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EXECUTIVE SUMMARY

Chemical characterization of hydraulic fracturing (HF) flowback and produced water (FPW) is important to the environmental sustainability of HF operations. In this work, we analysed and compared HF FPW samples from different well locations as well as FPW samples from a single well over time. The results provide vital information to assess the reusability of flowback water and guide treatment options. Additionally, this work has the potential to provide guidance on best practices for HF fluid additives for future reuse as well as provide a more complete understanding of FPW chemical makeup to guide treatment options. While reuse of FPW is desirable, it is not feasible in many operations. In these scenarios, transportation for offsite treatment or disposal increases the risk of an environmental spill of FPW. This work will provide data to aid clean-up efforts and determination of the environmental fate of FPW contaminants. Overall, this work will provide economic benefits to the oil and gas sector by increasing FPW reuse which decreases wastewater disposal costs and reduces environmental impacts of HF operations by decreasing the volume of used surface water and risk of FPW environmental spills.

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1.0 INTRODUCTION

Environmentally sustainable hydraulic fracturing (HF) is critical to the future of Canada's oil and gas sector. The combination of horizontal drilling and hydraulic fracturing is now widely used for the development of oil and gas reserves from low permeability rock (Kerr, 2010). Additionally, conventional wells that have run dry can be revived by horizontal drilling and HF to improve formation permeability and to access previously unreachable oil reserves. HF uses surface water mixed with proppants and HF fluid additives (0.5–3%) (Elsner and Hoelzer, 2016) followed by injection into a geological formation under high pressure. This process increases the size of natural fractures and generates new fractures in the formation, improving permeability of the formation and resulting in a higher flow of oil and gas. After HF is completed, the injected HF fluid and natural formation water flow to the surface. This water is known as hydraulic fracturing flowback and produced water (HF-FPW).

HF-FPW consists of a combination of the HF fluid and the formation water, which originates from the targeted formation. The HF fluid contains a complex mixture of chemical and physical additives while the formation water is highly saline and contains many dissolved minerals and trace metals that naturally occur in the formation (Luek and Gonsior, 2017). Due to the large number of unknown chemical compounds and highly saline nature of HF-FPW, proper disposal is vital to prevent environmental contamination (Goss, 2015). The most common disposal method is offsite deep-well injection (Alessi, 2017). However, this adds significant cost to the HF process and increases the risk of HF-FPW spills during transport to injection sites. In 2015, 113 environmental spills of HF-FPW occurred in the Duvernay shale region alone (Goss, 2015; AER, 2016; Alessi, 2017). Clean up of HF-FPW spills is challenging due to the unknown chemical nature of FPW (Shrestha, 2017).

Alternatively, FPW can be reused in future HF operations; however, reuse of flowback water is challenging as the largely unknown chemical make-up of FPW is not amenable for direct use as HF fluid (Ma *et al*, 2014). Therefore, FPW must undergo treatment before it can be reused. Treatment of FPW represents a major obstacle since the variable chemical nature of FPW is determined by the HF fluid additives used and the formation water; and both are highly variable from well to well (Mohammad-Pajooh *et al*, 2018). HF fluid additives may include clay stabilizers, breakers, biocides, surfactants, corrosion inhibitors, and surfactants (Elsner and

Hoelzer, 2016). Information on chemical additives is available from the FracFocus database; however, proprietary additives are not disclosed and many additives are only listed by generic chemical names. The nature of formation water varies greatly depending several factors, including the geological formation it originates from, ionic strength of the water, temperature, and pH. Due to the combination of HF fluid additives and the highly saline nature of formation waters, FPW contains a complex mixture of salts, geogenic compounds, HF fluid additives, and possibly transformation products formed downhole (Estrada and Bhamidimarri, 2016; Kahrilas *et al*, 2016). All these components complicate treatment options.

Chemical characterization of FPW is crucial to the environmental sustainability of HF operations. In this work, we analysed and compared FPW samples from different well locations as well as FPW samples from a single well over time. This provided vital information to assess the reusability of flowback water and guide treatment options. Additionally, this work has the potential to provide guidance on best practices for HF fluid additives for future reuse. While the reuse of FPW is desirable, it is not feasible in many operations due to high salinity and unknown soluble organics. In these scenarios, transportation for offsite treatment or disposal increases the risk of an environmental spill of FPW. This work will provide data to aid clean-up efforts and determination of environmental fate of FPW contaminants. Overall, this work will provide economic benefits to the oil and gas sector by increasing FPW reuse which decreases wastewater disposal costs and reduces environmental impacts of HF operations by decreasing the volume of used surface water and risk of FPW environmental spills.

2.0 REGIONAL GEOLOGY

Water samples were obtained from wells that were hydraulically fractured in the Duvernay Formation (Figure 1) in the Fox Creek and Three Hills areas of the Western Canadian Sedimentary Basin. The Duvernay Formation was deposited during the Frasnian stage of the Devonian and is part of the Woodbend Group (Switzer *et al.* 1994). The Duvernay consists of dark brown bituminous shale and limestone. It is both a reservoir and source rock formation (AER, 2019). The formation was the source rock for conventional hydrocarbon accumulations in other formations. The formation has a low permeability and hydraulic fracturing was needed to access hydrocarbons in the Duvernay.

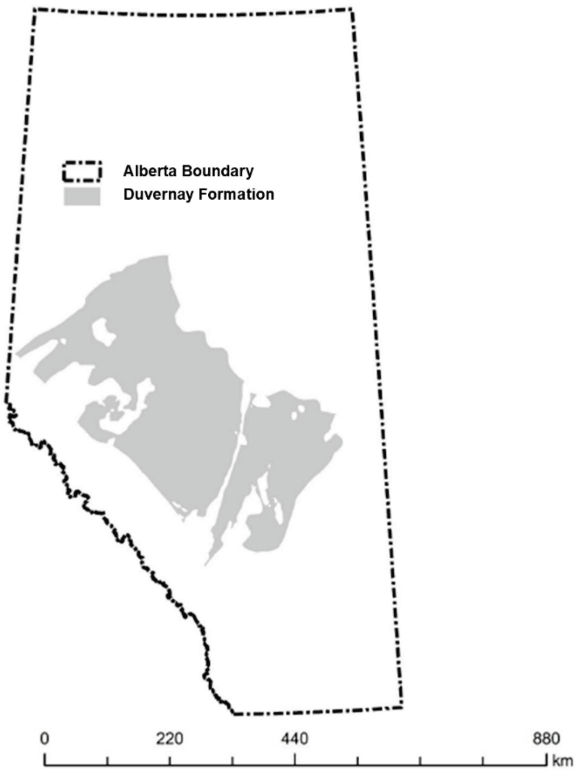


Figure 1 – Map of Duvernay formation in Alberta (adapted from AER, 2017)

3.0 METHODS

3.1. SAMPLING

Two series of FPW samples from the Duvernay Formation were collected for analysis. The first set of samples consisted of a series of single FPW samples collected from 17 different wells in the Fox Creek, Alberta area in November 2019. Each of these wells is completed in the Duvernay formation with borehole lengths (or measured depths from surface) ranging from 2800 to 6600 m. The second set of samples consisted of 24 FPW samples collected from December 2018 to November 2019 from a single well near Three Hills, Alberta. One sample was taken before shut-in and the remaining 23 samples were taken from 1 day to 7 months post shut-in flowback and production. This well was also completed in the Duvernay formation with a depth range of 2000 to 3900 m. All samples were collected from well heads and then transported to various collaborating laboratories before being received at CanmetENERGY Devon and stored at 4 °C. Figure 2 shows the well locations for both sets of samples.

