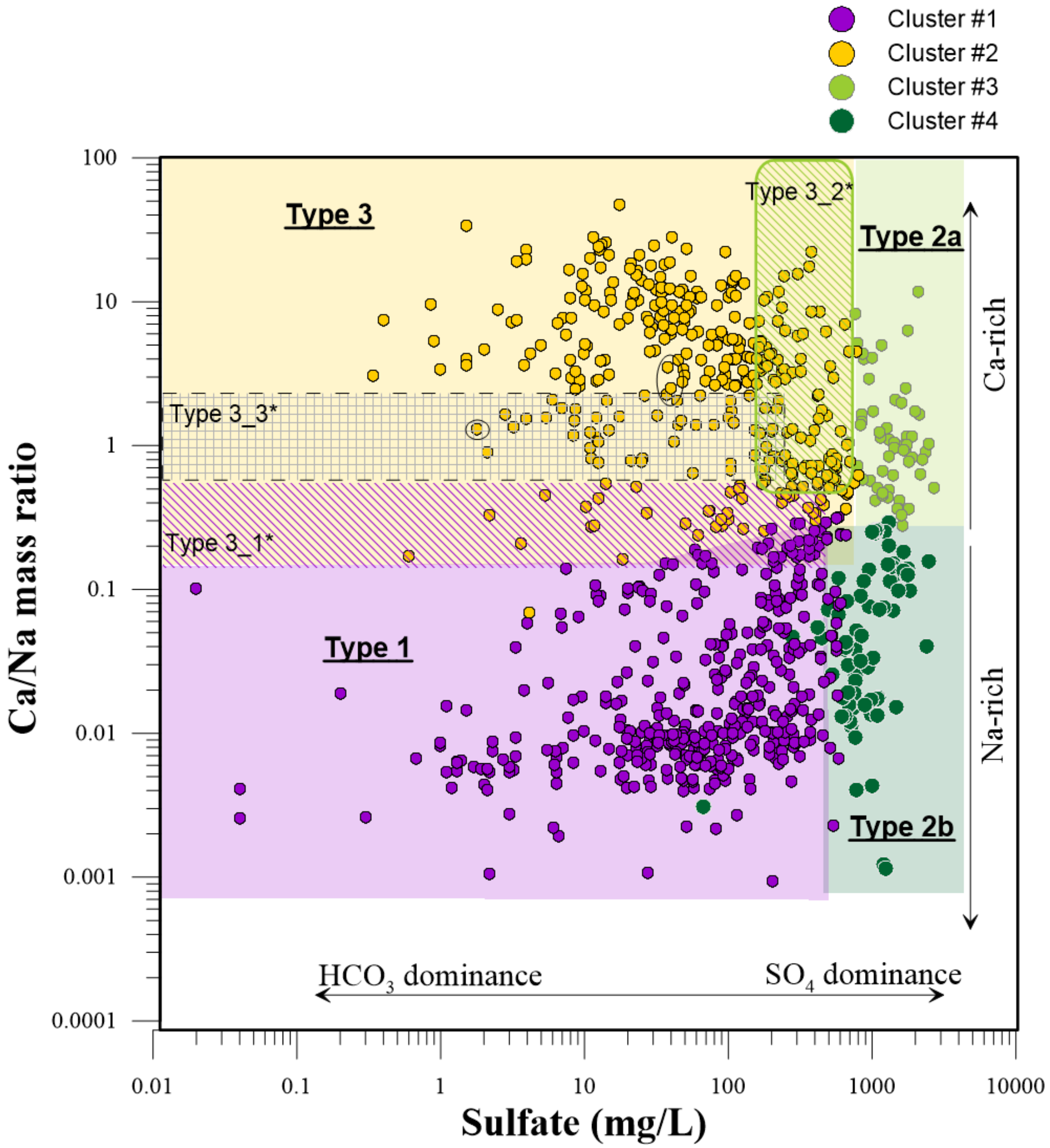

Figure 3.14: Graphical representation of the water type classification

Type 1 — Geochemically evolved groundwater (cluster 1)

The majority (93%) of the groundwater samples in this cluster is characterized by sodium-bicarbonate waters ($Na-HCO_3-(Cl)$). Ion exchange reactions in the subsurface are usually responsible for the increase in sodium concentrations in the groundwater. Cation exchange reactions have been revealed in the anti-correlation matrix between Ca and Na concentrations (Table 3.14). These groundwater samples are usually indicative of long groundwater residence times and thus more geochemically evolved groundwater. The water well depth for type 1 samples is not always reported but is on average 67 m (Fig. 3.19). This group of samples is called "**Type 1**".

As mentioned in the previous section, other minor hydrochemical facies have been found in this cluster e.g. $Na-HCO_3-SO_4$ (6.8%) which is representing the dominant hydrochemical facies of cluster 4. **Type 1*** thus describe the minor/overlapping hydrochemical facies among other clusters.

Types 2 — Mixed, sulfate rich groundwater (clusters 3 and 4)

Clusters 3 and 4 are both indicative of groundwater with elevated sulfate concentrations that is called **Type 2.** Clusters 3 and 4 differ from each other based on the cation contents with cluster 3 referring to SO_4-rich and Ca-rich water samples (Type 2a) while Cluster 4 characterizes SO_4-rich and Na-rich water samples (Type 2b). The water well depth is not always reported but is on average 29 m (Cluster 3 or Type 2a) and 69 m (Cluster 4 or Type 2b) (Fig. 3.15).

Type 2a: Calcium-Sulfate-rich waters (cluster 3) e.g. $Ca-Mg-Na-SO_4$, $Ca-SO_4$
Type 2b: Sodium-Sulfate-rich waters (cluster 4) e.g. $Na-HCO_3-SO_4$, $Na-SO_4$

Hydrochemical facies such as $Ca-SO_4$ or $Ca-Mg-SO_4$ in these waters may be indicative of water-rock interactions with anhydrite or gypsum. Water-rock interaction with pyrite e.g. pyrite oxidation would result in increased sulfate concentrations plus acidity that may be buffered by other reactions.

Type 2* refers to the minor hydrochemical facies that overlap other main clusters or types characteristics e.g. $Na-HCO_3$ (<5%).

Type 3: — Shallow freshly recharged groundwater (cluster 2)

The majority (> 55%) of the samples in this cluster is characterized by calcium-magnesium-bicarbonate waters ($Ca-(Mg)-HCO_3$). These water samples are usually typical for waters that have interacted with carbonate minerals and often have comparatively low total dissolved solids (TDS). The water well depth is not always reported but is on average 36 m (Fig. 3.15). This cluster is called **Type 3**.

The other minor hydrochemical facies reported that overlap the main characteristics of other water types will be reported as **Type 3***. Type 3* contains a various number hydrochemical facies that differ from $Ca-Mg-HCO_3$. Including $Na-HCO_3$ hydrochemical facies that belong to type 1 (<13%) that will be named Type 3_1*; SO4-rich water types e.g. $Ca-Mg-Na-SO_4$ (<16%) belonging to Type 2 that will be named Type 3_2* and a number of mixed hydrochemical facies e.g. Ca-Na-HCO_3 (<16%) that will be named Type 3_3*. These Type3* are presented in Fig. 3.14.

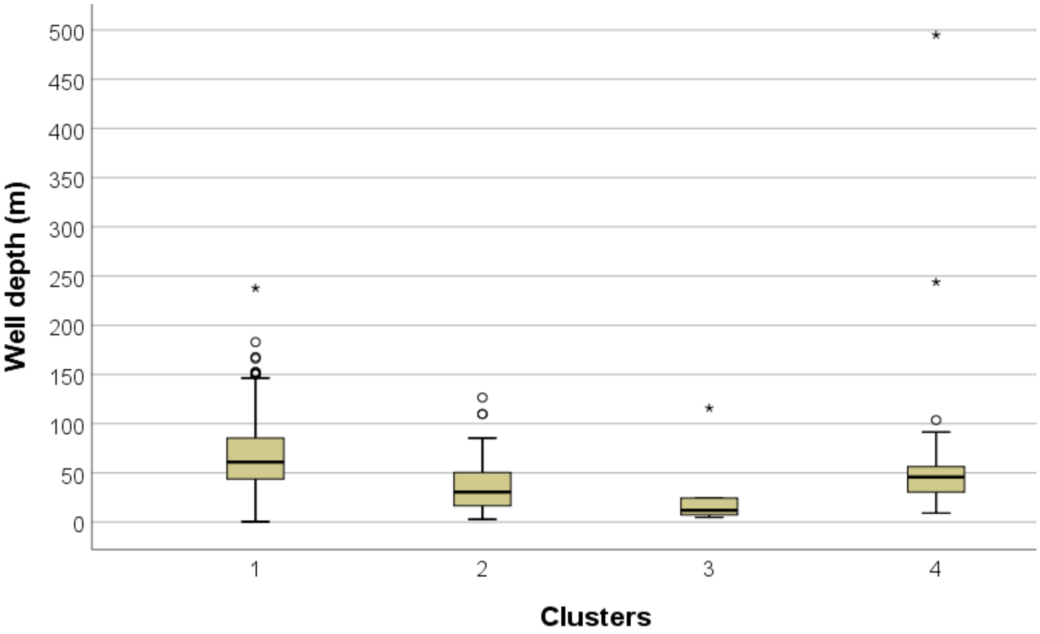

Figure 3.15: Water well depth distributions among the four clusters.

A summary table of the geochemical classification is presented in Table 2.19. We used a geochemical classification using multivariate analyses, to establish a framework to direct aquifer assessment/mapping and help identifying strategic/vulnerable zones regarding potential contaminations. Three main types of groundwater characteristics have been defined:

- **Type 1**: more geochemically evolved, mature groundwater typically of Na-HCO_3 type;
- **Type 2**: mixed, sulfate rich groundwater (type 2a: Na-SO_4 rich, type 2b, Ca-SO_4 rich) with a wide range of groundwater ages;
- **Type 3**: Shallow, freshly recharged and modern groundwater typically of Ca-(Mg)-HCO_3 type due to water-rock-interaction with carbonate minerals, often from wells completed in quaternary sediments.

Table 3.19: Summary of classification

Parameters	Type 1	Type 2		Type 3
		Type 2a	Type 2b	
Description	More geochem. evolved water	SO_4-rich groundwater		Shallow fresh/modern groundwater
	Anoxic	Anoxic-oxic		Anoxic-oxic
Ca/Na ratio	<0.1	>0.1	<0.1	>0.1
Dominance of redox species	SO_4< 500mg/L	SO_4>500mg/L		SO_4<160 mg/L 2.1 mmol/L
Average Depth (m)*	67	29	69	36

* not all water samples have information on the water well depth (mainly Alberta dataset)

Type: expect of low methane concentration unless water dis-equilibrated with respect to redox (SO_4)

Type: expect high concentration of methane

3.5 Assessing the spatial and temporal geochemical databases variability

3.5.1 Temporal variability

Alberta

From 2006 to 2019, 9 GOWN wells have been visited frequently resulting in time series monitoring of geochemical data. Most of the samples have been collected between July and September. The temporal variability of the main major ions is illustrated in Fig. 3.16. The coefficient of variation (CV) is used here to quantify the temporal variability per groundwater well. The CV is expressed as a percentage and defined as the ratio of the standard deviation to the mean. The CVs for the major ions are <25% indicating low temporal variability. Exceptions are SO_4 and DIC that show a CV >50% for well 338.

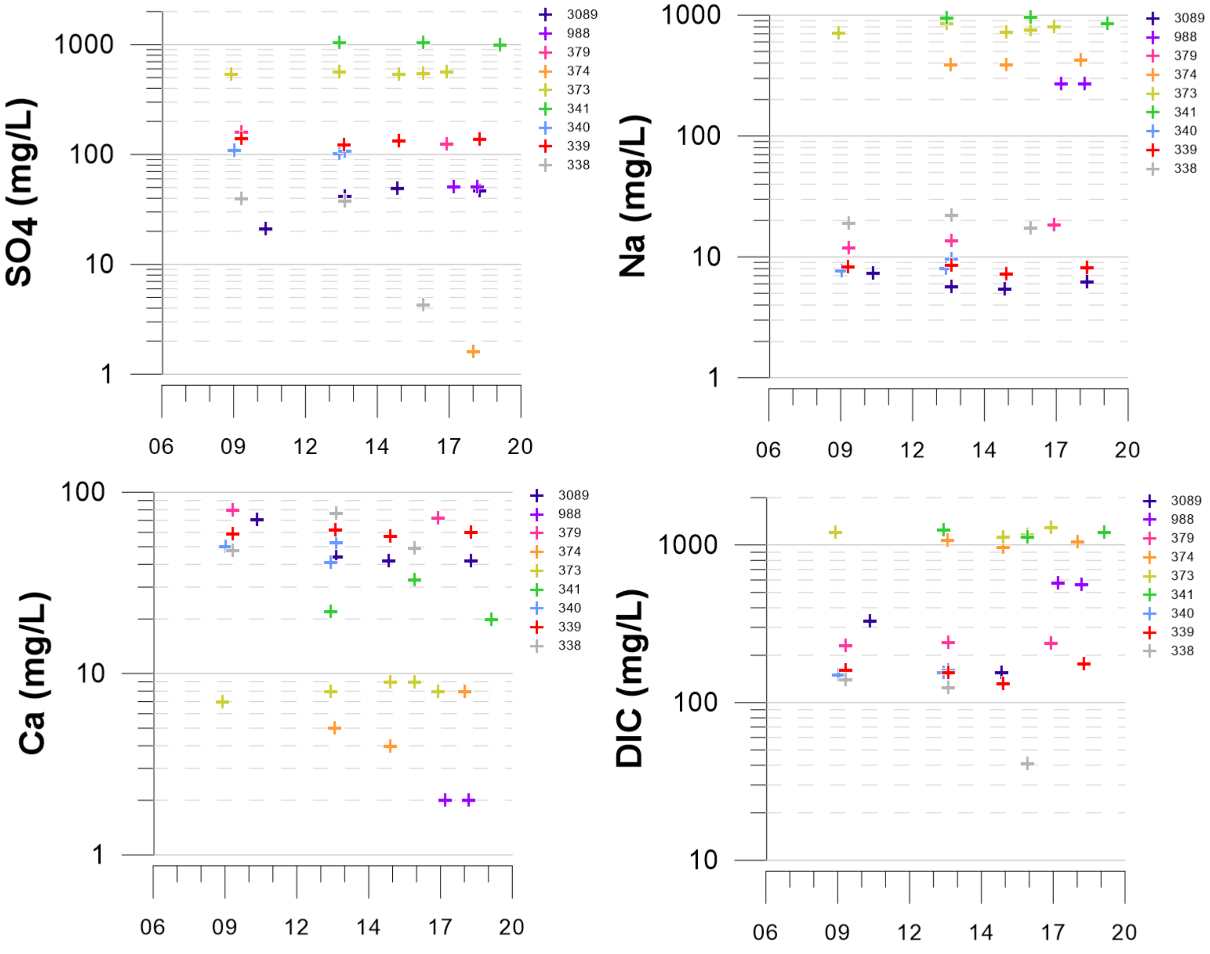

Figure 3.16: Temporal variability of Ca, Na, SO_4 and DIC concentrations versus time (year expressed as 2-digit: yy) from the GOWN samples.

British Columbia

The wells presenting time-series monitoring of groundwater geochemistry were selected. A total of 12 wells from the Northern Health Authority dataset were selected for assessing temporal variability of geochemical data. Some of the wells report very long records of geochemical data that have been analyzed in the 80s. However the frequency of the sampling campaign for each well is quite low meaning that most of the wells have been visited every 2-5 years. Such large time interval between sampling campaigns limit a refined temporal evaluation of the geochemical data. There are four exceptions where wells have been sampled during summer and winter season of the same year e.g. #60796, #60768, #60345, #60053. Those wells are presented in black symbols in the Fig. 3.17.