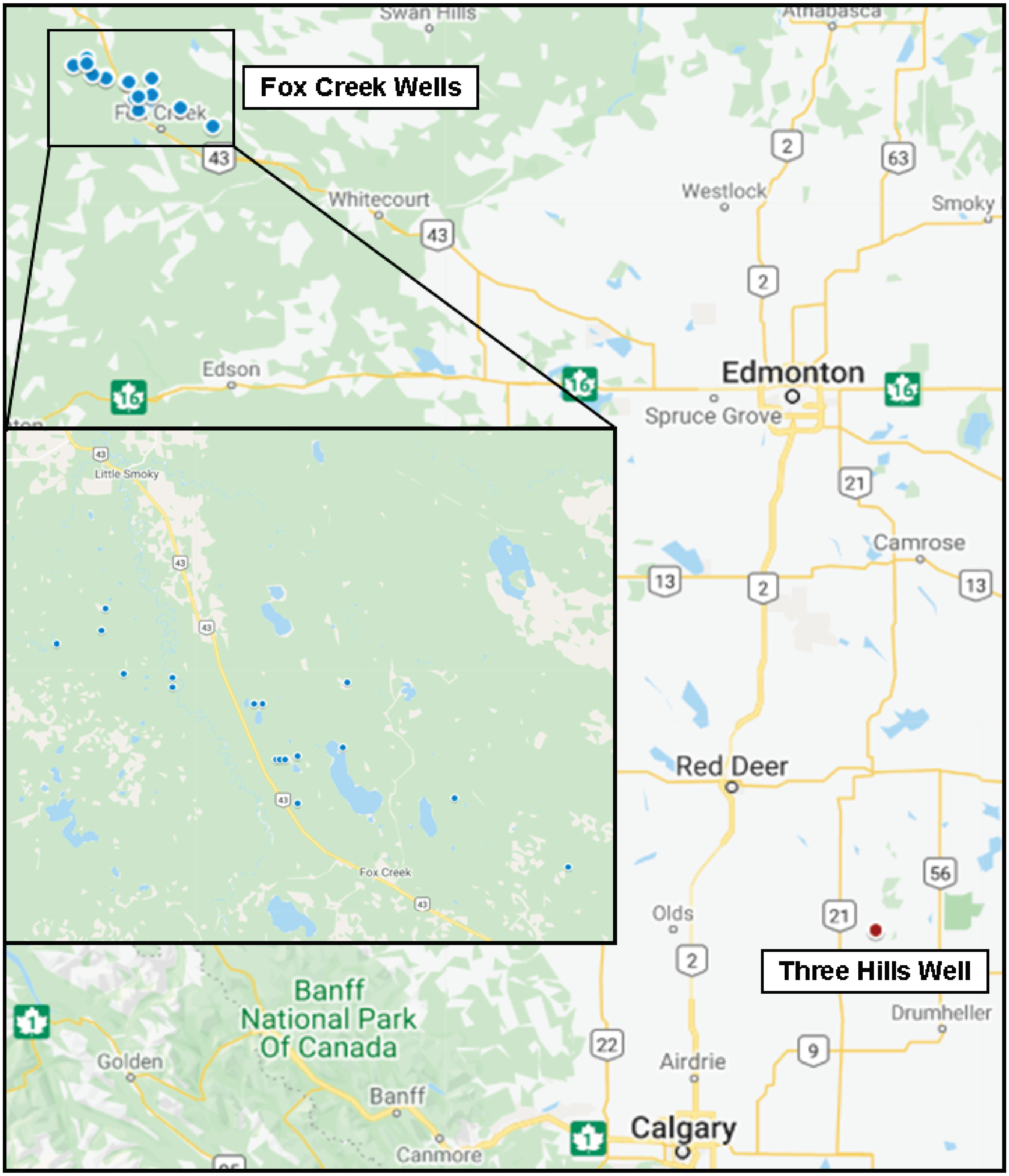


Figure 2 – Map of horizontal well locations (basemap from Google Maps)

3.2. SAMPLE PREPARATION AND ANALYSIS

A Varian Vista-Pro 725 radial simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES) equipped with a SPS3 auto-sampler was used to determine concentrations of dissolved calcium, sodium, potassium, magnesium, and sulfur. Working standards of each analyte were prepared using certified standard stock solutions.

Alkalinity, pH and electrical conductivity were measured with a Man-Tech Associates PC-Titrate instrument equipped with a Titrasip module, which was calibrated using an ERA Waters P272-506 standard.

Chloride and sulfate concentrations were measured with a Thermo-Fisher ICS 3000 ion chromatograph (IC) system. Working standards of each analyte were prepared using certified standards diluted with deionized water. A commercial standard of 100 ppm sulfate and 50 ppm chloride was used as a quality control standard.

Dissolved trace metals were measured on an Agilent 8800 ICP-MS triple quadrupole using a collision gas to remove isobaric interferences. A solution of 2 % HNO_3 and 0.5 % HCl was used to perform standard and sample dilutions. To monitor and correct for any instrument drift, a SPEX CertiPrep Instrument Check Standard 3 (CL-ICS-3) was measured every 10 samples, and one calibration standard was measured three times (beginning, middle and end) throughout the analysis.

The total soluble organic carbon (TOC) was determined using a Shimadzu TOC V-CPH instrument. The calibration standards used were 0, 50, 100, 250, 500, and 1000 mg/L of carbon, according to ASTM D7573. For inorganic carbon analysis sodium bicarbonate was used as standards, for organic carbon analysis potassium hydrogen phthalate was used as standards.

3.3. STATISTICAL ANALYSIS

Principal component analysis (PCA) and hierarchical clustering were used to identify groupings observed at two different geographic locations as well as throughout the flowback period at Three Hills using JMP 9. An eigenvalue greater than three was used to determine the number of principal components based on the screen plot of correlation matrix (Astel *et al*., 2007; Engle and Rowan, 2014; Ouyang, 2005). Hierarchical clustering was used to identify relatively homogeneous variables and confirm PCA results (Oetjen *et al* 2018). The hierarchical clustering analysis was performed using Ward’s minimum variance method (Ward *et al* 1963). In Ward's minimum variance method, the distance between two clusters is the ANOVA sum of squares between the two clusters added up over all the variables.

In addition, multivariate analysis was applied to show the correlation among different water chemistry parameters.

3.4. GEOCHEMIST'S WORKBENCH ANALYSIS

Geochemist's Workbench® 10 (GWB) was used to calculate the saturation indices of the minerals in the flowback water samples. This software calculates the expected equilibrium chemistry of a system based on thermodynamic parameters. "Thermo" dataset of thermodynamic data for GWB programs is applied in this modeling which is based on the "debye-huckel" activity model.

4.0 RESULTS

4.1. GENERAL WATER CHEMISTRY

Table 1 shows averaged standard water parameters for both the Fox Creek region and Three Hills region samples. The total dissolved solids (TDS), conductivity, and pH of the two regions' FPW samples are very close. For example, samples from both regions had the same average TDS of 229 g/L.

The similarities between the two sampling regions are further illustrated by the piper plot in Figure 3 This data shows large similarities in dissolved ion chemistry for both regions. Since both regions are derived from the same formation, the formation water component of the FPW is expected to be similar, which is confirmed by the similar FPW water chemistry seen here.

Table 1 – Standard water parameters

Parameter	**Fox Creek Region (N=17)**		**Three Hills Region (N=24)**	
	Average	Standard Deviation	Average	Standard Deviation
Conductivity (mS/cm)	214	± 16	216	± 1
TDS (g/L)	229	± 40	229	± 14
pH	5.9	± 0.3	5.7	± 0.3
Sodium (mg/L)	66000	± 7000	66000	± 3000
Magnesium (mg/L)	1420	± 450	2360	± 160

Sulfur (mg/L)	580	± 390	490	± 240
Chloride (mg/L)	143000	± 26000	141000	± 13000
Potassium (mg/L)	1380	± 160	3220	± 100
Calcium (mg/L)	17000	± 6200	15600	± 860
Bicarbonate (mg/L)	53	± 27	28	± 10
Sulfate (mg/L)	375	± 71	863	± 79
TOC (mg/L)	231	NA	106	NA

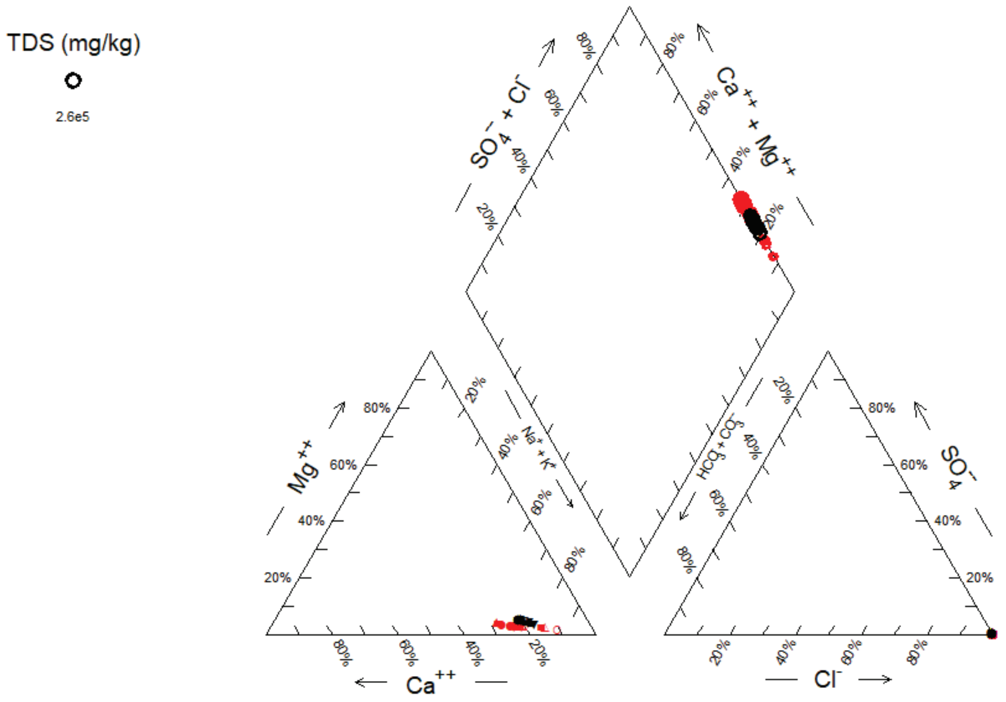


Figure 3 – Piper plot of major ions in FPW samples. Red is fox creek and black is three hills samples

Concentrations of individual dissolved ions from the Fox Creek region and Three Hills region samples are compared in Figure 4. The Fox creek region has lower concentrations of K, Mg, and SO_4 (Figure 4). Other dissolved anions were measured but were determined to be below method detection limits: Br (<0.5 mg/L), F (<0.15 mg/L), NO_3 (<0.5 mg/L), NO_2 (<0.01 mg/L), PO_4 (<0.05 mg/L).

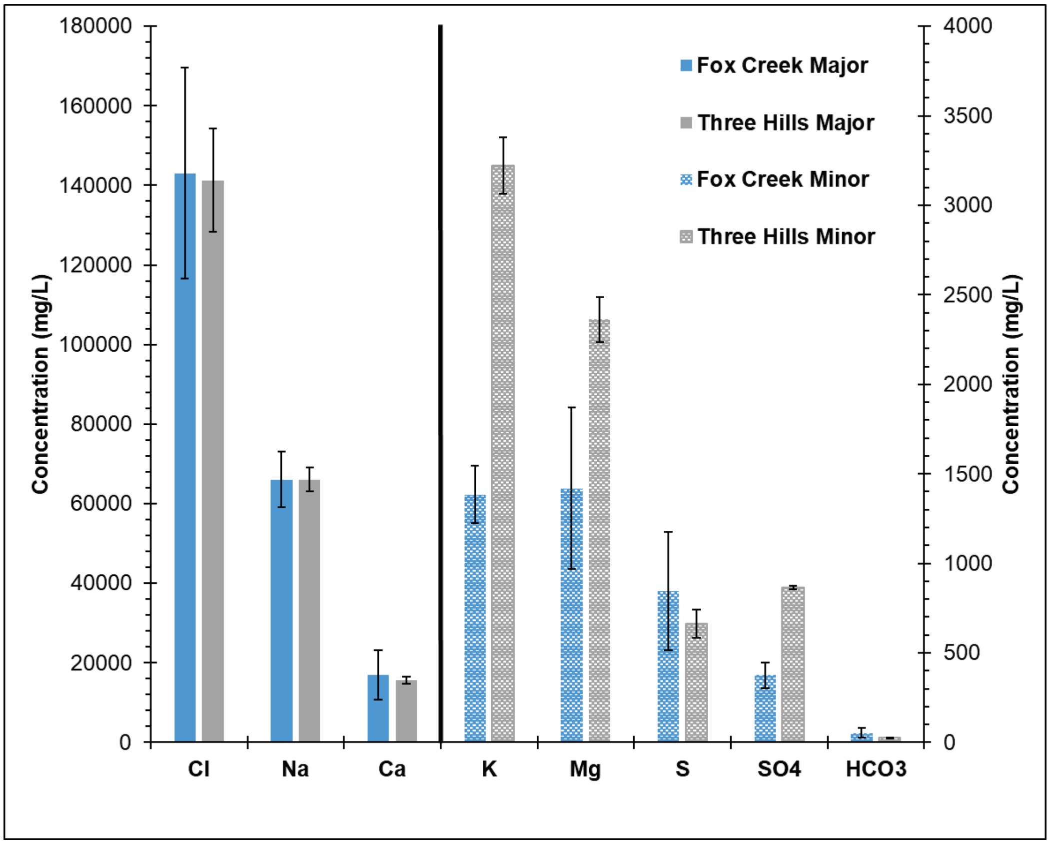


Figure 4 – Concentrations of dissolved ions in FPW samples. (Note: dotted bar values are plotted on the right hand y-axis).

We investigated correlations between ions found in FPW samples. Figure 5 shows the positive correlation between the Mg and Ca concentrations in FPW for both sample regions. Additionally, the concentration of Mg, Ca, and Na are all positively correlated with the concentration of Cl in Fox Creek region FPW samples, while only Na shows a weak positive correlation with Cl in Three Hills region FPW. Fox Creek FPW samples show positive correlations between concentrations of Ca and Mg with Na, while the Three Hills region samples do not. Fox Creek FPW samples show a negative correlation between the concentration of bicarbonate and concentrations of Na, Mg, and Ca, while Three Hills FPW samples show no such correlation (Figure 6). Other dissolved ions investigated showed little to no correlation (Appendix A).

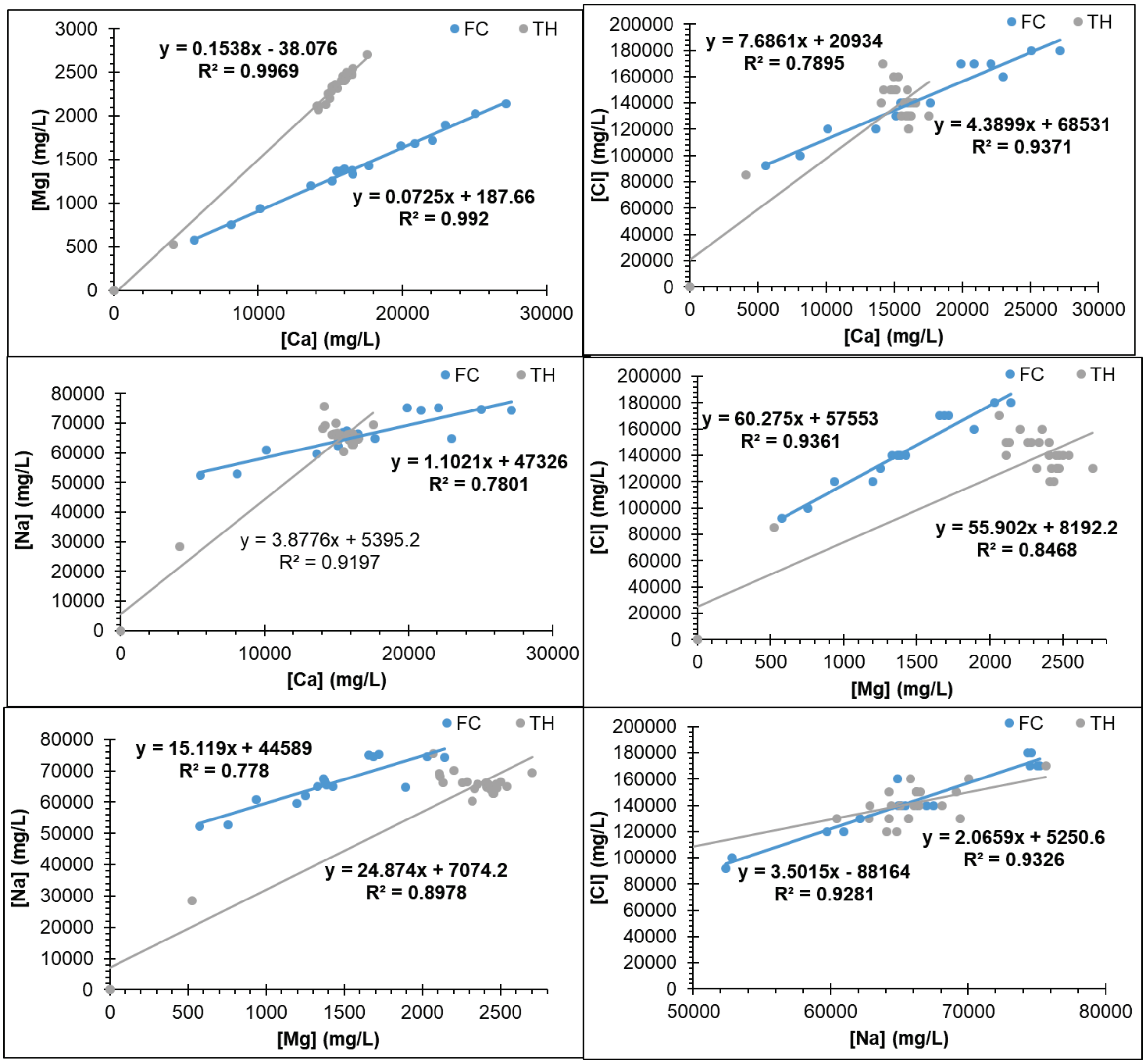


Figure 5 – Positive correlations found in Duvernay FPW samples

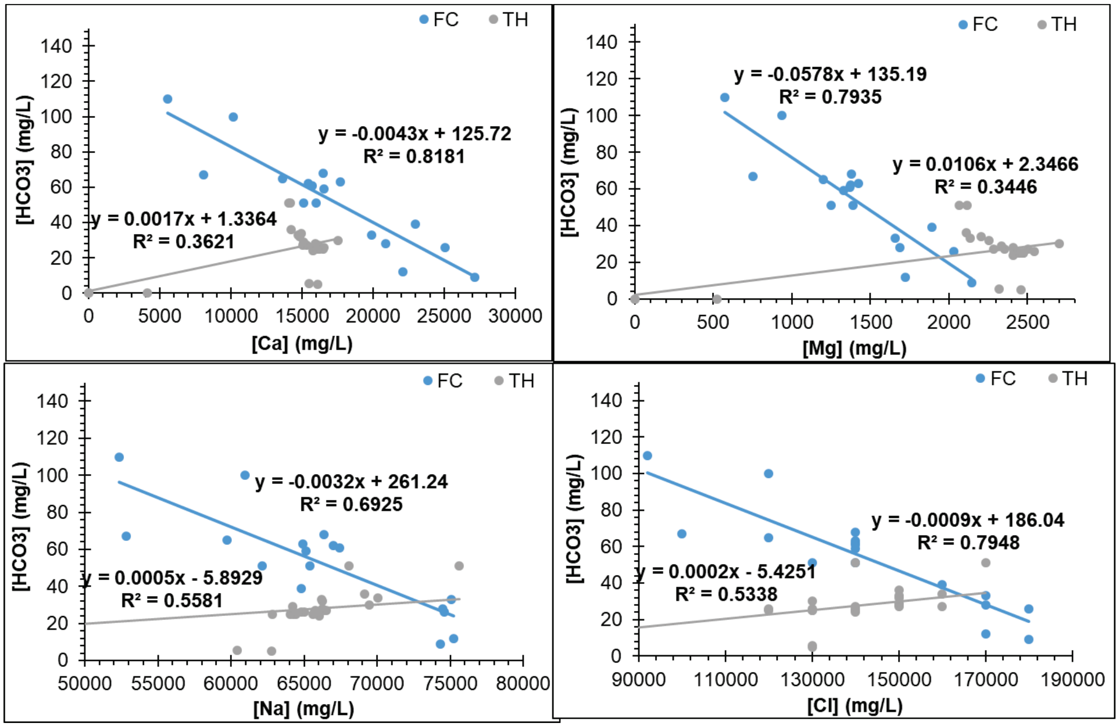


Figure 6 – Negative correlations found in Duvernay FPW samples

4.2. DISSOLVED TRACE METALS

In addition to major element water chemistry, trace element concentrations in all samples were measured. Figure 7 shows the average concentrations of trace elements for both the Fox Creek and Three Hills samples. Both regions show very similar concentrations of trace element with all values being within one order-of-magnitude, except for the Three Hills samples showing much higher concentrations of chromium and cadmium, and the Fox Creek samples showing much higher concentrations of iron. Smaller differences were seen for other elements, such as the Fox Creek region showing higher concentrations of manganese, zinc, barium, boron, silicon, cobalt, nickel, and strontium. The Three hills region showed higher concentrations of aluminum, phosphorus, and vanadium.