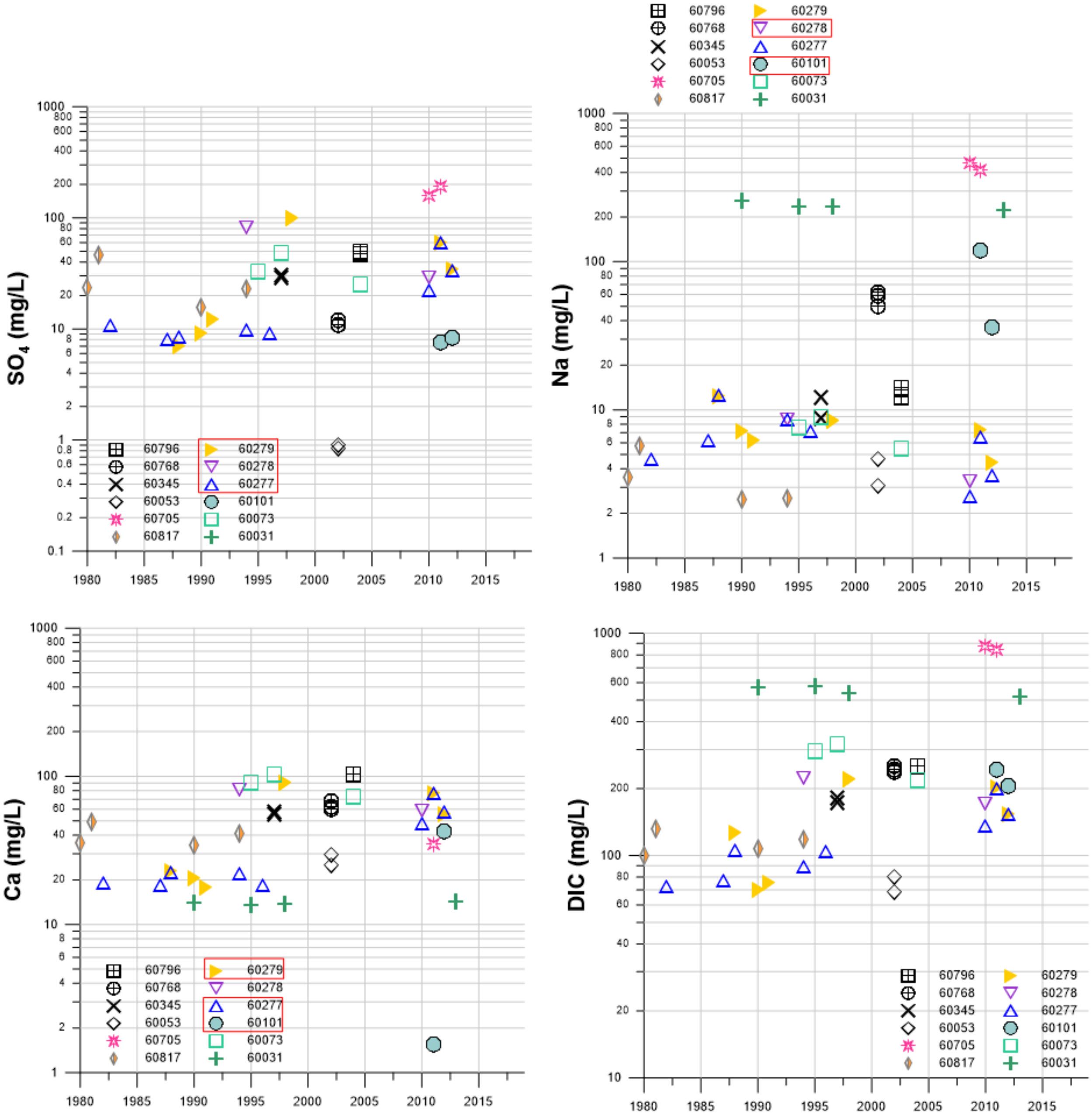

Figure 3.17: Temporal variability of Ca, Na, SO_4 and DIC concentrations versus time (year) from the NHA samples.

For each well, coefficient of variation (CV) was used to express the temporal variability of the geochemical data. For most of the major ions i.e. Ca, Na, Mg, SO_4, DIC the CV are < 33% for the majority of the groundwater wells. Few exceptions for 3 wells are found with CV that are > 50% for certain parameters such as Ca, Na, Mg and SO_4 where the concentrations double. Those exceptions are highlighted in red in the legend of Fig. 3.16. The CVs of the 4 wells that have been re-sampled in the same year have a very low variability with CV < 20%. Even if a low temporal variability has been detected for those wells, only two samples per well have been collected, which limits the detection of seasonal patterns/effects.

3.5.2 Geospatial variability: Alberta versus British Columbia water samples

3.5.2.1 Major ions geospatial variability: example of sulfate concentration

Different maps showing the spatial distribution of the major ions are provided in Appendix B. The distribution of sulfate concentration has been presented in Fig. 3.18. Jenks natural breaks optimization classification method is used to create concentration intervals. Such algorithm is designed to maximize the similarity of numbers in groups while maximizing the distance between the groups.

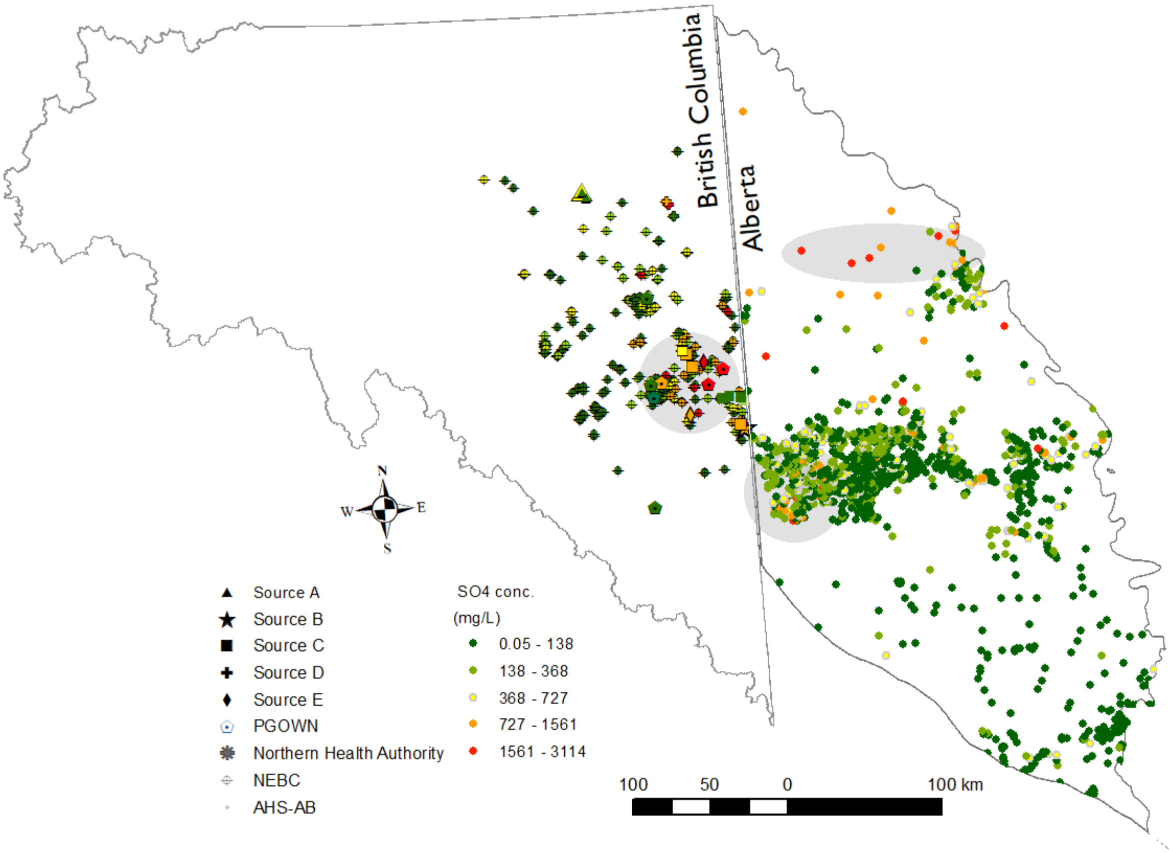

Figure 3.18: Spatial distribution of sulfate concentrations in the groundwater samples located above the Montney extent in British Columbia – Alberta. The AHS sulfate concentrations are averaged/section. The SO_4 concentration intervals are defined according to Jenks natural breaks optimization classification method.

On the Alberta side, the AHS dataset shows a spatial limitation due to the ATS system used for location of the different groundwater wells. The precision of this ATS coordinate system is at the section (1 mile or 1.6 km) order. Multiple wells have thus identical ATS coordinates. The AHS geochemical variability within the section was studied. Sulfate concentrations reported in groundwater samples was used as a proxy to illustrate the spatial variability. The sulfate concentration in Alberta from AHS dataset is averaged per section. A wide range of concentration and spatial heterogeneity are illustrated in the water samples from British Columbia to Alberta. Some cluster samples with elevated concentration of sulfate have been found and are highlighted in a grey circle in Fig. 3.18. A further exploration using geochemical and isotope data constraints in the next Milestones will permit to emit hypothesis regarding the origin of sulfate in these areas.

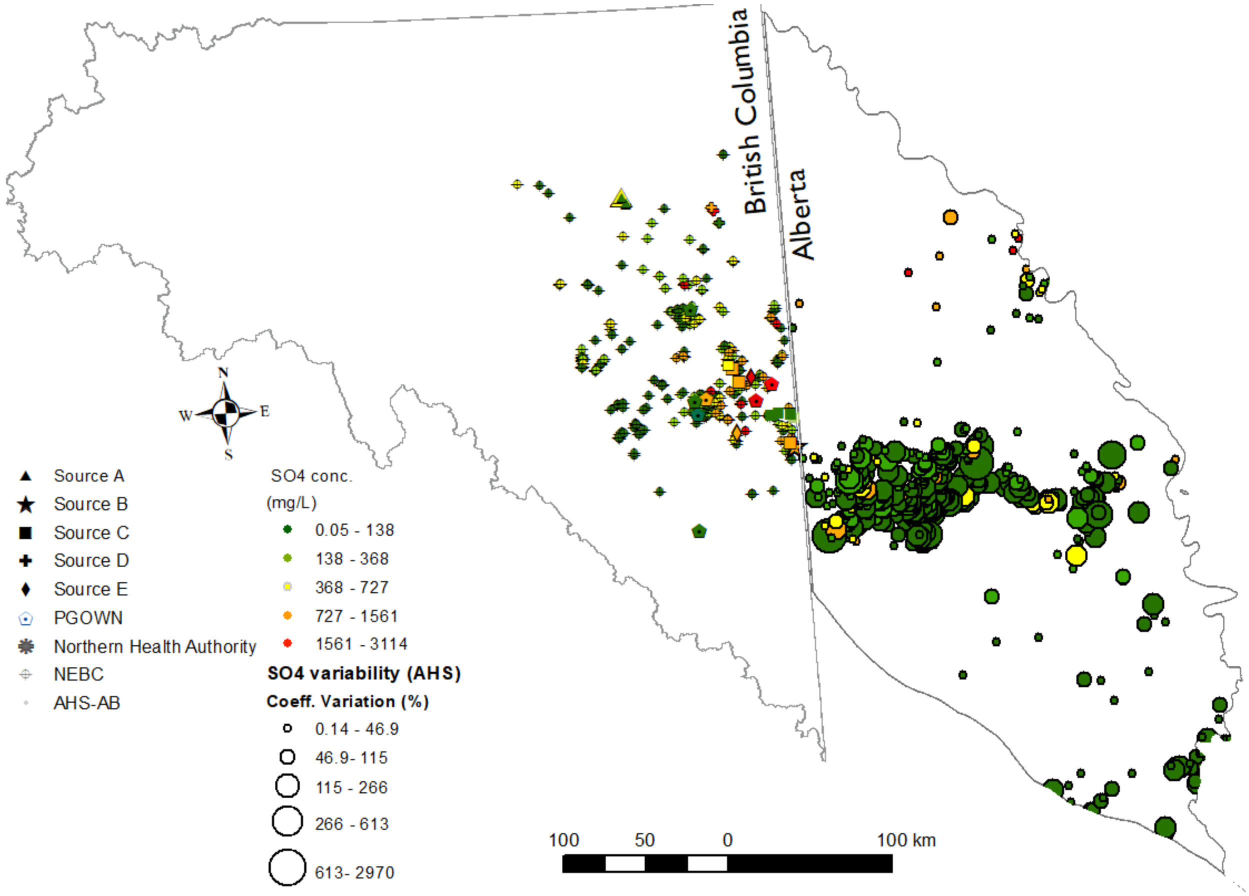

Figure 3.19: Variability (Coefficient of Variation %) of sulfate concentrations within a section (Alberta Township System)

The dispersion of sulfate concentration/section is represented with the coefficient of variation (CV). Only sections containing ≥ 2 wells were part of the CV calculation. The results are mapped in Fig. 3.19, the wider circles representing the largest CV. For clarity reasons the CV are plotted into a histogram (Fig. 3.20). The CV varies from 0.14% to > 2900%. Over 72% of the sections containing minimum two wells have a CV < 100% (Fig 3.20). A CV= 100% indicates that the concentration of sulfate can double.

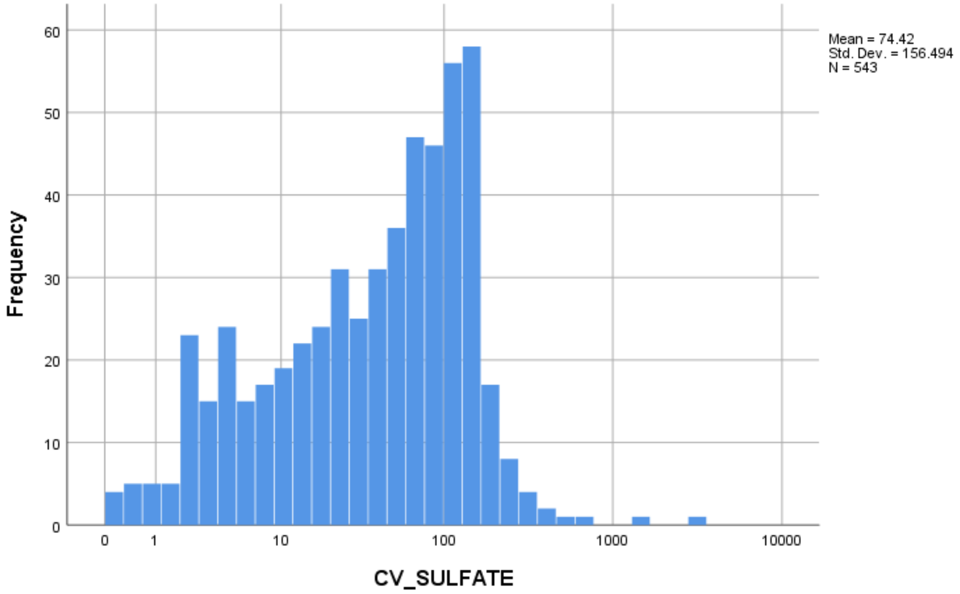

Figure 3.20: Histograms of coefficient of variation of sulfate for AHS dataset for sections* with ≥ 2 wells (* grid of 1mile precision in the ATS coordinates definition

3.5.2.2 Spatial analyst - density toolset

The map of the data shows regions of high (Grande Prairie area) or low event occurrence of water wells and spatial outliers (Fig. 3.21). The density of the wells has been estimated and is represented in Fig. 3.21. The average highest density of >0.2 wells/km^2 indicates that in the denser areas an average of 10 wells would be found within a circle-radius of 7 km. Other areas have a lower density of wells. A great imbalance in term of density is observed between the two provinces. One problem that may occur is the impact when event occurrences are non-uniform and how to compare event density maps.

Imbalanced datasets have been treated previously by using a resampling (bootstrap) method. A map is shown below to represent the location of the randomly selected water samples (Fig. 3.22). The re-sampling method permitted not only to balance the size of the datasets (BC and AB) but as well permit to balance the well density across the two provinces.

Differences regarding density events with areas with high event occurrence (Grande Prairie area, AB) and low event occurrence or spatial outliers exist. The re-sampling method permitted to balance not only the size difference between the data of the two provinces but as well smooth the well density discrepancies across the provinces. In addition, we have identified among the groundwater samples across the different databases, spatial and geochemical variabilities sometimes within <2 km radius. Such variability (i) will affect any spatial interpolations as well the confidence of any predictions regarding potential contamination for these groundwater systems (ii) will affect any potential water quality parameters deviation with time.

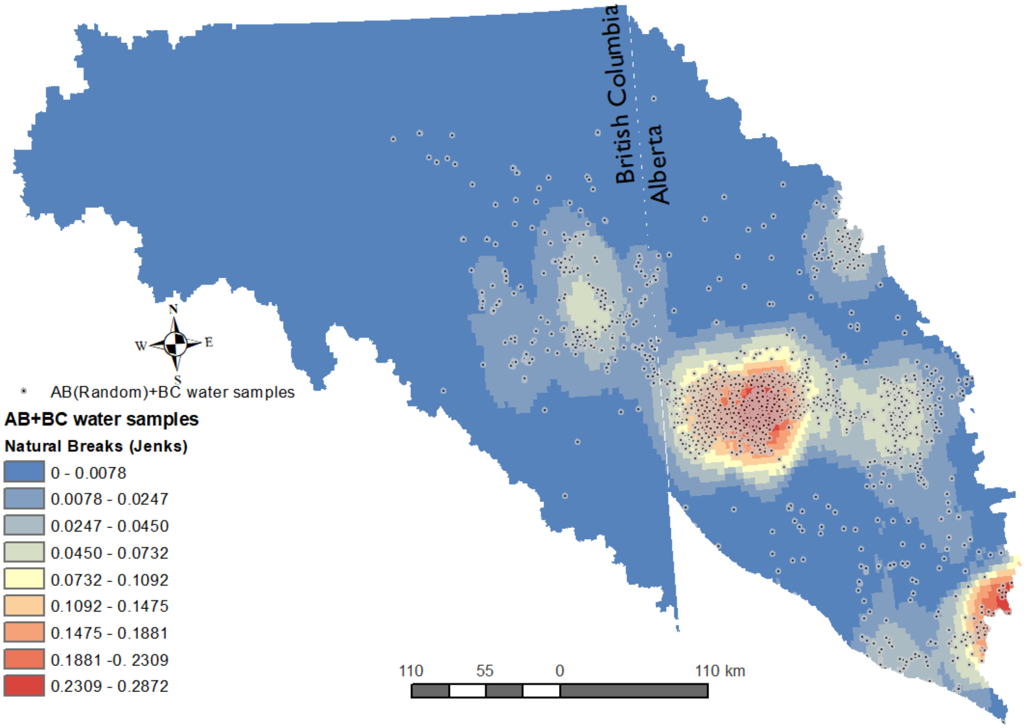

Figure 3.21: High and low event occurrence of the water samples location (density expressed in square kilometers).

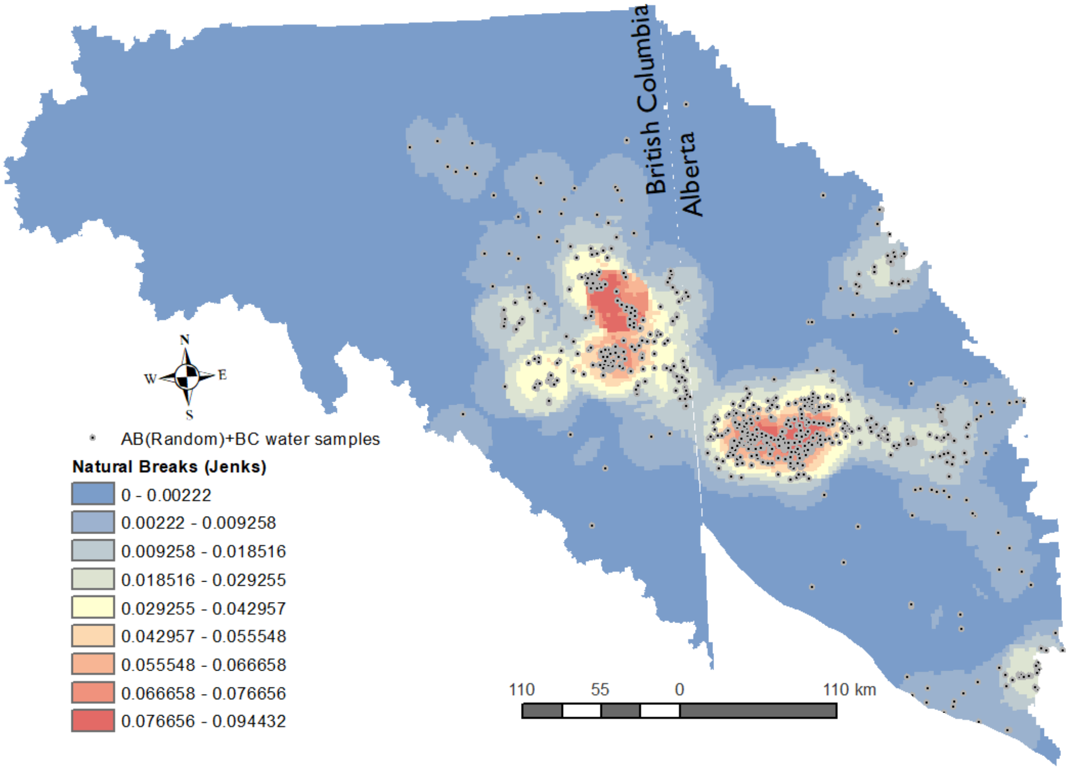

Figure 3.22: Density (wells/km^2) of the groundwater wells after the re-sampling method for the Alberta dataset.

4. Milestone 3: Occurrence of methane

4.1 Occurrence of methane and other higher alkanes in groundwater samples

- Guidelines for assessing methane occurrence

The explosive level of methane in air is between 5% to 15% by volume (50,000 to 150,000 ppmv). This range was used to characterize measured free-gas methane concentrations. For dissolved methane, Henry's Law relates the dissolved methane concentrations (C_w) to gas pressure C_g expressed as $C_w=K_H*C_g$. For illustration, at 20°C and atmospheric pressure (101.325 kPa), using $K_H=1.4\cdot 10^{-3}$ mol.m^{-3}.Pa^{-1}, a dissolved methane concentration of 1.2 mg/L could theoretically generate a lower explosive limit for CH_4 in air (5% by volume). This scenario would require confined conditions where "an unlimited quantity of aerated water is sprayed into an unventilated chamber" (Edwards, 1991). These conditions are unlikely to be encountered in practice.

There are few established guidelines for dissolved methane concentration in water. A CH_4 risk "action level" was proposed at 10 mg/L by Eltschlager et al. (2011). Other guidelines considered explosion/safety issues related to exsolution of dissolved methane into potentially confined, air-filled spaces. The Colorado Oil & Gas Conservation Commission (COGCC) reported a hazard threshold for dissolved methane concentration > 10 mg/L and a hazard mitigation level of 28 mg/L similar to the US Department of the Interior, Office of Surface Mining (2001). The Quebec Ministry of Environment and the Pennsylvania Department of Environmental Protection both set a threshold value of 7 mg/L for dissolved methane in groundwater. The Ontario Ministry of Environment and Energy proposed a methane volumetric guideline set at 3 L/m^3 corresponding to ~2 mg/L defined in the maximum desirable concentration parameters related to aesthetic quality (source: agrienvarchive.ca).

For this study, elevated concentration of methane will be defined as any concentration of methane > 1 mg/L.

- Industrial datasets

Dissolved methane concentrations have been reported for all industrial data sets except for source B.

For source A

Methane has been analyzed in the 7 samples. 2 of 7 samples had no methane detected. For the other 5 samples, methane concentrations vary from 0.1 mg/l and 9.63 mg/L. Only one sample has a concentration of methane > 1 mg/L.

For source C

Methane has been analyzed for 6 samples and 3 samples had no methane detected. For the other 3 samples the concentrations of methane vary from 0.004 to 0.006 mg/L.

For source D

Methane has been analyzed for 3 samples. The concentrations of methane vary from 0.005 mg/L to 11.9 mg/L. One sample has a concentration of methane > 1 mg/L.

Across the different industrial sources, methane has been detected (> LQ) in 70% of all the samples submitted for gas composition analyses, but only 2 samples had elevated methane concentrations > 1 mg/L. No higher alkanes (e.g. ethane, propane) have been detected.

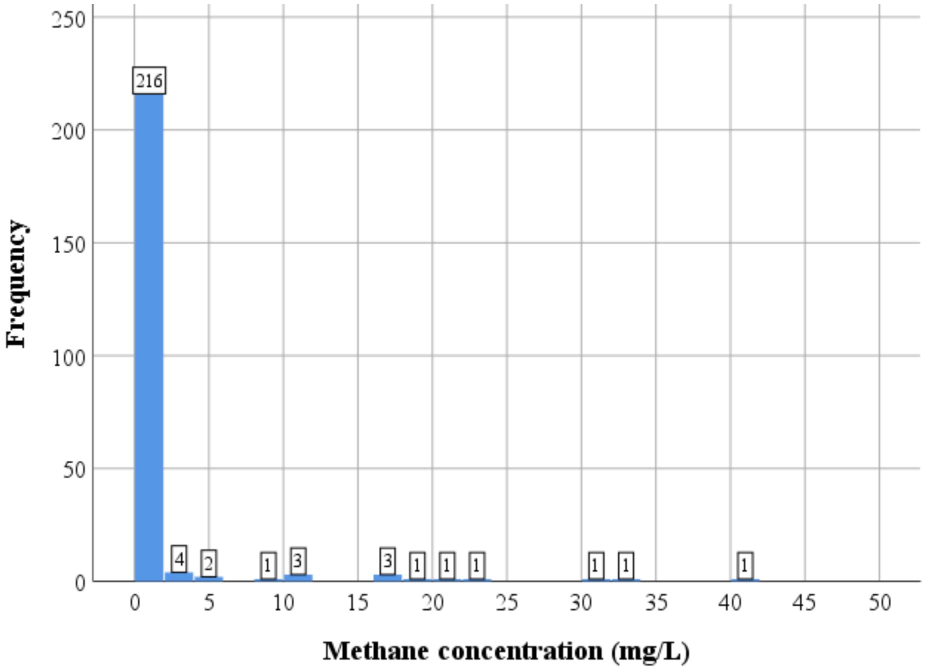

Figure 4.1: Frequency plot of methane concentrations distribution from the SFU dataset (n= 235 samples).

- Additional datasets

Groundwater collected by SFU provided methane concentrations for 264 samples. Methane was not detected in 29 samples. For the 235 remaining samples, the methane concentration varied from 0.0002 to > 40 mg/L. A total of 29 of 235 samples (12%) had methane concentrations > 1 mg/L (Fig. 4.1). Highest methane concentrations are found in groundwater obtained from monitoring wells completed in bedrock formations (bedrock #1, Fig. 4.2) and the lowest methane concentrations were observed in samples collected from springs.

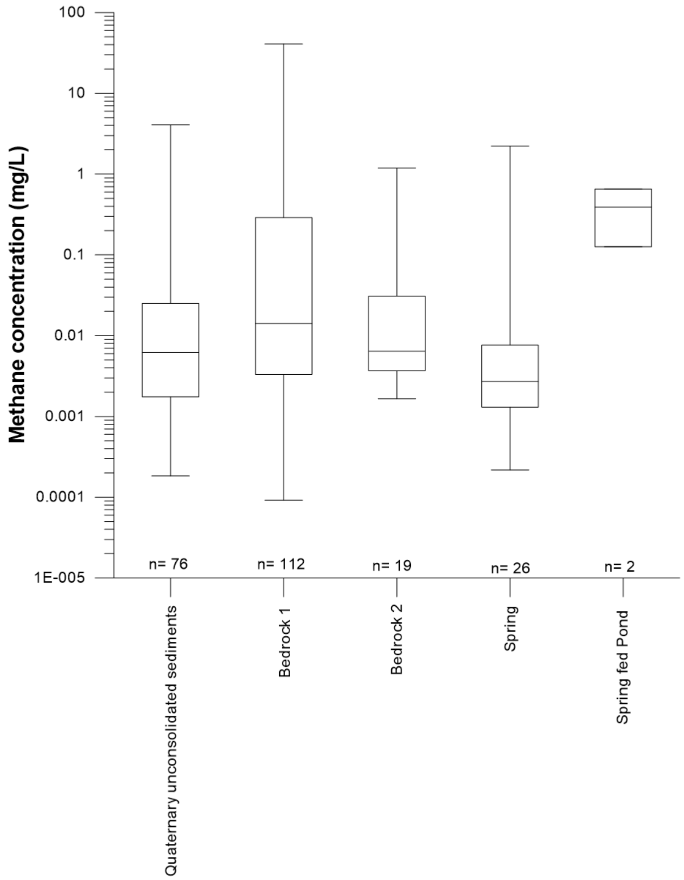

Figure 4.2: Methane concentration distribution among the different sampling points (SFU source).

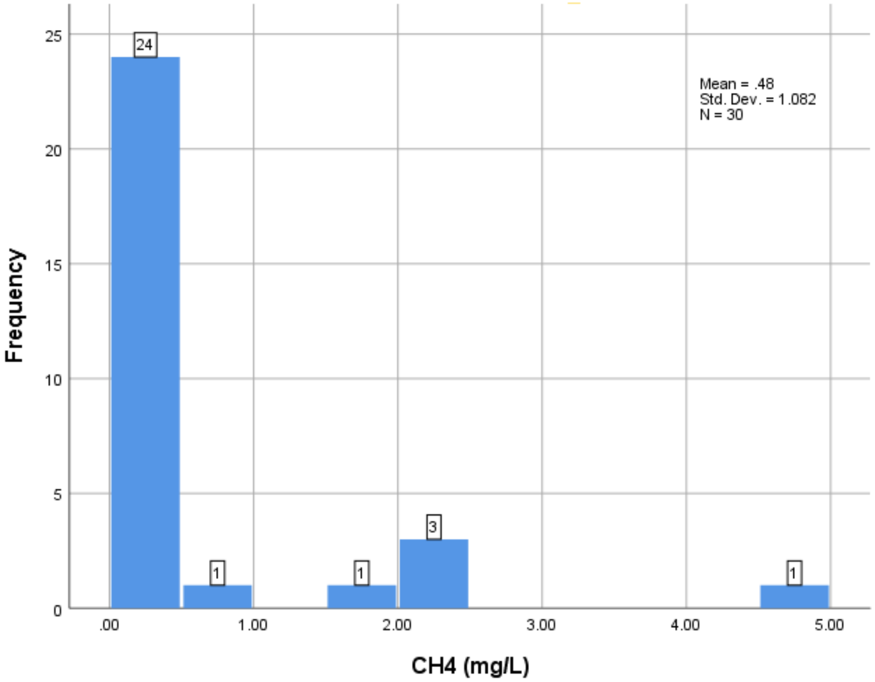

Figure 4.3: Frequency plot of methane concentration distribution from the GOWN-AB dataset (n= 30 samples).

The dissolved gas samples from GOWN-AB wells have been analyzed for gas composition. Methane concentrations varied from 0.0004 to 4.69 mg/L. A total of 25 samples of 30 samples (83%) had methane concentration < 1 mg/L, while 5 samples had elevated methane concentrations exceeding 1 mg/L (Fig. 4.3).

A spatial distribution of methane occurrence is presented in Fig. 4.4. There is no distinct distribution pattern in the elevated methane (> 1 mg/L) occurrences. In general, methane occurrence in groundwater is highly variable between groundwater wells sites.