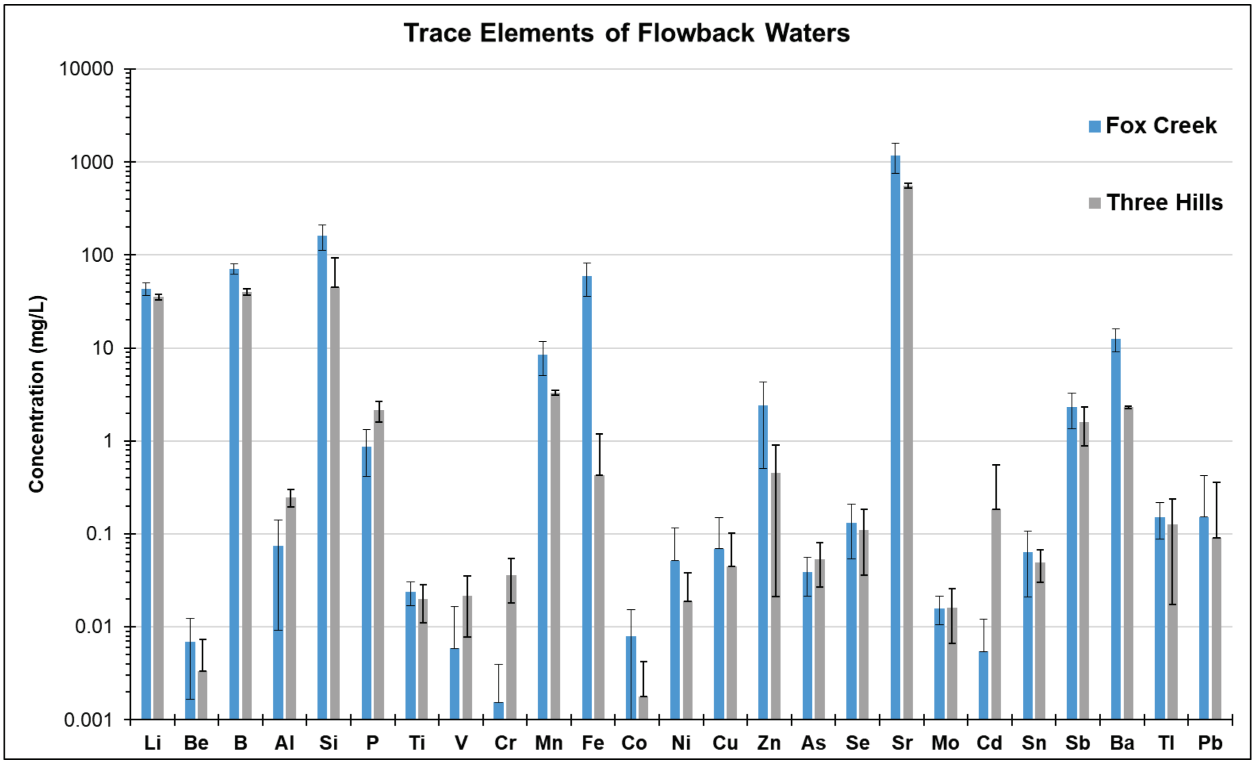


Figure 7 – Average trace element composition of FPW samples from the Fox Creek and Three Hills region wells

4.3. CHANGE IN CHEMISTRY OVER TIME

The second aspect of this study is to analyze FPW over time from a single well in order to observe changes in FPW chemistry in relation to the time since fracturing. A single well from the Three Hills region was sampled immediately after ceasing fracturing, and then sampled on a weekly basis after about four months of shut-in and up until 7 months after fracturing operations.

Water chemistry over the course of about 7 months shows no major changes and are always dominated by NaCl (Figure 8). Cl is the dominant anion, accounting for 99% (Meq) of anions detected. In addition to Cl, small amounts of SO_4 (~0.4 %) and HCO_3 (~0.01 %) were detected. The average cation profile is Na (73 %) and Ca (20 %) with small amounts of Mg (5 %) and K (2 %). Water quality parameters including pH, conductivity, and TDS remained approximately constant for four months during the flowback and production stages (Figure 9). While overall water chemistry remained approximately constant, Ca and Mg concentrations show a gradual increase, while SO_4^- shows a decreasing trend (Figure 10). Other major dissolved ions showed little to no change over the sampling period (Appendix B).

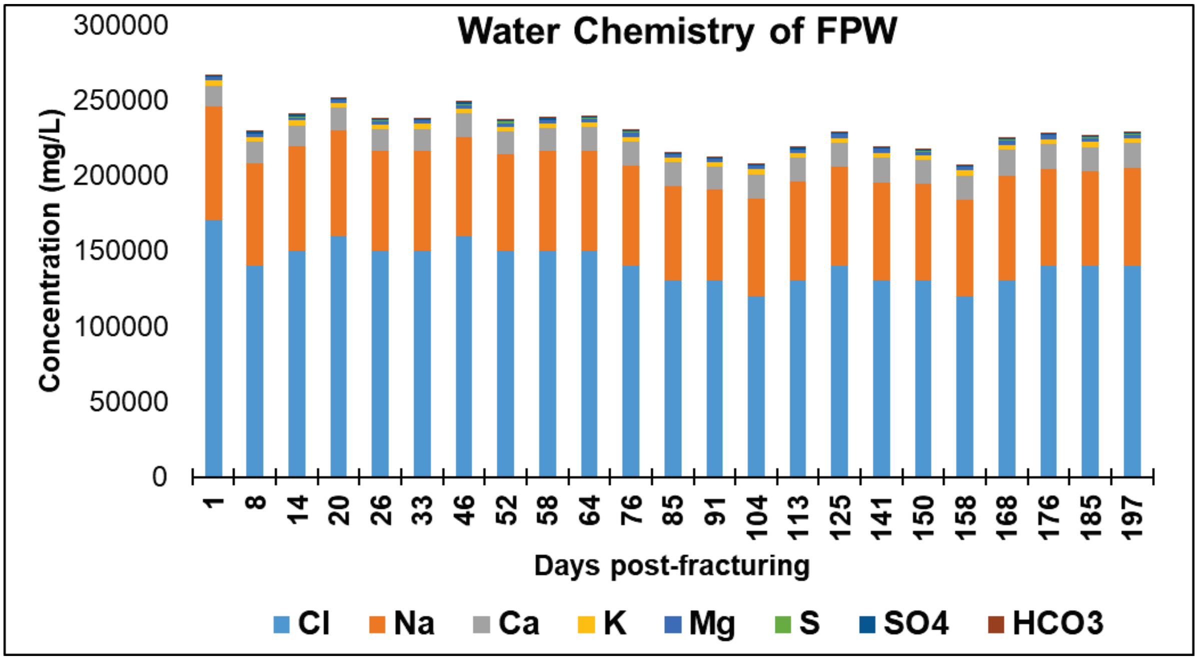


Figure 8 – Ion profile of FPW from a single well in the Three Hills region over the course of 7 months post fracturing

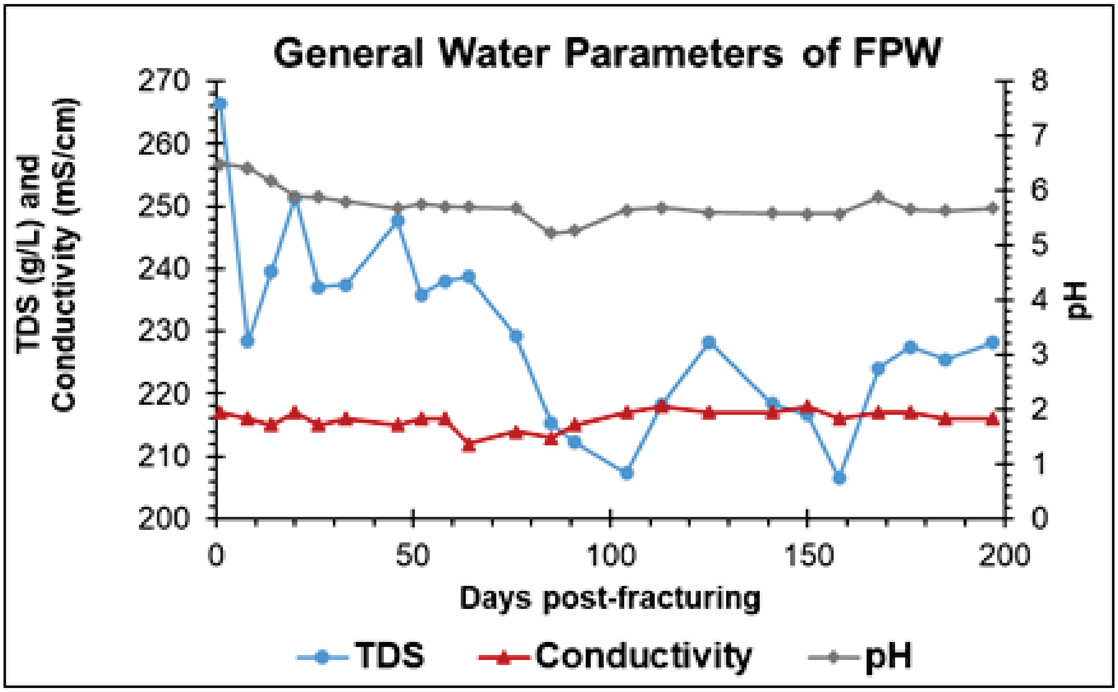


Figure 9 – Change in total dissolved solids, conductivity, and pH of Three Hills region FPW samples

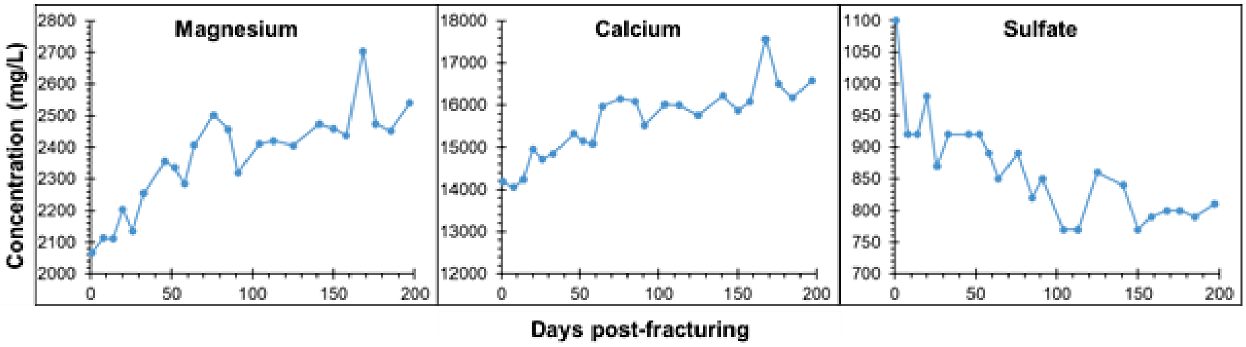


Figure 10 – Time profiles of major ions in Three Hills region FPW that show gradual change post-fracturing

4.4. TRACE METAL CONCENTRATIONS OVER TIME

The FPW from the Three Hills well showed moderate changes in many trace elements over time. Figure 11 shows increases in lithium, boron, vanadium, chromium, and strontium over the 7-month sampling period. Figure 12 shows eight elements that exhibit decreasing concentrations over the sampling period. Copper, zinc, thallium, and lead were initially present in relatively high concentrations before sharp decreases, followed by steady levels for the remainder of the sampling period (Figure 13). These dramatic drops in concentration occur within the first two weeks of flowback/production. Other trace elements showed little to no change over time (Appendix C).

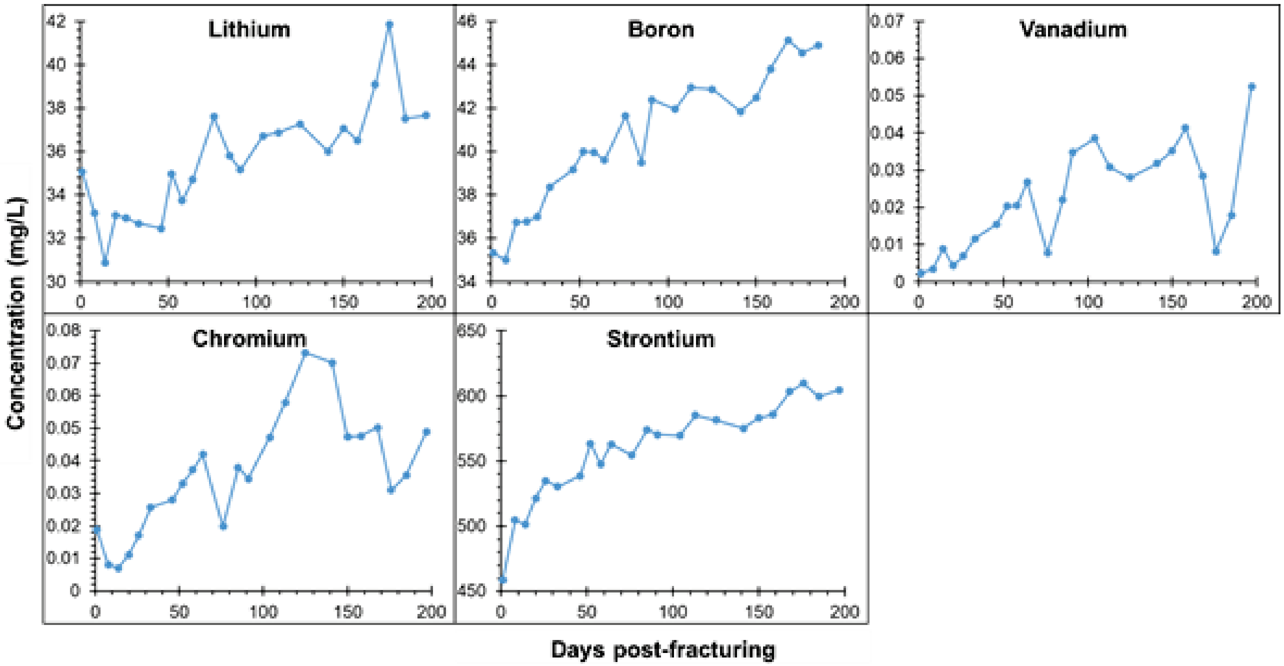


Figure 11 – Time profiles of trace elements in Three Hills region FPW that show gradual increases post-fracturing

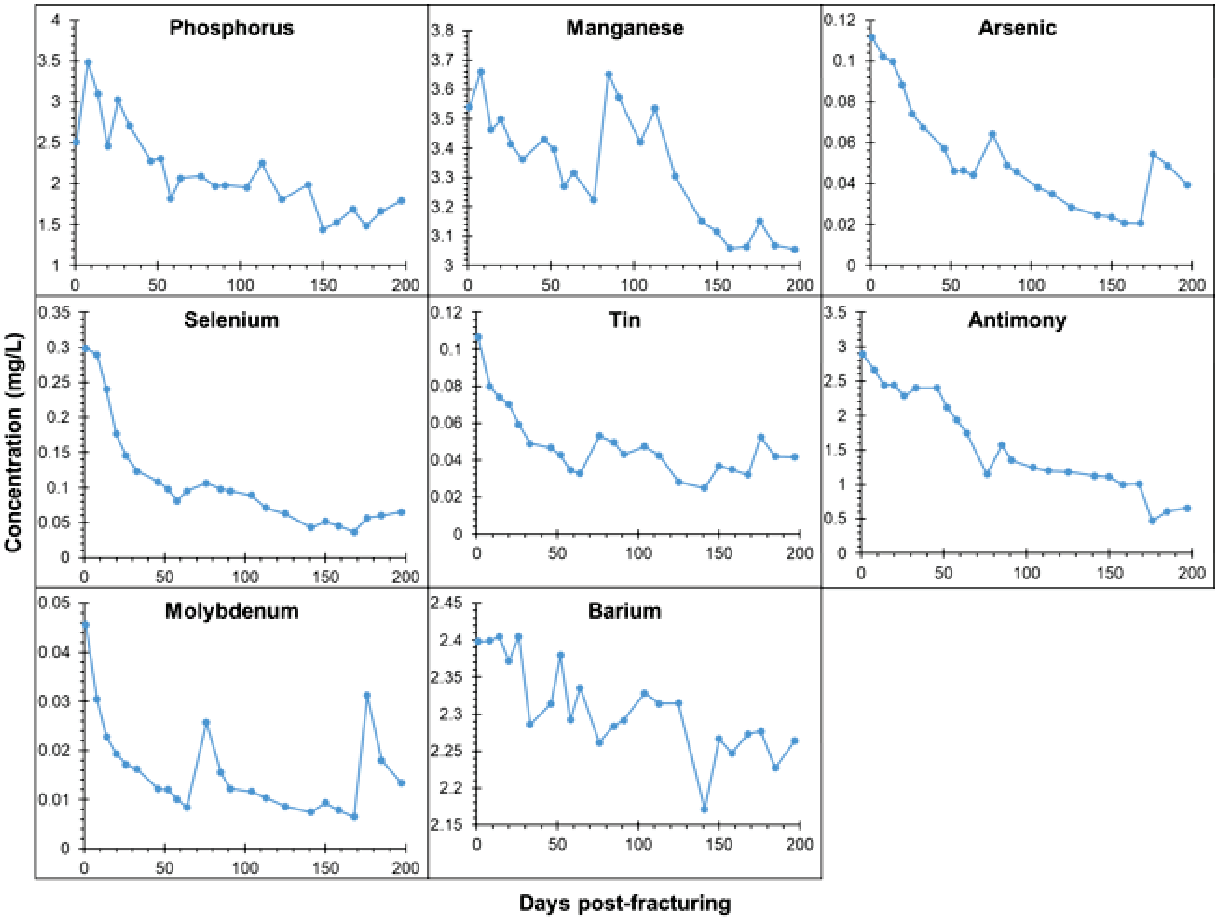


Figure 12 – Time profiles of trace elements in Three Hills region FPW that show a gradual decrease during flowback and/or production

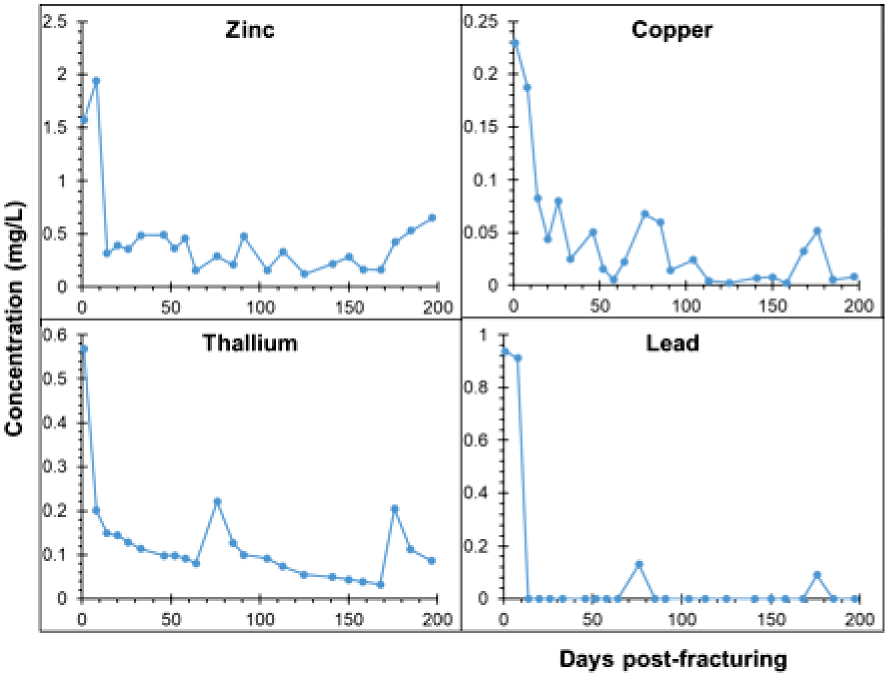


Figure 13 – Time profiles of trace elements in Three Hills region FPW that show a rapid decrease post-fracturing