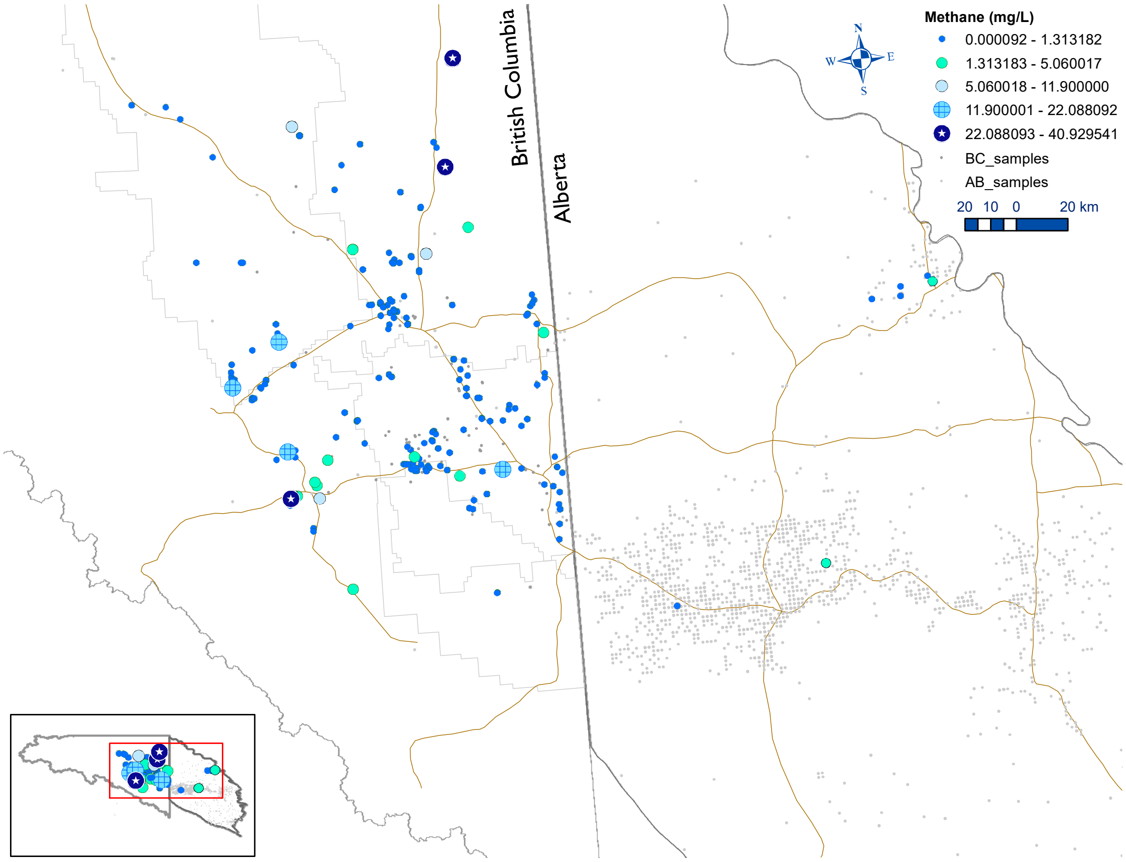

Figure 4.4: Spatial distribution of methane in the groundwater samples detected in Alberta and British-Columbia.

4.2 Relationship between methane occurrence and geochemical/statistical classification

We were interested in assessing any potential relationship between methane occurrence and the hydrochemical types. The previous section had identified different main geochemical and statistical types (Types 1, 2, and 3). Any deviation from this concept would permit to identify anomalies in methane.

Table 4.1: Distribution of the methane-containing samples across the different hydrochemical water types 1, 2, 3 and 4.

	Type 1		**Type 2**			**Type 3**			
	Type 1	**Type 1***	**Type2a**	**Type 2b**	**Type 2***	**Type 3**	**Type 3*_1**	**Type 3*_2**	**Type 3*_3**
Mean (mg/L)	4.66	0.00	0.02	0.28	18.34	0.09	0.54	0.01	0.79
Standard deviation	8.33		0.05	1.10	16.87	0.53	1.20	0.02	1.92
Median (mg/L)	0.31	0	0.01	0.01	16.19	0.01	0.01	0	0.03
N	48	1	28	21	4	61	11	24	25
Sub-total	223								
Non-detected	13	1	12	1	0	17	5	16	9
Sub-total	74								
Grand total	297								
N >1 mg/L	20	0	0	1	3	1	2	0	6
Sub-total	33								
	60.6%	0.0%	0.0%	3.0%	9.1%	3.0%	6.1%	0.0%	18.2%
N >2 mg/L	13	0	0	1	3	1	2	0	3
Sub-total	23								
	56.5%	0.0%	0.0%	4.3%	13.0%	4.3%	8.7%	0.0%	13.0%
N >7 mg/L	12	0	0	0	3	0	0	0	1
Sub-total	16								
	75.0%	0.0%	0.0%	0.0%	18.8%	0.0%	0.0%	0.0%	6.3%
N >10 mg/L	10	0	0	0	3	0	0	0	0
Sub-total	13								
	76.9%	0.0%	0.0%	0.0%	23.1%	0.0%	0.0%	0.0%	0.0%
Type 1	*Type 1*	*More geochemically evolved – mainly (>93%) Na-HCO$_3$-Cl hydrochemical facies*							
	*Type 1**	*Deviation from main hydrochemical facies e.g. Na-HCO$_3$-SO$_4$*							
Type 2	*Type 2a*	*Mainly Ca-SO$_4$ rich waters*							
	Type 2b	*Mainly Na-SO$_4$ rich waters*							
	*Type 2**	*Deviation from main hydrochemical facies e.g. Na-HCO$_3$-Cl*							
Type 3	*Type 3*	*Freshly recharged water mainly Ca-Mg-HCO$_3$*							
	*Type 3*_1*	*Deviation from main hydrochemical facies e.g. Na-HCO$_3$-(Cl) (<13%)*							
	*Type 3*_2*	*Deviation from main hydrochemical facies e.g. Ca-Na-SO$_4$-rich waters (<16%)*							
	*Type 3*_3*	*Deviation from main hydrochemical facies e.g. Ca-Na-HCO$_3$-Cl (<16%)*							

The Type 1 groundwater samples contain the most elevated concentration of methane with mean and median values of 4.66 mg/l and 0.31 mg/l respectively. Type 1 contains the majority i.e. 61%, 56%, 75% and 97%, of all methane-containing samples with methane concentrations > 1 mg/L, > 2 mg/L, >7 mg/L, >10 mg/L respectively. Type 2 and more specifically Type 2* is described by elevated average concentration of methane > 15 mg/L (n=4). Type 2* represents a deviation from Type 2 as the hydrochemical facies differ from Ca-Mg-HCO$_3$. Those four samples belonging to Type 2* are describing a Na-HCO$_3$-Cl hydrochemical facies.

Types 2 and 3 have different statistics regarding methane occurrence than type 1. They both contain samples with the lowest methane concentration mean and median values. The mean and median values of methane concentration in Type 2a are 0.02 and 0.01 mg/L respectively. The mean and median values of methane concentration in Type 2b are 0.28 and 0.01 mg/L respectively. The water type 2 describes SO_4 rich water where elevated concentration of methane should not be expected. As mentioned previously, Type 2* contains water samples that describe rather a Na-HCO_3-Cl hydrochemical facies that differs from the SO_4-rich characteristic of Type 2 waters.

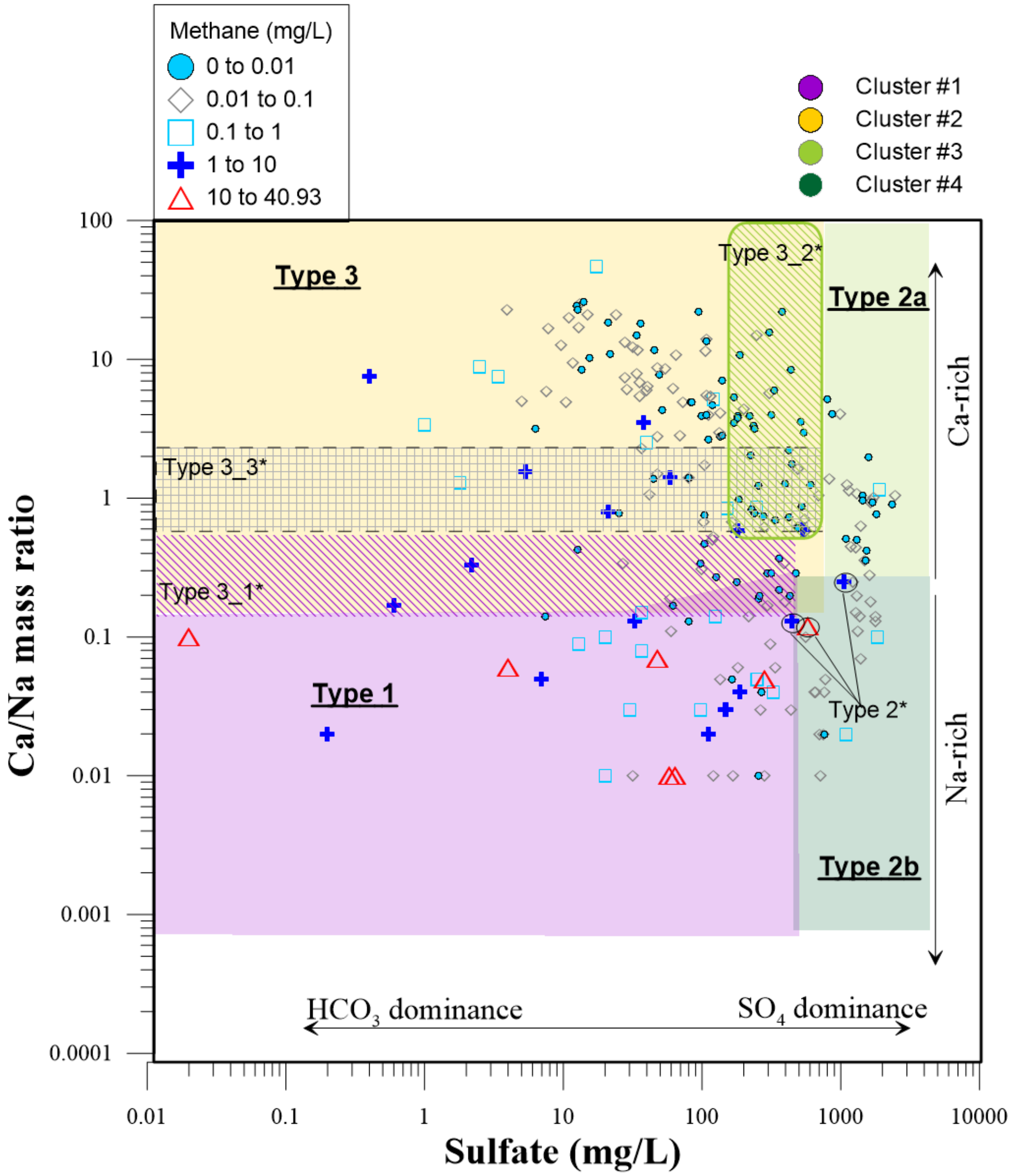

Figure 4.7: Methane concentration distribution within the hydrochemical facies framework. >75% of all groundwater samples with methane concentrations >1 mg/L belong to Na-HCO_3-Cl (Type 1, Type 3*_1).

The mean and median values of methane concentration in Type 3 are 0.09 and 0.01 mg/L respectively. Deviations from Type 3 called Type 3*_1, Type 3*_2, Type 3*_3 have been identified and are representative of minor hydrochemical facies that differ from the Ca-Mg-HCO_3 hydrochemical facies that comprise mainly the Type 3. A relatively large proportion of elevated methane concentration have been found in the Type 3*_1 and Type 3*_3 of 6% and 18% that are representative of Na-HCO_3 hydrochemical facies and mixed anoxic hydrochemical facies of Ca-Na-HCO_3-Cl types respectively.

Type 2 and Type 3 contain the majority of the samples that did not detect methane.

Methane occurrence is common in all groundwater samples however its occurrence and accumulation is associated with groundwater samples of Na-HCO_3-Cl hydrochemical facies (Type 1, Type 2*, Type 3*_1). This facies is often associated with long residence time (see section 2.11).

Consistent with the redox ladder concept, methane occurs when most of the electron acceptors have been consumed e.g. SO_4. This explains why SO_4-rich waters (Type 2, Type 3*_2) contain lower methane concentrations than in the geochemically evolved/mature groundwater samples Na-HCO_3-Cl (Type 1, Type 2*, Type 3*_1). The groundwater samples characterized by freshly recharged groundwater (Type 3) do not contain elevated methane concentrations. Exceptions (<6%) with elevated methane concentrations have been found in Types 2 and 3 that could indicate a **metastable state regarding redox conditions** potentially as a consequence of methane migration into more oxidizing conditions that will be studied in detail in the next milestone.
The distribution of methane-containing samples within the Types 1, 2 and 3 and respective deviations (marked with *) is illustrated in Figure 4.7.

Summary:

Across the different datasets there is a wide range of concentration of methane in the water samples. More than 85% of the samples with detectable methane content had methane concentration <1 mg/L. The hydrochemical facies is an important characteristic/control regarding the presence/absence of methane. The highest concentrations of methane belong to older/mature sodium-bicarbonate to sodium-chloride water systems. The lowest concentrations of methane belong to mixed cations-bicarbonate-sulfate waters. More than 75% of methane with concentration > 1 mg/L belong to Na-HCO_3-Cl and 18% belong to the Type 3*_3 (mixture water). About 6% of the groundwater samples with elevated concentration of methane belong to the SO_4-rich and Ca-Mg-HCO_3 waters.

5. Milestone 4: Redox conditions/control on source and fate of methane

5.1 Occurrence of redox sensitive species

5.1.1 Occurrence of O_2, NO_3, Fe, Mn and SO_4 in groundwater samples

- Industrial datasets

Different redox sensitive species have been reported for all different industrial data.

For source A:

Dissolved O_2 concentration has not been reported.

A total of 3 out of 7 samples analyses do not detect nitrate (below DL). The concentration of NO_3 has a mean of 0.17 ± 0.05 mg/L and median value is 0.2 mg/L. The mean and median concentrations of Fe and Mn are 0.17±0.06 mg/L and 0.2 mg/L, 0.19±0.29 and 0.02 mg/L respectively. The concentrations of SO_4 vary from 7.00 to 407 mg/L and the median value is 20 mg/L.

For source B

The groundwater sample collected from a shallow well has dissolved O_2 concentration reported of 8.05 mg/L. No nitrate has been detected during analysis (below DL). The concentrations of Fe and Mn are 0.8 and 0.4 mg/L respectively. The concentration of SO_4 is 1300 mg/L.

For source C

Dissolved O_2 concentration has not been reported.

A total of 8 out of 12 samples analyses do not detect nitrate (below DL). The concentration of NO_3 is 1.47 ± 2.27 mg/L and the median value is 0.05 mg/L. The mean and median concentrations of Fe and Mn are 0.78±0.84 mg/L and 0.47 mg/L, 0.31±0.39 mg/L and 0.12 mg/L respectively. The concentration of SO_4 is 616±572 mg/L and the median value is 433 mg/L.

For source D

Dissolved O_2 concentration reported is in average 3.12±3.71 mg/L and the median value is 1.78 mg/L. The lowest O_2 concentration of 0.26 mg/L is found in Na-HCO_3. Redox potentials (ORP) have been reported and vary from -19 mV to -213 mV. The concentration of NO_3 is 0.22 ± 0.08 mg/L and median value is 0.27 mg/L. The mean and median concentrations of Fe and Mn are 0.23±0.21 mg/L and 0.24 mg/L, 1.10±1.59 mg/L and 0.38 mg/L respectively. The mean and median values of concentration of SO_4 are 994±873 mg/L and 1330 mg/L respectively.

For source E

Dissolved O_2 concentration has not been reported. Both samples analyses do not detect nitrate (below DL). When detected, the concentrations of Fe and Mn are 1.6 mg/L and 0.65±0.02 respectively. The concentration of SO_4 is 1590 ± 183.8 mg/L.