4.5. STATISTICAL ANALYSIS

To understand the observed variability between the two geological locations (i.e., Fox Creek and Three Hills), a PCA was performed on the chemical data and on variables above the detection limit. The results are shown in Figure 14. In total, 37 variables were used. Three principal components were observed, with principal component 1 (PC1) accounting for 39% of the variability, while principal component 2 (PC2) and 3 (PC3) accounted for 21% and 15% of the variability, respectively (Appendix D). Using this approach, it appears that Three Hills and Fox Creek are significantly different from each other. Hierarchical clustering analysis has confirmed the clusters observed by PCA analysis (as shown in Figure 15). This difference appears to be driven by conductivity, Fe, Ba, K, S and Sulfate. The difference observed at the two geological locations could be likely due to the different fracking chemicals used at two regions or the different formation water chemistry when mixing with the fracturing fluids during the flowback process.

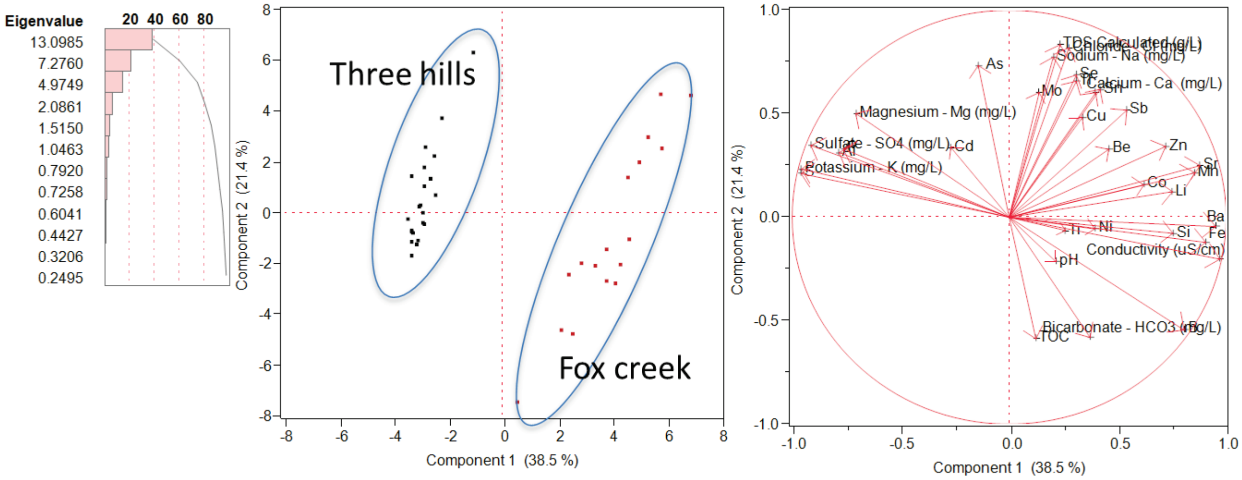


Figure 14 – Principal component analysis for the flowback water samples from Three Hills and Fox Creek

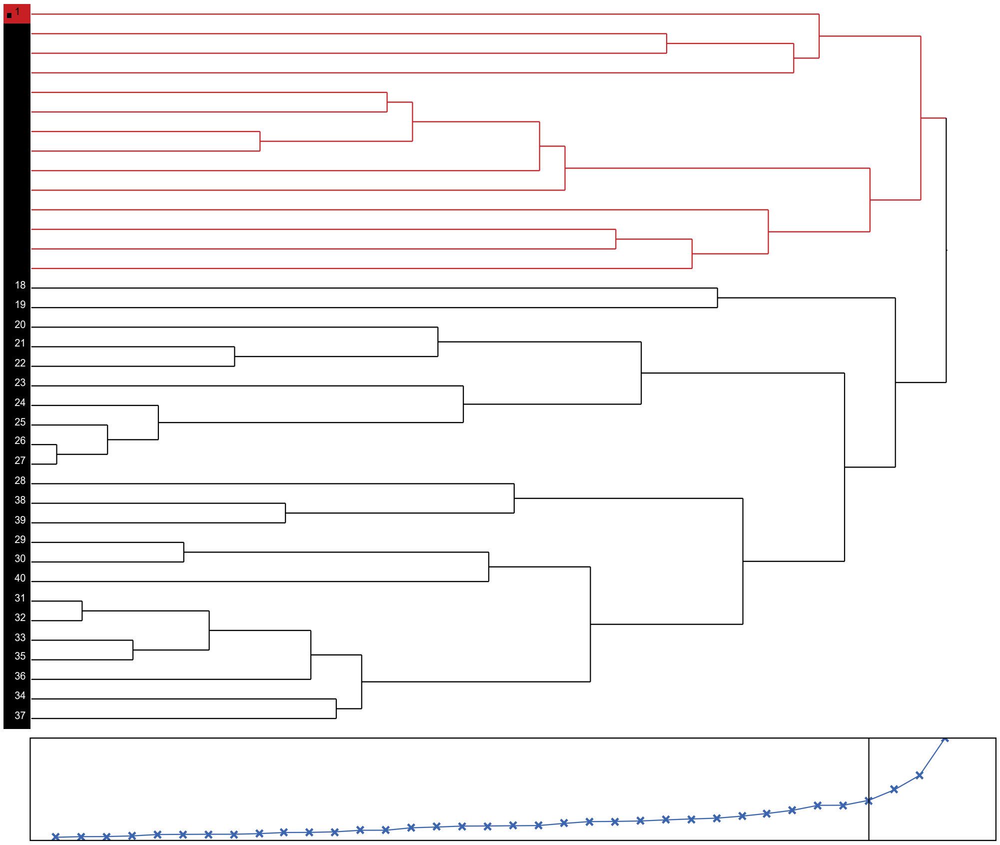


Figure 15 – Hierarchical clustering analysis for the flowback water samples from Three Hills and Fox Creek. Numbers on the left are sample numbers. Samples 1-17 are Fox Creek flowback water samples and Samples 18-40 are Three Hills water samples.

Using a similar approach, Three Hills flowback water samples were analyzed by PCA analysis during the entire flowback period. Two principal components were observed, with principal component 1 (PC1) accounting for 51% of the variability, while principal component 2 (PC2) accounted for 11% of the variability, respectively. It appears that PC1 has differentiated the water samples into 3 dominant clusters based on flowback periods (Figure 16). This difference appears to be driven primarily by the metals (such as As, Se, Sn, Sb, S, B, Sr, Ca, Mg, SO4). The difference observed at different flowback periods could be likely due to the delayed mixing of formation water with the fracturing fluids during the flowback process. Hierarchical clustering analysis has also confirmed the clusters observed by PCA analysis Figure 17).

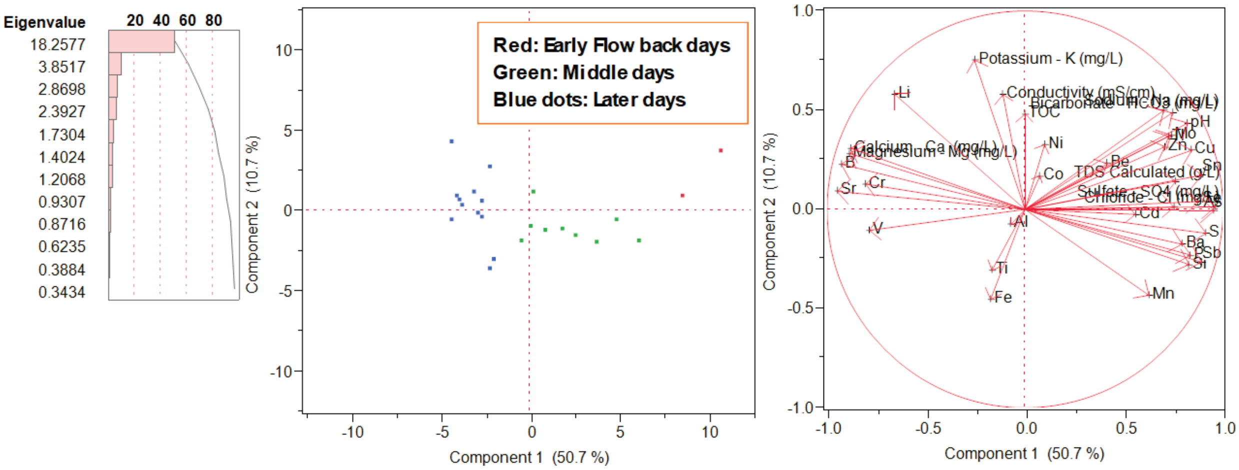


Figure 16 – Principal component analysis for the flowback water samples from Three Hills at different flowback periods