- Additional datasets

For PGOWN-BC data

Dissolved O_2 concentration has been reported for two samples with respective concentration of 2.1 and 8.5 mg/L. The concentration of NO_3 is on average 0.02± 0.03 mg/L and median value of 0.017 mg/L. When detected, the concentrations of Fe and Mn are 3.00± 5.53 mg/L associated with a median value of 0.379 mg/L, 0.23±0.31 and 0.09 mg/L respectively. The concentration of SO_4 is 839±1140 mg/L the median value is 94.9 mg/L. Descriptive statistics of redox sensitive species per hydrochemical facies can be found in Table 3.6.

For NHA dataset

Dissolved O_2 concentration has not been reported. A total of 17 samples analyses do not have nitrate detected. The concentration of NO_3 is in average 1.49 ± 2.99 mg/L and the median value is 0.33 mg/L. A total of 90% of the samples show a concentration in $NO_3 < 4$ mg/L. The highest concentrations of nitrate are associated with hydrochemical facies Ca-HCO_3. When detected, the mean and median values of concentrations of Fe and Mn are 0.59 ± 1.53 mg/L and 0.98 mg/L, 19.7 ± 26.12 and 11.1 mg/L respectively. The mean and median values for concentration of SO_4 are 90.2 ±188 mg/L and 32 mg/L. Descriptive statistics of redox sensitive species per hydrochemical facies can be found in Table 3.7.

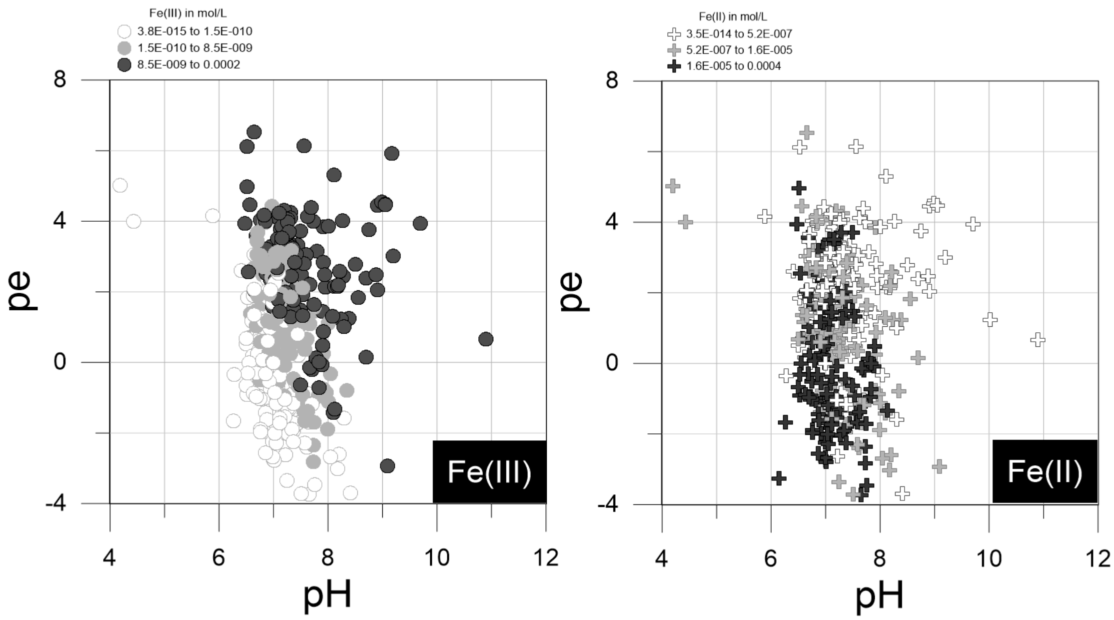

Figure 5.1: Diagram pe versus pH and geochemical speciation of iron in the groundwater samples of SFU dataset using PHREEQC

For SFU dataset

Dissolved O_2 concentration is in average 3.02 ± 4.51 mg/L. The hydrochemical facies Ca-Mg-HCO_3 are associated with the highest O_2 content. In addition, redox potentials (ORP) are provided for each sample. The concentration of NO_3 is on average 2.24 ± 3.72 mg/L and the median value is 1.2 mg/L. An outlier value of 539 mg/L is found in one sample. The mean and median concentrations of Fe and Mn are 1.67±3.36 and 0.16 mg/L, 0.36 ± 0.85 mg/L and 0.08 mg/L respectively. Manganese exists mainly in groundwater samples as Mn(II), the primary soluble form of Mn. Geochemical speciation has been performed using PHREEQC. Results from geochemical speciation are presented in Fig. 5.1 showing the distribution of Fe(II) versus Fe(III) in a stability diagram pe versus pH. As for Eh, high positive values of pe indicate oxidizing conditions and low negative values of pe, reducing conditions. The relation between pe and Eh is:

$$\mathrm{Eh} = \frac{2.303\,RT}{F}\,\mathrm{pe}$$

with R gas constant, T temperature and F Faraday constant.

The concentration of SO_4 is on average 416 ± 539 mg/L and the median value is 182 mg/L. Descriptive statistics of redox sensitive species per hydrochemical facies can be found in Table 3.8.

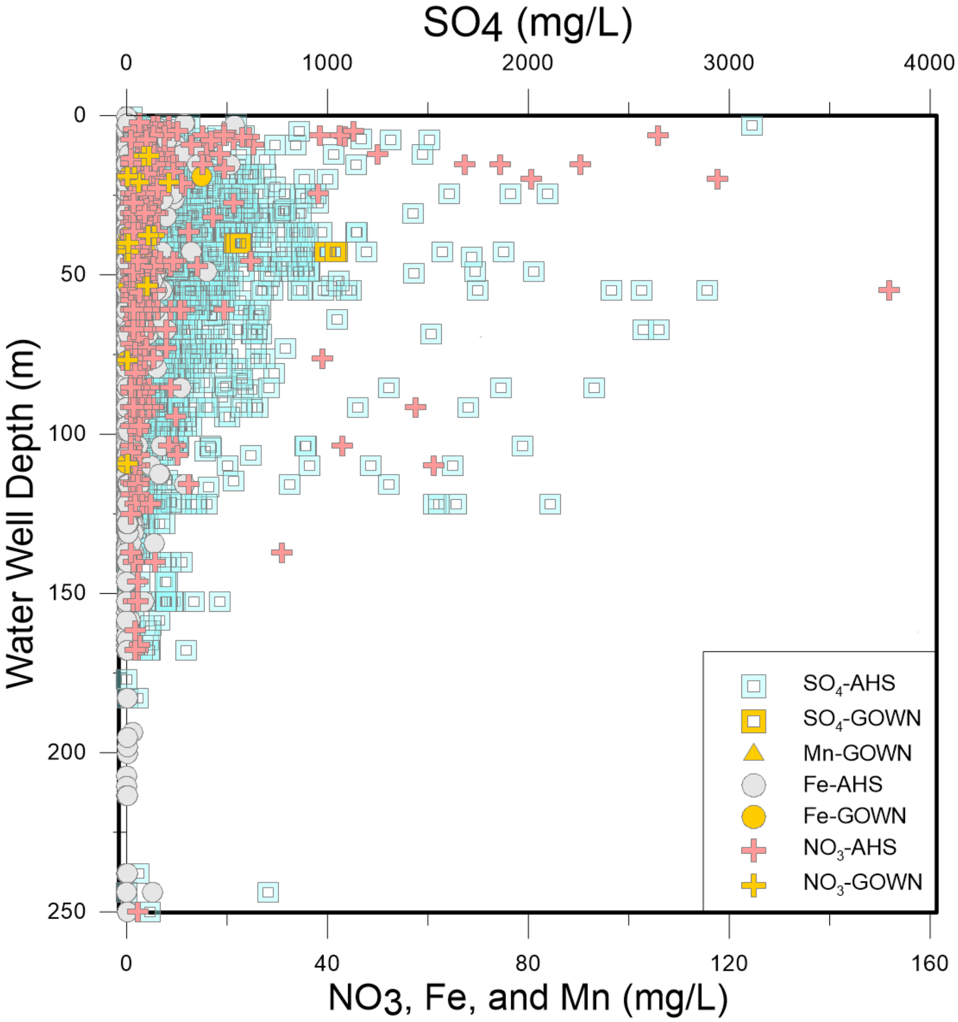

Figure 5.2: Redox sensitive species versus water well depth for the groundwater samples (AHS + GOWN samples)

For AHS

Dissolved O_2 concentration has not been reported for this dataset. The average nitrate concentration is 5.48 ± 12.9 mg/L, with 77% of groundwater samples having a nitrate concentration < 4 mg/L. The Fe concentration is in average 0.52 ± 1.99 mg/L and median value of 0.08 mg/L. Sulfate concentration has a mean and median values of 182 ± 287 mg/L and 82 mg/L respectively.

For GOWN-AB

Field dissolved O_2 parameter has not been reported for this dataset. The mean and median nitrate concentration values are 2.14 ± 2.40 mg/L and 0.43 mg/L respectively. The Fe and Mn concentrations have mean and median values of 1.59 ± 3.34 mg/L and 0.36 mg/L, 0.17 ± 0.32 mg/L and 0.036 mg/L. Sulfate concentration has a mean and median values of 265.8 ± 326.9 mg/L and 121 mg/L.

The Fig. 5.2 presents the distribution of the redox sensitive species of both AHS and GOWN samples on a depth profile. It is interesting to note there is a vertical **trend in which the availability of electron acceptors decreases with depth.**

5.1.2 Relationships between methane and other redox sensitive species occurrences

Anti-correlations have been found between methane and elector acceptor species e.g. NO_3, Mn, Fe, and SO_4. Across the dataset, it is found that the occurrence of elevated concentration of methane (>1 mg/L) was identified in groundwater samples where nitrate, iron, manganese and sulfate were either not present or only in small amount. The 90th and 95th percentile methods have been used to define redox sensitive species thresholds (Table 5.1).

Table 5.1: Percentile methods to define different thresholds regarding occurrence of redox sensitive species.

		Threshold expressed in mg/L			
		NO_3	Mn	Fe	SO_4
99th percentile	Threshold	3.1	0.01	0.34	32.8
	Proportion CH_4> 1mg/L below the threshold	80%	14%	91%	49%
95th percentile	Threshold	2.5	0.02	0.66	158.1
	Proportion CH_4> 1mg/L below the threshold	77%	60%	94%	83%
90th percentile	Threshold	2.6	0.03	0.82	119.2
	Proportion CH_4> 1mg/L below the threshold	71%	71%	94%	77%

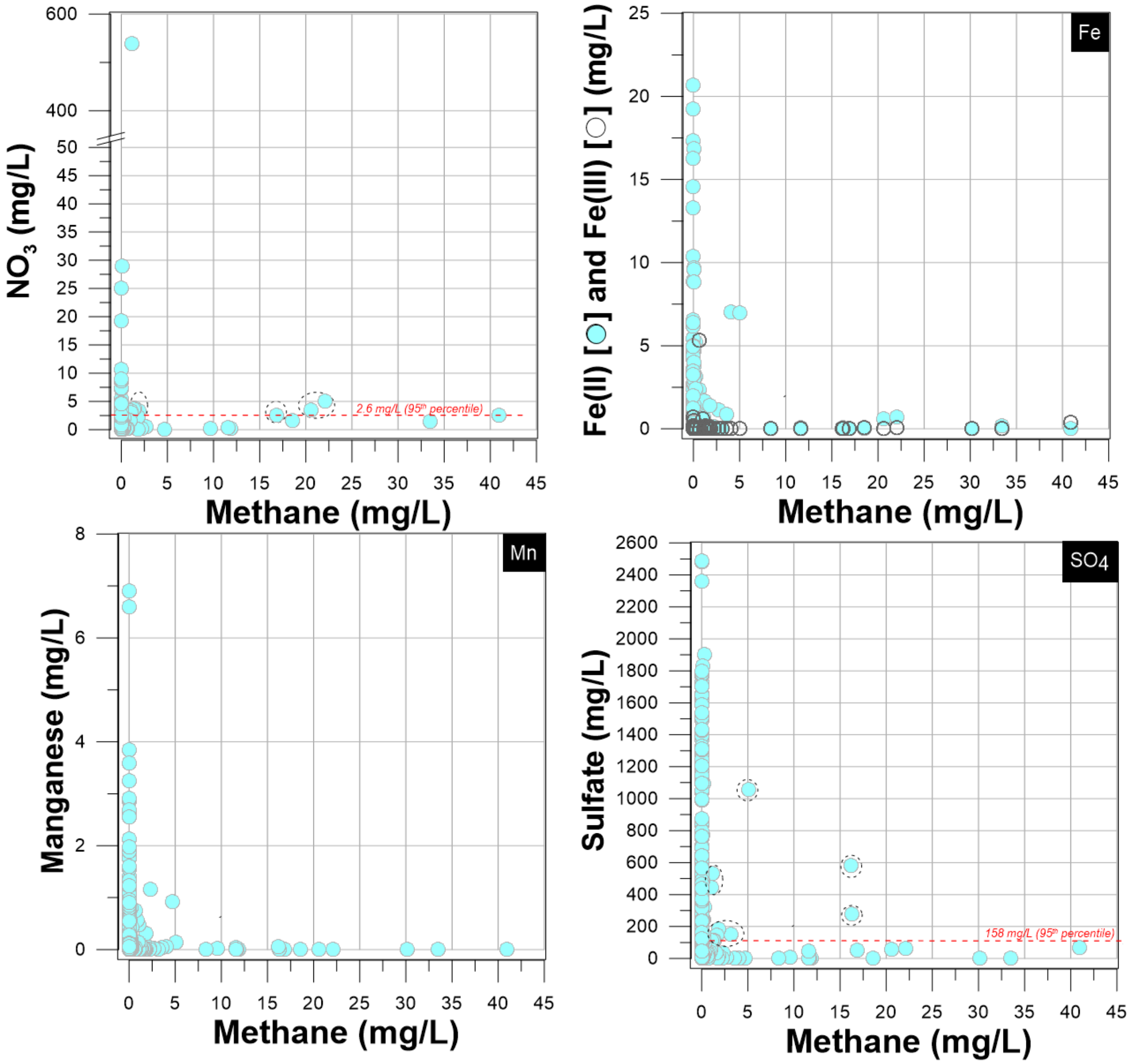

Figure 5.3: Distribution of redox sensitive species versus methane across the different datasets

Based on Fig. 5.3 the following observations have been made:

- A total of 71% and 77% of groundwater samples with methane > 1 mg/L are found when $NO_3 < 2.6$ mg/L and <2.5 mg/L (90th and 95th percentile);
- 71% and 60% of groundwater samples with methane > 1 mg/L are found when Mn < 0.03 and 0.02 mg/L respectively (90th and 95th percentile);
- 94% of groundwater samples with methane > 1 mg/L are found when Fe < 0.82 mg/L and Fe < 0.66 mg/L respectively (90th and 95th percentile);
- A total of 77% and 83% of the groundwater samples with methane > 1 mg/L when $SO_4 <$ 119 mg/L and <158 mg/L (90th and 95th percentile).

The next section characterizes the redox state of the different groundwater samples.

5.2 Redox state/sequencing of the different groundwater systems

The redox conditions of groundwater strongly affect the mobility and persistence of many contaminants. Knowing the redox conditions is important factor to determine the vulnerability of groundwater to contamination. As groundwater migrates from recharge zones to areas of discharge, different stages in the redox sequence may be recognized. Groundwater systems are often characterized by redox reactions and the availability of redox sensitive species such as O_2, NO_3, Mn^2+, Fe^{2+}, SO_4^{2-} and CH_4. Redox processes change the geochemical conditions of a hydrochemical system and may lead to secondary reactions. Oxidation and reduction processes can occur along the groundwater flow pathway. The redox reactions generally proceed from the highest energy yield (consumption of dissolved oxygen) downwards to the zone of methanogenesis. The resulting redox zone is characterized by either the presence or absence of the redox sensitive species.

5.2.1 Redox classification model

To enable the identification of the dominant redox processes in an aquifer, the classification table developed for the PTAC-AB project, has been applied for this datasets project and is shown in Table 5.2. The groundwater samples from this study were classified into redox categories depending on the concentration of terminal electron acceptors (TEAPs) such as O_2, NO_3, Mn, Fe and SO_4 participating in redox reactions. The redox zoning thresholds obtained previously by the 95th percentile method, have been incorporated into the classification approach. This redox category classification has multiple objectives: (1) identify the dominant and ongoing redox processes such as nitrate reduction, manganese and/or iron reduction, sulfate reduction and methanogenesis; (2) assign a redox state to the groundwater samples based on water-quality parameters that are commonly measured such as NO_3, Mn, Fe and SO_4; (3) evaluate proportions of redox states in the aquifers of Alberta using the redox classes assignments and statistics tools; (4) focus on the identification of methanic redox zones.

Table 5.2 shows the different redox classifications used for the investigated groundwater samples. Using this approach, redox states such as oxic, anoxic or mixed redox conditions were identified, and the predominant redox processes were identified based on the dissolved redox sensitive species concentrations. The redox categories are described as follows:

Nitrate-reduction zone containing nitrate concentrations above the threshold of 2 mg/L and with manganese and iron concentration below their respective thresholds; sulfate concentrations can be below (named NO3red) or above its concentration threshold (named NO3red-SO4red).

Manganese(IV)-reduction zone containing manganese concentrations above its threshold, while nitrate and iron concentrations are below their respective thresholds and sulfate concentrations can be below (named Mn(IV)red) or above its concentration threshold (named Mn(IV)red-SO4red). In the scenario where manganese is the only dissolved constituent above its respective thresholds (named Mn(IV)red), the manganese(IV)reduction zone may contain methane explaining the abbreviation Mn(IV)red or CH4fm.

Iron(III)-reduction zone containing iron concentration above its threshold while nitrate concentrations are below its threshold, manganese and sulfate concentrations can be below or above their concentration thresholds. Three combinations can be possible; (1) iron and sulfate concentrations are above their concentrations threshold (named Fe(III)red-SO4red), (2) iron, sulfate and manganese concentrations are above their concentrations threshold (named Mn(IV)red-Fe(III)red-SO4red), (3) iron and manganese concentrations are above their threshold concentrations (Mn(IV)red-Fe(III)red). In the scenario where iron is the only dissolved constituent above its respective thresholds (named Fe(III)red), the iron(III)reduction zone may contain methane explaining the abbreviation Fe(III)red or CH4fm.

Bacterial sulfate reduction zone: containing sulfate concentration above its threshold while nitrate, manganese, and iron concentrations are below their respective thresholds (named SO4red). In addition to sulfate concentration above its threshold and similarly to iron(III), Mn(IV) reduction zones, the presence of iron and/or manganese as reduced form is not incompatible with the sulfate reduction zone (combinations named Fe(III)red-SO4red, Mn(IV)red-SO4red, Mn(IV)red-Fe(III)red-SO4red).

Methanogenesis or methanic zone constrained by concentration of nitrate and sulfate below their respective thresholds. The presence of iron and manganese concentration above their respective thresholds is possible within a methanic zone because the Fe- Mn- reduction could entail elevated Fe(II), Mn(IV) concentrations as mentioned previously and in these cases the redox category are named Mn(IV)red or CH4fm, Fe(III)red or CH4fm, Mn(IV)red-Fe(III)red.

All the other scenarios that do not fit the previous redox zoning description are described as mixed process indicating redox heterogeneity in the studied system.

In order to test the redox category classification, the datasets reported methane analyses have been used e.g. sources A, C, D from the industrial sources and SFU, GOWN-AB from the additional datasets.

Table 5.2: Redox category classifications for groundwater from aquifers in Alberta.

Criteria used for assigning redox categories to groundwater from Alberta and British Columbia: identifying dominant ongoing redox process(es)				**Nitrate**	**Manganese**	**Iron**	**Sulfate**
			Threshold [mgl/L]	**2.6**	0.02	0.66	158
General	**Redox processes favorable #1**	**Redox processes favorable #2**	**Abbreviation**				
Anoxic	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	Mn(IV)-reducing/SO_4reducing (mixed process)	Mn(IV)red or Mn(IV)red-SO4red	<	≥	<	≥
Anoxic	Mn(IV)-reducing	Methanogenesis	Mn(IV)red or CH4fm	<	≥	<	<
Anoxic	Fe(III)-reducing SO_4-reducing	Fe(III)reducing/ SO4reducing (mixed process)	Fe(III)red or Fe(III)red-SO4red	<	<	≥	≥
Anoxic	Fe(III)-reducing SO_4-reducing	Fe(III)-Mn(IV)reducing/ SO4reducing (mixed process)	Mn(IV)red-Fe(III)red-SO_4red	<	≥	≥	≥
Anoxic	SO_4-reducing		SO_4red	<	<	<	≥
Anoxic	Fe(III)-reducing	Methanogenesis (mixed process)	Fe(III)red or CH4fm	<	<	≥	<
Anoxic	Methanogenesis		CH_4fm	<	<	<	<
Anoxic	Methanogenesis	Fe(III)-Mn(IV)reducing	Mn(IV)red-Fe(III)red	<	≥	≥	<
Mixed-Anoxic (Heterogeneity)	Mixed process		NO_3red-Mn(IV)red	≥	≥	<	<
Mixed-Anoxic (Heterogeneity)	Mixed process		NO_3red-Mn(IV)red-SO_4red	≥	≥	<	≥
Mixed-Anoxic (Heterogeneity)	Mixed process		NO_3red-Fe(III)red	≥	<	≥	<
Mixed-Anoxic (Heterogeneity)	Mixed process		NO_3red-Fe(III)red-SO_4red	≥	<	≥	≥
Mixed-Anoxic (Heterogeneity)	Mixed process		NO_3red-Mn(IV)red-Fe(III)red	≥	≥	≥	<

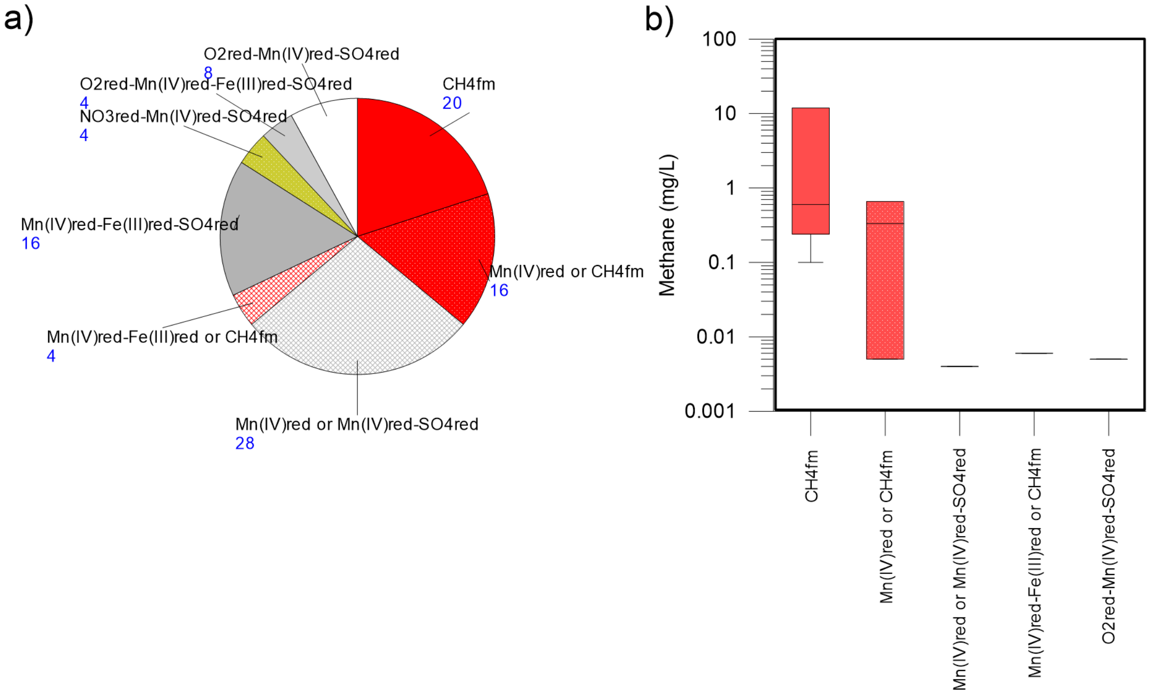

Figure 5.4: a) Redox category assignments for industrial samples, name of redox category and percentage (blue number) are listed; b) occurrence of methane in the different redox categories.

5.2.2 Industrial datasets: Redox Assignments

The results are shown in Fig. 5.4a. Over 20% of the samples (n=5) belong to the methanic zone where NO_3, Mn, Fe and SO_4 are below their respective threshold concentrations (*abbr.* CH4fm). A total of 20% (n=5) of the samples belong to the redox zone where Fe(II) and Mn(IV) are present indicating the occurrence of Fe(III)-reduction Mn(IV)-reduction and/or a mixed redox zone where methanogenesis occurs as well as Fe-reduction (*abbr.* Mn(IV)red and Mn(IV)red-Fe(III)red or CH_4fm). A total of 44% (n=11) of the samples belong to the mixed redox zone where Mn(IV) and Fe(II) and SO_4 are present indicating the occurrence of Fe(III)-reduction Mn(IV)-reduction and SO_4-reduction (*abbr.* Mn(IV)red or Mn(IV)red-SO4red and Mn(IV)red-Fe(III)red-SO_4red).The remaining samples belong to mixed and oxic redox zones indicating O_2 consumption, NO_3-reduction, Mn(IV)reduction, Fe(III) reduction and SO_4reduction (*abbr.* NO_3red-Mn(IV)red-SO_4red, O_2red-Mn(IV)red-SO_4red and O_2red-Mn(IV)red-Fe(III)red-SO_4red) processes occur (Fig. 5.4a). Fig. 5.4b presents the distribution of methane throughout the different redox categories. The most elevated methane concentrations belong to the CH_4fm zones.

5.2.3 Additional datasets Redox Assignments: example of the SFU dataset

The results are shown in Fig. 5.5a and Table 5.3. Based on the redox classification, different main redox zones have been identified:

- Oxic-Anoxic mixed redox zones

Over 38% samples belong to mixed and oxic redox zones indicating O_2 consumption, NO_3-reduction, Mn(IV)-reduction, Fe(III)-reduction and/or SO4-reduction (*abbr.* NO_3red-Mn(IV)red-SO_4red, O2red-Mn(IV)red-SO_4red and O_2red-Mn(IV)red-Fe(III)red-SO_4red etc.) processes occur.

- Sulfate zones

Over 6% (n=22) belong to the sulfate zone where SO_4 is present indicating the occurrence of SO4 reduction (*abbr.* SO_4red*)*

- Anoxic mixed redox zones

Over 20% samples belong to mixed redox zones indicating Mn(IV) reduction, Fe(III)-reduction and/or SO_4reduction (*abbr.* Mn(IV)red-SO_4red, Mn(IV)red-SO_4red and Mn(IV)red-Fe(III)red-SO_4red etc.) processes occur.

- Methane zones

Over 9% of the samples (n=33) belong to the methanic zone where NO_3, Mn, Fe and SO_4 are below their respective threshold concentrations (*abbr.* CH4fm).

A total of 14% (n=52) of the samples belong to the redox zone where Fe(II) and Mn(IV) are present indicating the occurrence of Fe(III)-reduction Mn(IV)-reduction and/or a mixed redox zone where methanogenesis occur as well as Fe(III)-reduction and Mn(IV)-reduction (*abbr.* Mn(IV)red-Fe(III)red or CH_4fm). A total of 7% (n=26) of the samples belong to the redox zone where Mn(IV) is present indicating the occurrence of Mn(IV)-reduction and/or a mixed redox zone where methanogenesis occurs as well as Mn(IV)-reduction (*abbr.* Mn(IV)red or CH_4fm).

A total of 17 out of 29 (59%) samples containing elevated concentrations of methane (>1mg/L) were correctly associated with redox zones e.g. CH4fm. A total of 169 out of 235 (72%) samples containing low concentration of methane (<1 mg/L) were correctly classified e.g. more oxidizing redox conditions (Table 5.3).

- Redox state of groundwater versus hydrochemical facies

It seems that groundwater age is often related to redox conditions. It has been observed that the young, recently recharged groundwater is likely to be oxic, and older groundwater – groundwater that recharged thousands or even more years ago is more likely to be anoxic. Indeed, the most reducing conditions e.g. CH4fm are mainly associated with the hydrochemical Na-HCO_3-Cl facies (type I) for >60% of the cases. The oxic-anoxic mixed groundwaters are associated with Ca-Mg-HCO_3 (40%) and SO_4-rich groundwater hydrochemical facies (40%). This indicates that older groundwater is more likely to be anoxic than younger groundwater because there more time for chemical reactions that consume electron acceptor. However, redox conditions can vary a lot across different aquifers.

Table 5.3: Results for redox assignment for SFU datasets

	Redox assignment_SFU			**Methane_ descriptive statistics**					**Sensitivity and specificity**	
	n_tot	%	%cumul	n_CH_4	median	mean	n_CH4> 1 mg/L	n_CH_4<1 mg/L	% CH_4>1 mg/L	% CH_4<1 mg/L
Mn(IV)red-Fe(III)red or CH_4fm	52	14	14	36	0.01	0.38	4	32	14	14
Mn(IV)red-Fe(III)red-SO_4red	43	11	25	29	0.01	0.21	1	28	3	12
Mn(IV)red or Mn(IV)red-SO_4red	35	9	34	26	0.01	0.03	0	26	0	11
CH_4fm	33	9	42	26	0.42	6.91	11	15	38	6
O_2red-SO_4red	29	8	50	22	0.00	0.00	0	22	0	9
O_2red-Mn(IV)red-SO_4red	27	7	57	8	0.00	2.02	1	7	3	3
Mn(IV)red or CH_4fm	26	7	64	21	0.01	0.69	2	19	7	8
O_2red-Mn(IV)red-Fe(III)red-SO_4red	26	7	70	14	0.00	0.03	0	14	0	6
O_2red	22	6	76	17	0.00	0.01	0	17	0	7
SO_4red	22	6	82	16	0.01	1.03	1	15	3	6
O_2red-Mn(IV)red-Fe(III)red	14	4	85	8	0.03	0.15	1	7	3	3
O_2red-Mn(IV)red	13	3	89	8	0.00	0.03	0	8	0	3
O_2red-NO_3red	9	2	91	7	0.01	0.01	0	7	0	3
NO_3red	5	1	92	5	1.09	4.65	3	2	10	1
O_2red-NO_3red-SO_4red	5	1	94	5	0.00	0.01	0	5	0	2
NO_3red-Mn(IV)red-SO_4red	4	1	95	3	0.00	0.00	0	3	0	1
O_2red-NO_3red-Mn(IV)red-SO_4red	4	1	96	1	0.00	0.00	0	1	0	0
NO_3red-Mn(IV)red-Fe(III)red-SO_4red	3	1	97	2	1.14	1.14	2	0	7	0
Fe(III)red or Fe(III)red-SO_4red	2	1	97	2	0.02	0.02	0	2	0	1
NO_3red or NO_3red-SO_4red	2	1	98	2	0.95	0.95	1	1	3	0
NO_3red-Mn(IV)red	2	1	98	2	0.67	0.67	1	1	3	0
O_2red-NO_3red-Mn(IV)red-Fe(III)red-SO_4red	2	1	99	1	0.00	0.00	0	1	0	0
Fe(III)red or CH_4fm	1	0	99	1	0.31		0	1	0	0
NO_3red-Fe(III)red	1	0	99	1	22.09		1	0	3	0
NO_3red-Mn(IV)red-Fe(III)red	1	0	99	1	0.01		0	1	0	0
O_2red-Fe(III)red	1	0	100					0	0	0
O_2red-NO_3red-Mn(IV)red-Fe(III)red	1	0	100					0	0	0
Total	385			264			29	235	**59%**	**28%**
									41%	**72%**