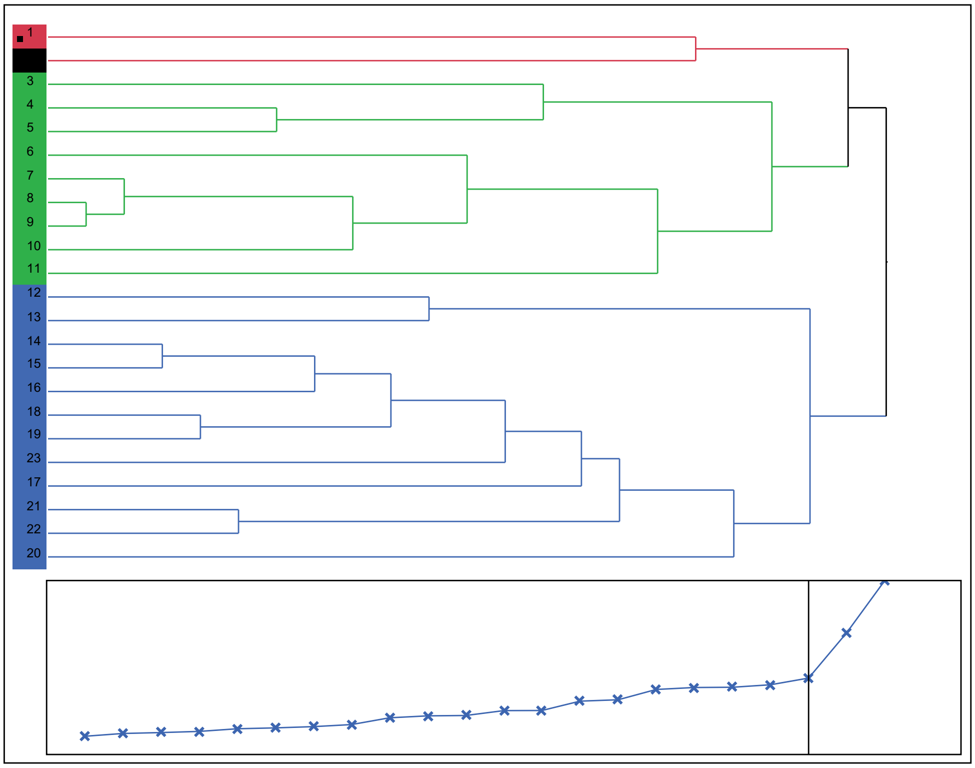


Figure 17 – Hierarchical clustering analysis for the flowback water samples from Three Hills at different flowback periods. Samples 1-2 are early flowback days, samples 3-11 are intermediate flowback days, samples 12-20 are late flowback days.

In addition, correlations between different factors for Three Hills flowback water samples were analyzed as shown in Figure 18 and Figure 19. Clearly, there is strong positive correlation among B, Sr, Ca and Mg; whereas these four elements are negatively correlated with Sb, P, S, As, Se, Cu, Sn and Pb, which are positively correlated among themselves. The correlations among different factors are shown in Appendix E.

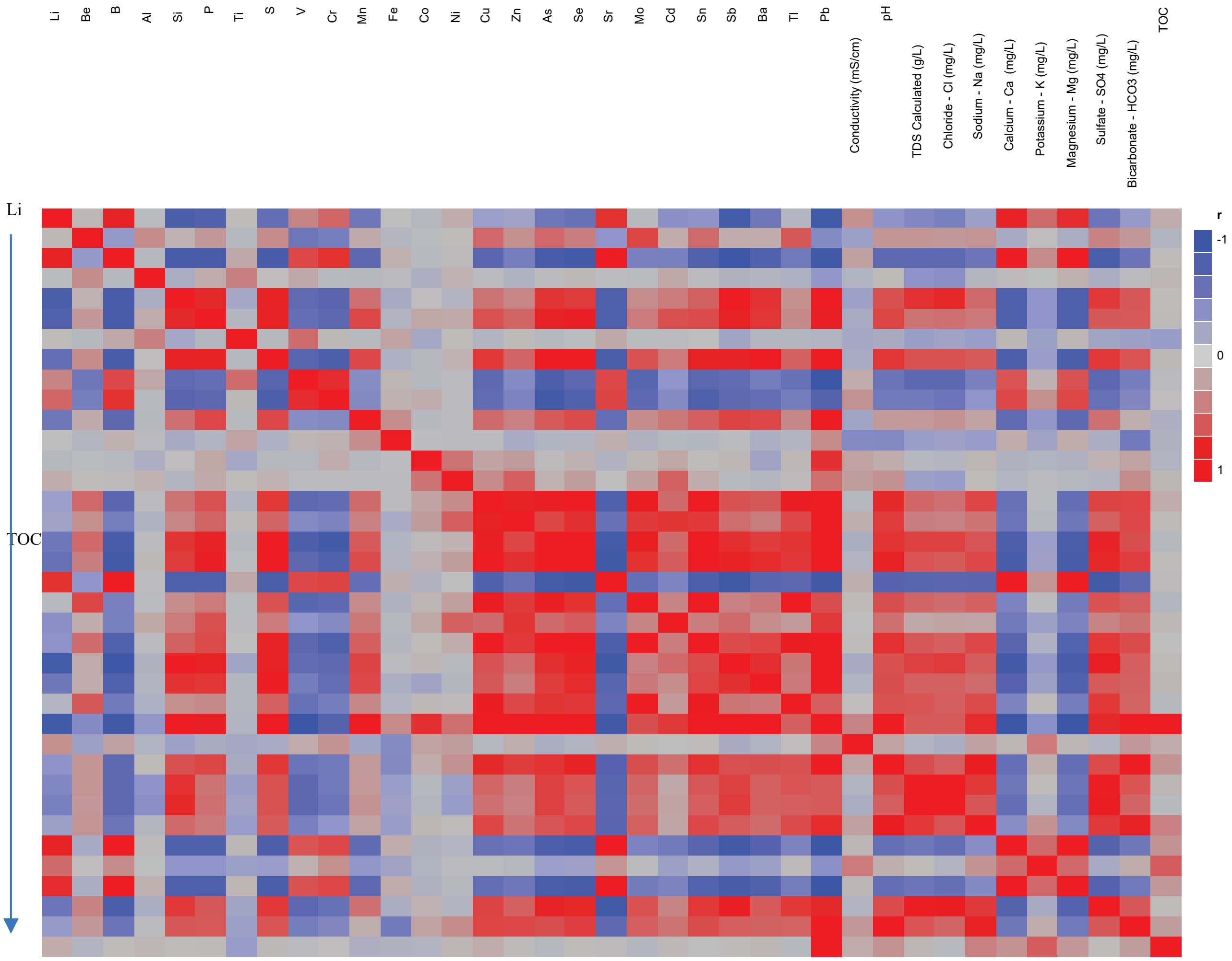


Figure 18 – Correlation between different variables including both general chemistry data and trace metals of the Three Hills flowback water. Blue means negative correlation and red means positive correlation.

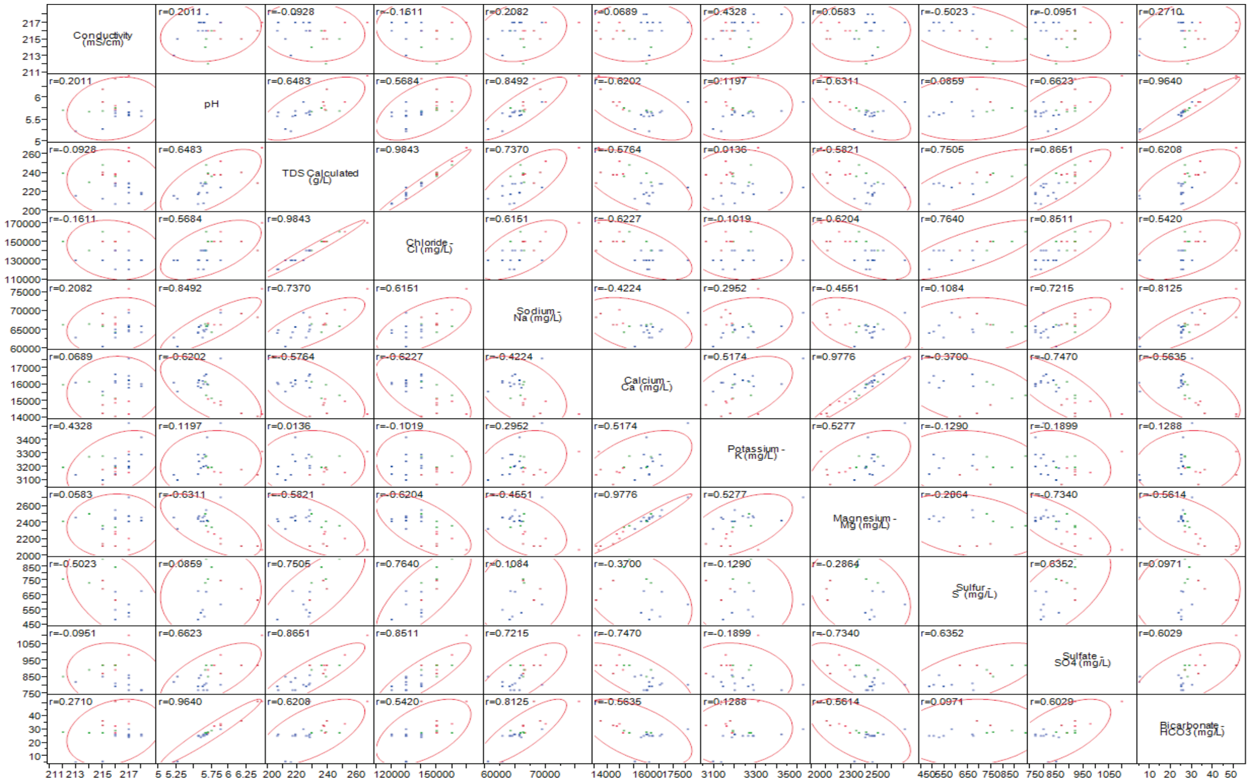


Figure 19 – Scatterplot matrix of multivariate analysis to show the correlations among different variables using general chemistry data of Three Hills flowback water as an example. Correlation between two variables is shown as r along with density eclipses in the graph.