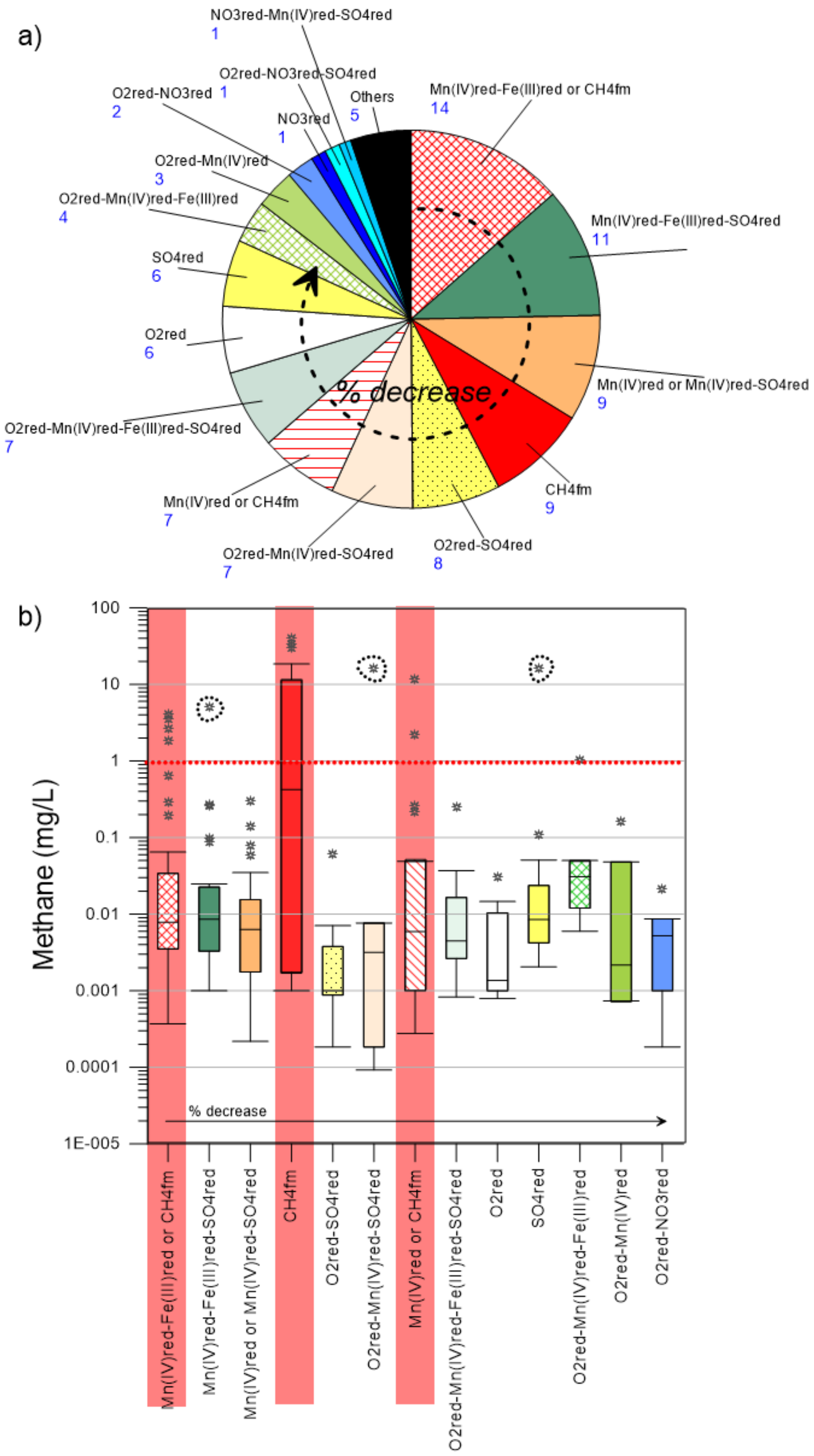

Figure 5.5: a) Redox category assignments for SFU samples, name of redox category and percentage (blue number) are listed; b) occurrence of methane in the different redox categories.

5.3 Isotopic characteristics of methane in groundwater samples

5.3.1 Stable isotopes of methane

The SFU and GOWN datasets have been reporting stable isotopes of methane. A total of 157 isotopic fingerprints has been compiled. Samples from SFU had $\delta^{13}C_{CH4}$ of –146.7 to –17.6‰ (n=144). The median and mean of $\delta^{13}C_{CH4}$ values are –65.6 and –63.8‰ respectively (n=144). The 25th and 75th percentile values (e.g. 25% and 75% of the data are below these values) are –77.6‰ and –48.8‰ respectively. Only 12 samples are associated with $\delta^{2}H_{CH4}$ values. The mean and median values are –250.8‰ and –306.8‰ respectively.

For comparison, the samples from GOWN had $\delta^{13}C_{CH4}$ of –99.5 to –54.7‰ (n=13). The median and mean of $\delta^{13}C_{CH4}$ values are –69.2 and –72.3‰ respectively (n=13). The 25th and 75th percentile values (e.g. 25% and 75% of the data are below these values) are –81.6‰ and –55.9‰ respectively. Only 4 samples are associated with $\delta^{2}H_{CH4}$ values. The mean and median values are –343.4‰ and –334.1‰ respectively.

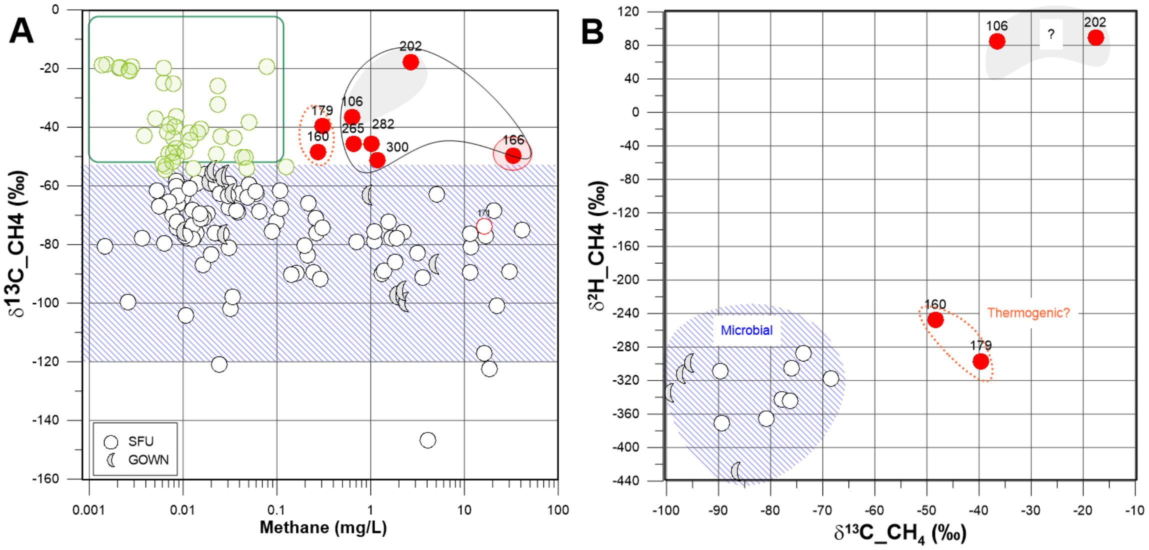

Figure 5.6: Diagrams for classification of microbial and thermogenic gas based on $\delta^{13}C_{CH4}$, δD_{CH4} and concentration of methane for SFU and GOWN datasets. Red symbols were used to identify the groundwater samples associated with elevated methane concentrations with $\delta^{13}C_{CH4}$>–55‰. The well ID # were reported to keep track of the subset of samples. The green symbol identify the groundwater samples associated with low concentrations of methane associated with $\delta^{13}C_{CH4}$>–55‰.

5.4 Sources and sinks of methane in groundwater

Hydrocarbon molecular and isotopic compositions have been used in several studies to determine sources of methane in groundwater (Whiticar, 1999). Microbial methane is isotopically lighter than thermogenic methane because microbes preferentially utilize lighter isotopes. The isotopic signature of methane is also related to thermal maturity. In general, $\delta^{13}C_{CH4}$ > –50 to –45‰ is characteristic of thermogenic methane and $\delta^{13}C_{CH4}$ < –60 to –55‰ would be diagnostic as microbial methane (Whiticar, 1999). Different processes such as mixing or methane oxidation can affect the original isotopic signatures of methane and can mislead the interpretation of methane origin.

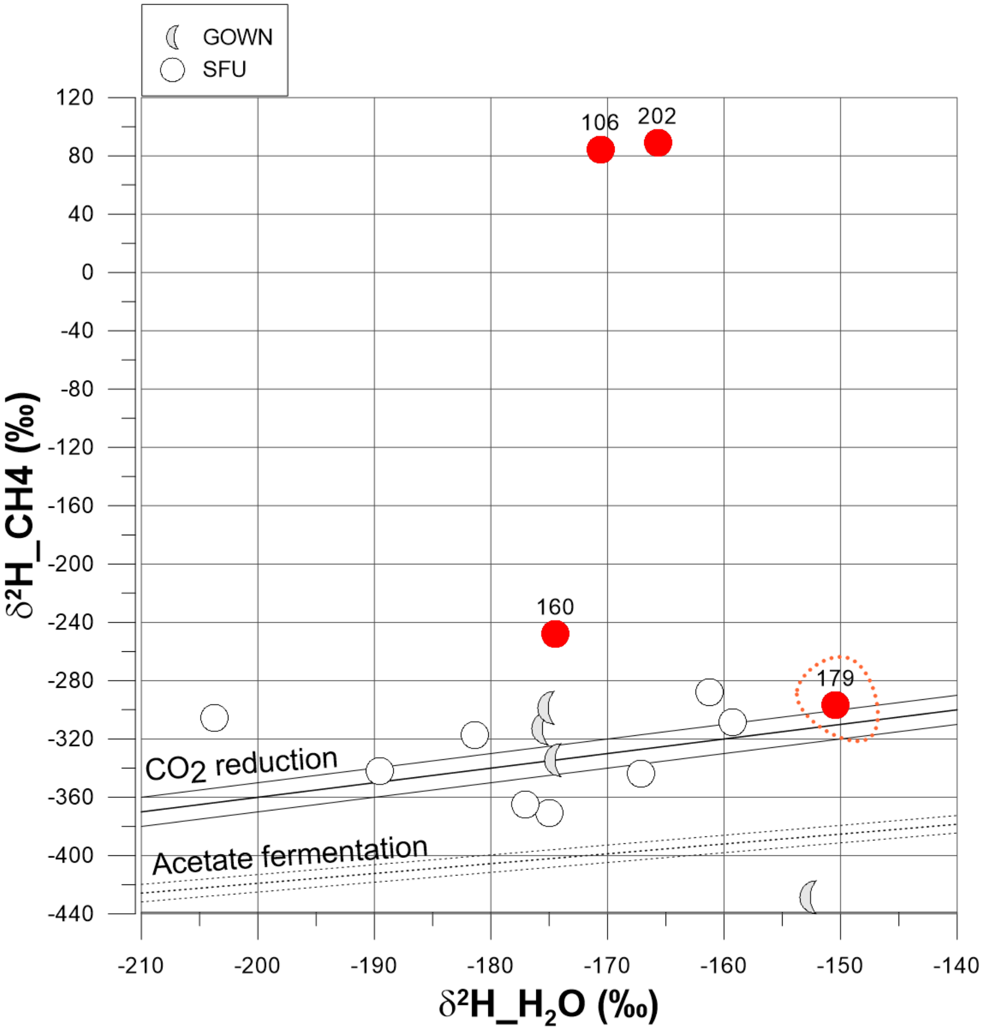

Figure 5.7: Relation between the stable hydrogen isotopic signature of water and methane for samples from groundwater wells (SFU and GOWN datasets). CO_2 reduction: $\delta D_{CH4} = \delta D_{H2O} -160(\pm10)$ from Schoell (1980) and acetate fermentation $\delta D_{CH4} = 0.675*\delta D_{H2O} -284(\pm6)$ from Waldron et al. (1999). Red symbols were used to identify the groundwater samples associated with elevated methane concentrations with $\delta^{13}C_{CH4} > –55‰$. The well ID # were reported to keep track of the subset of samples.

5.4.1 Isotopic characteristics of microbial methane

Microbial methane forms during the final stages of decomposition of organic matter in anaerobic environments. It has been observed in the previous section that the conditions favorable for microbial methanogenesis include lack of electron acceptors such as O_2, NO_3, and SO_4 and the presence of microbial communities capable of breaking down complex organic matter into compounds methanogens can use. A total of 96/157 samples or 61.2% and 106/157 or 67.5% from both SFU and GOWN have $\delta^{13}C_{CH4} < –60$ to –55‰ respectively, associated with a wide range of methane concentration (Fig. 5.6a) and a total of 12/16 samples seems to plot in the fields from microbial methane (Fig. 5.6b). The isotopic composition of methane is related to $\delta^{13}C$ of the organic precursor, δ^2H of coexisting water and the predominant microbial process that created methane. There are two primary pathways of microbial methanogenesis – acetate fermentation and CO_2 reduction.

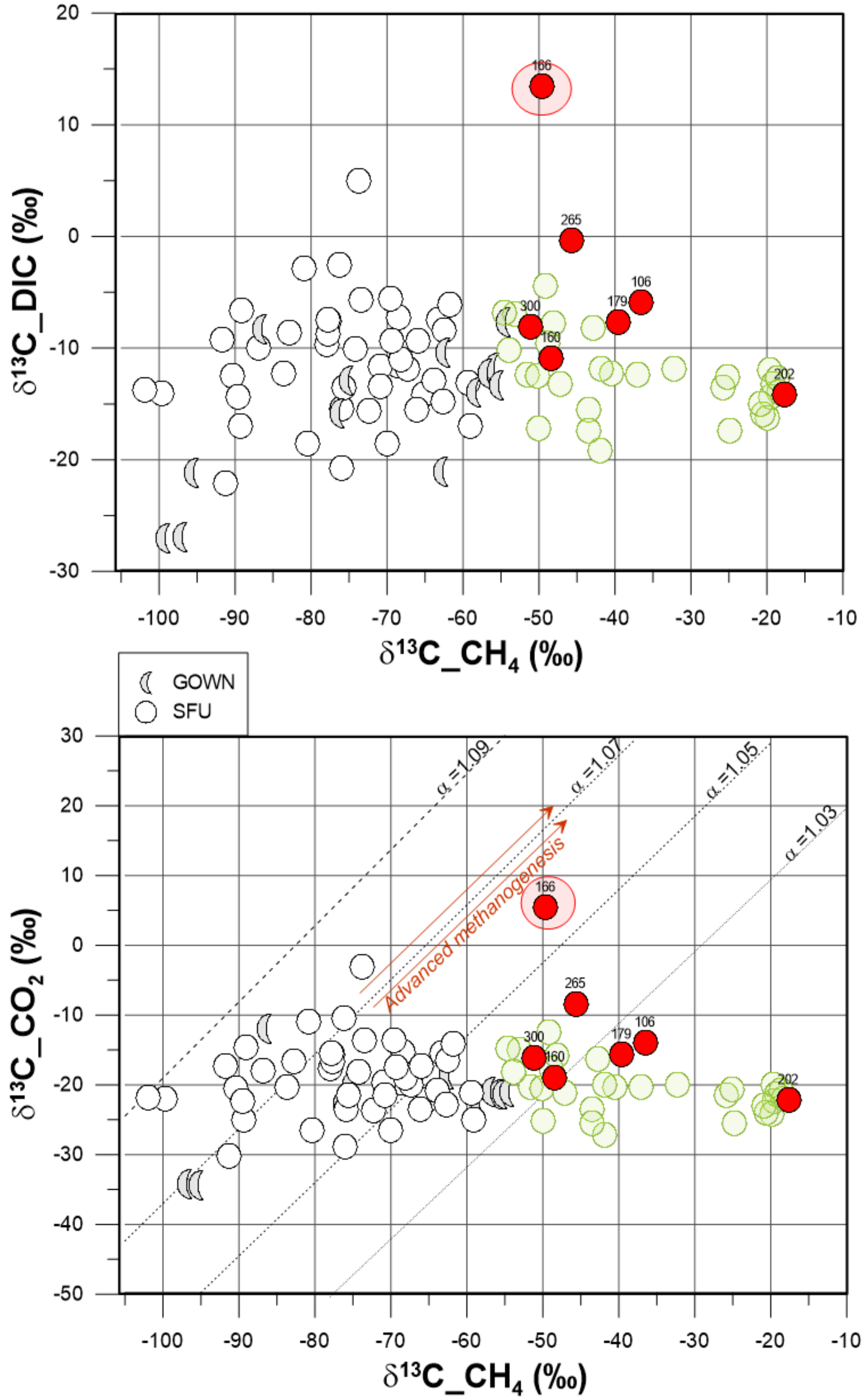

Figure 5.8: Stable carbon isotopic signature of methane in relation to DIC. Fractionation factor between CO_2 and CH_4 ($\alpha^{13}C_{CO2\text{-}CH4}$). Red symbols were used to identify the groundwater samples associated with elevated methane concentrations with $\delta^{13}C_{CH4}$>–55‰. The well ID # were reported to keep track of the subset of samples. The green symbol identify the groundwater samples associated with low concentrations of methane associated with $\delta^{13}C_{CH4}$>–55‰.

For the CO_2 reduction pathway, all the H in CH_4 is derived from coexisting water, while during acetate fermentation hydrogen is derived from water and acetate. In Fig. 5.7 δD_{CH4} and δD_{H2O} are shown in relation to trends for acetate fermentation and CO_2 reduction. Most of the samples plot near the trend for CO_2 reduction which indicates that CO_2 reduction is the main methanogenesis pathway. The wide range in $\delta^{13}C$ values observed in the different methane samples can be related to a combination of isotopic effects occurring during methanogenesis. Whiticar (1999) have reported that ^{13}C fractionation factors of 1.049-1.095 were consistent with CO_2 reduction and values of 1.039-1.058 were consistent with acetate fermentation. The samples compiled in the SFU dataset were analyzed for $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CO2}$ was estimated based on the equilibrium isotopic fractionation between CO_2 and HCO_3^-. The $\delta^{13}C_{DIC}$ values vary from < –25 ‰ to > +10‰ as a consequence $\delta^{13}C_{CO2}$ values vary from < –30 ‰ to > +5‰. A majority of the samples have $\alpha < 1.05$ that could be consistent with CO_2 reduction (Fig. 5.8). Most of the groundwater samples $\delta^{13}C_{DIC}$ values are between –10‰ and –20‰. The $\delta^{13}C_{DIC}$ of groundwater reflect the relative contribution between two sources of DIC (1) microbial degradation of soil or aquifer-derived organic carbon and (2) dissolution of carbonate minerals. Only one sample has $\delta^{13}C_{DIC}$ > +10‰ and is highlighted in red.

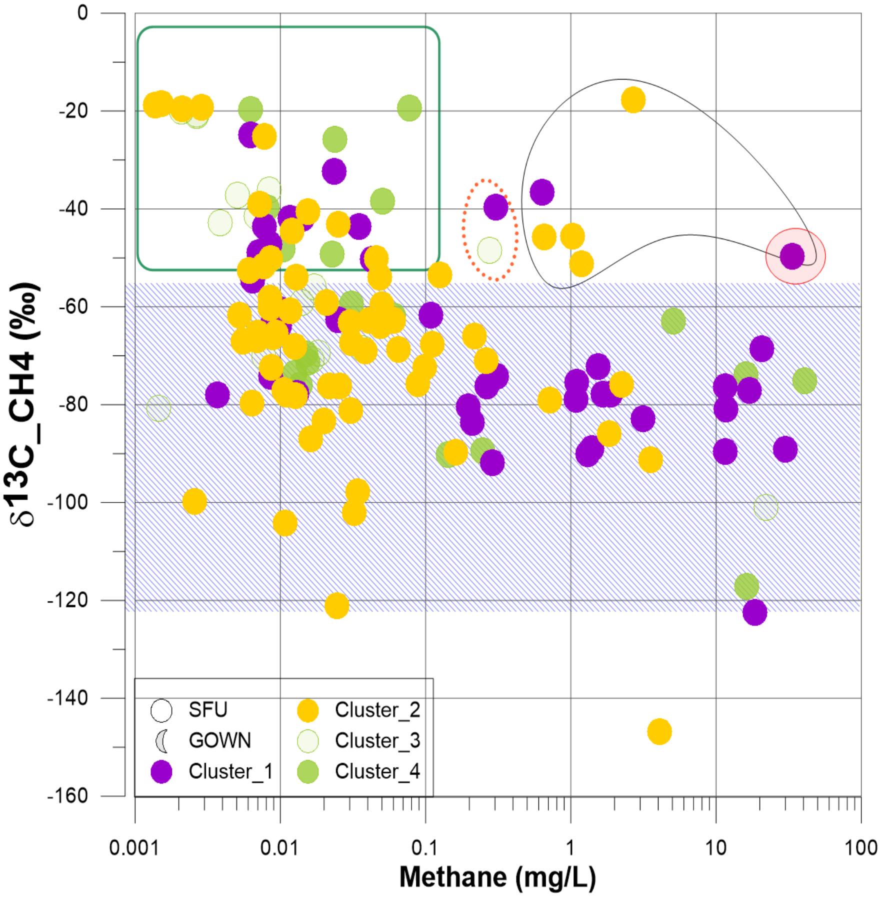

Figure 5.9: Stable carbon isotopic signature of methane versus methane concentration in relation to the different clusters identified in the previous section.

In a closed system, advanced methanogenesis through CO_2 reduction results in a progressive isotopic enrichment of the precursor (CO_2) and product (CH_4). In combination with a CH_4 concentration > 10 mg/L and $\delta^{13}C_{CH4} > -50$ ‰ and $\delta^{13}C_{DIC} > +10$‰, the sample #166 associated with Na-HCO_3 hydrochemical facies (Cluster 1, in Fig.5.9), is indicative of advanced methanogenesis and could have been misinterpreted as thermogenesis if only interpreting its $\delta^{13}C_{CH4}$.

5.4.2 Isotopic characteristics of thermogenic or pseudo-thermogenic methane?

Hypothesis of methane oxidation coupled with sulfate reduction

The isotopic composition of methane and sulfate in groundwater provides evidence for biogeochemical processes involving methane and sulfate. When methane is available as the electron donor, microorganisms can oxidize it and in some cases sulfate can be reduced by coupling with oxidation of methane, as shown in Eq. 1:

$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$ (Equation 1)

Table 5.4: Distribution of C- isotope ratios of methane and classification among methane potential sources.

		Criteria 1		**Criteria 2**		
	Microbial	**Thermogenic**	**Pseudo-thermogenic**	**Thermogenic**	**Pseudo-thermogenic**	Total
Domain	$\delta^{13}C_{CH4} < -60$ to –55‰	$CH_4 > 0.1$ mg/L; $\delta^{13}C_{CH4} > -55$‰	$CH_4 < 0.1$ mg/L; $\delta^{13}C_{CH4} > -55$‰	$CH_4 > 1$ mg/L; $\delta^{13}C_{CH4} > -55$‰	$CH_4 > 1$ mg/L; $\delta^{13}C_{CH4} > -55$‰	
n	106	9	42	4	47	157
%	68	6	27	3	30	
Mean	–76.5	–43.1	–38.7	–41.0	–39.3	
SD	15.6	10.9	12.5	15.7	12.2	
Median	–75.2	–45.7	–41.9	–47.6	–41.9	

A trend toward enriched (more positive values) isotopic values is observed in Fig. 5.6a associated with low methane concentration. A cluster of 42 out of 157 samples (green colored symbol, Figs. 5.7 and 5.8) are associated with methane concentration < 0.1 mg/L and $\delta^{13}C_{CH4} > -55$ ‰ and could be associated with methane oxidation process. Depending on the extent of reaction, methane oxidation generates ^{13}C-depleted DIC leaving ^{13}C-enriched residual methane. In addition, a ^{13}C fractionation factors range of 1.0005-1.03 is found in Fig. 4.8 that is indicative of methane oxidation or thermogenic methane (Whiticar, 1999). Those samples belong mainly to Cluster 2,3 and 4 that are indicating of fresh recharged groundwater and mixed groundwater SO_4-rich that are not experiencing conditions conducive to methanogenesis (Fig. 5.9). The hypothesis of migrating methane toward more oxidizing conditions and successively being oxidized is formulated for those samples. Such advanced processes leave ^{13}C enriched residual methane that could be misinterpreted as “thermogenic methane”. These samples with evidence of methane oxidation have been identified as “pseudo-thermogenic” methane signature (Table 5.4.). It is not excluded that methane oxidation process has happened in the blue zone area defined as microbial where the extent of methane oxidation could be not as advanced and /or the initial source being highly ^{13}C-depleted, potentially increasing the current proportion of identified pseudo-thermogenic methane (Table 5.4). **Methane oxidation process plays an important role in the**

groundwater systems. It is not excluded that methane oxidation during the sampling/storage could have occurred.

The isotopic composition of sulfate is provided in the SFU and GOWN-AB datasets. The $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ vary from –17.4‰ to +24.4‰, and, –19.4‰ to +27.0‰ respectively. Sulfate may originate from oxidation of reduced sulfur compounds (Fig. 5.10). A trend toward enriched (more positive values) isotopic values is observed in Fig. 5.11 associated with low sulfate concentrations and high methane concentration. During bacterial sulfate reduction, a decrease of dissolved sulfate concentration coupled with isotopic enrichment of both ^{34}S and ^{18}O in the dissolved sulfate is expected because sulfate-reducing bacteria discriminate against the heavy isotope.

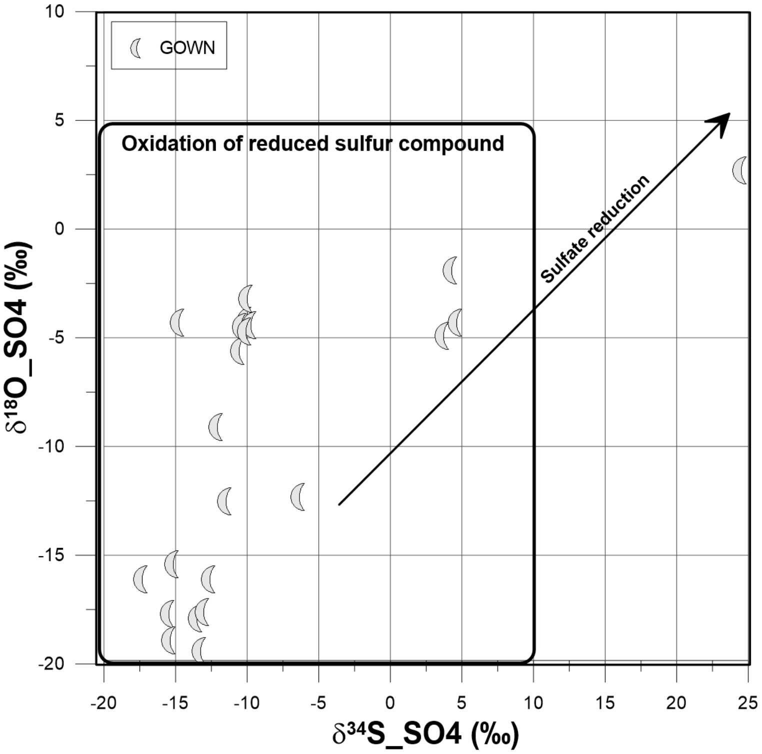

Figure 5.10: $\delta^{34}S$ versus $\delta^{18}O$ of dissolved SO_4 in groundwater from GOWN dataset against the typical sources and trends of biogeochemical processes.

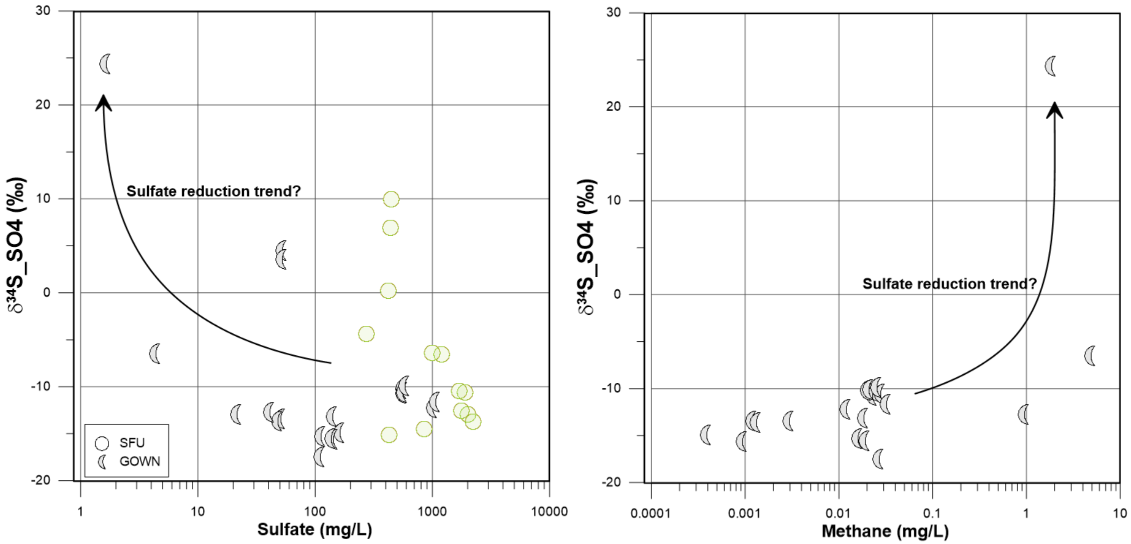

Figure 5.11: $\delta^{34}S$ versus dissolved (left) SO_4 concentration (right) CH_4 concentrations in groundwater from GOWN and SFU datasets. The green symbol identify the groundwater samples associated with low concentrations of methane associated with $\delta^{13}C_{CH4}$>–55‰.

Thermogenic mixed gas origin?

Thermogenic gas is usually isotopically heavier than microbial methane. While groundwater samples with low methane concentrations < 0.1 mg/L and $\delta^{13}C_{CH4}$ > –55 ‰ have been identified as pseudo-thermogenic as a consequence of methane oxidation processes, another cluster of samples seem to indicate an apparent thermogenic component methane signature with both elevated methane concentration and $\delta^{13}C_{CH4}$ > –55 ‰ (Fig. 5.6A, red color symbol). A total of 9 samples have $\delta^{13}C_{CH4}$ > –55 ‰ with CH_4 concentration > 0.1 mg/L (=9/157 or 6%) with a mean of –43.1±10.9 ‰ (Table 5.4, Figs. 5.6). A total of 4 samples have $\delta^{13}C_{CH4}$ > –55 ‰ with CH_4 concentration > 1 mg/L (4/157 or 3 %) with a mean of –41.0±15.7 ‰ (Table 5.4, Figs. 4.6). Compiling $\delta^{13}C$ and $\delta^{2}H$ of methane, some of the samples plot in the thermogenic field (#179 and #160) while other samples such as #106 and #202 present very positive $\delta^{2}H\_CH_4$ values up to +80‰. No relation between $\delta^{2}H_{CH4}$ and $\delta^{2}H_{H2O}$ is found for those samples (Fig. 5.7) with the exception of #179. One sample #166 has been identified as microbial methane produced in-situ and in a closed system. Lack of additional data such as the occurrence of potential higher alkane would be needed to agree upon the potential apparent thermogenic versus pseudo-thermogenic methane signatures.

Microbial origin of methane seems to be the predominant source of methane in the groundwater samples from GOWN and SFU. A significant portion (>30%) of groundwater samples seems to show that additional processes, such as methane oxidation process most probably coupled with sulfate reduction, have altered the concentration and isotopic composition of methane. Such alteration process would indicate an allochthonous source of methane, that migrated under most oxidizing conditions. It would be of value to perform further analyses such as identifying if microbial communities e.g. presence of methanogens,

methanotrophs could be identified to support the biogeochemical processes highlighted in this section.

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