For Fox Creek flowback water chemistry, although there is still strong positive correlation between Ca and Mg, there is no positive correlation between B and Sr. In fact, B is negatively correlated with Ca, Mg, Sr and some other trace metals (Figure 20). pH shows negative correlations with the majority of the elements, meaning the dissolution of the minerals underground likely happened during the fracking process. The detailed correlations among different factors are shown in Appendix E. The difference in the multivariate analysis of the flowback water between two geological locations demonstrates the difference in the fracking fluids applied in the field as well as formation water chemistry. It appears that the correlation can also be potentially used as an indication of the mixing ratio of the formation water and fracking fluids.

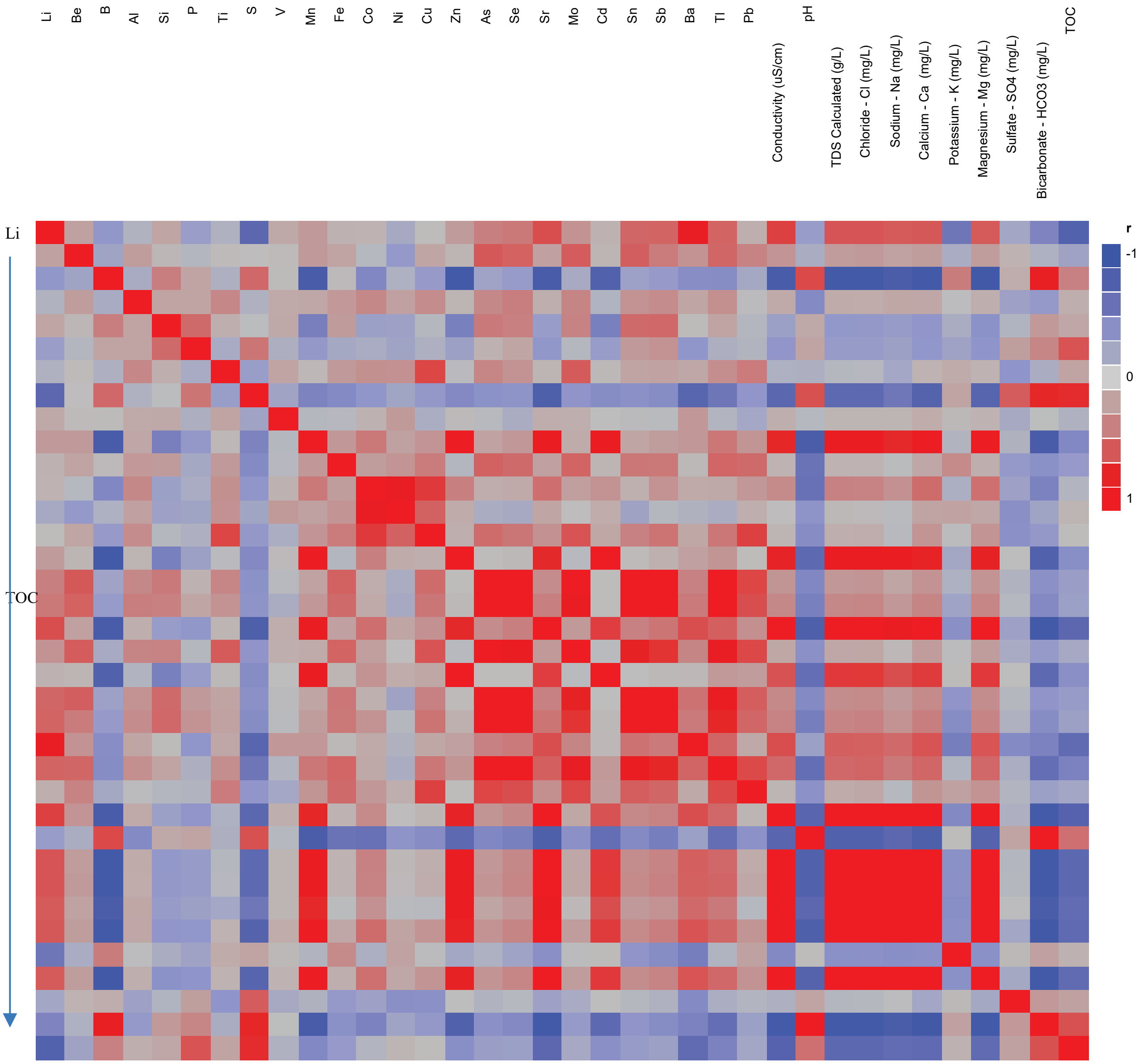
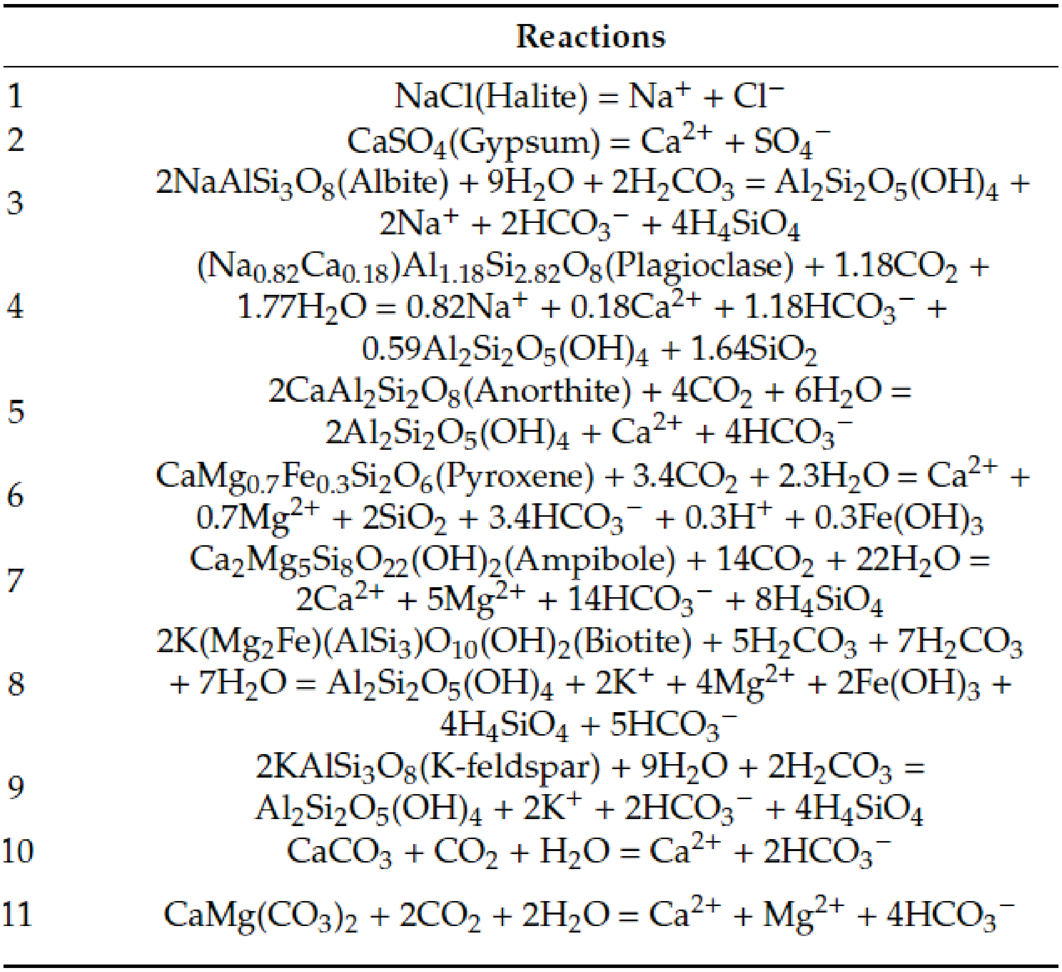


Figure 20 – Correlation between different variables including both general chemistry data and trace metals of the Fox Creek flowback water

The strong correlation between Ca and Mg of all the flowback water samples is an indication of dolomite minerals in the formation. And a strong correlation (0.9643 as shown in Appendix E) between Na and Cl for Fox Creek flowback water samples is likely an indication of halite minerals in the formation. In addition, it is found that the molar ratio of Na+/Cl- in all of the HF flowback water samples is less than 1, which indicates that halite dissolution is not the main contribution to Cl- concentration in groundwater and there is an anthropogenic disturbance by fracturing fluids. The potential mineral dissolution reaction underground is shown below in Figure 21 as an example. The ion ratio observed in the HF flowback water samples is different from the mineral dissolution reactions, which indicates the mixing of the formation water and the fracking fluids as well as the potential scale formation underground.



	Reactions
1	$NaCl(Halite) = Na^+ + Cl^-$
2	$CaSO_4(Gypsum) = Ca^{2+} + SO_4^-$
3	$2NaAlSi_3O_8(Albite) + 9H_2O + 2H_2CO_3 = Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$
4	$(Na_{0.82}Ca_{0.18})Al_{1.18}Si_{2.82}O_8(Plagioclase) + 1.18CO_2 + 1.77H_2O = 0.82Na^+ + 0.18Ca^{2+} + 1.18HCO_3^- + 0.59Al_2Si_2O_5(OH)_4 + 1.64SiO_2$
5	$2CaAl_2Si_2O_8(Anorthite) + 4CO_2 + 6H_2O = 2Al_2Si_2O_5(OH)_4 + Ca^{2+} + 4HCO_3^-$
6	$CaMg_{0.7}Fe_{0.3}Si_2O_6(Pyroxene) + 3.4CO_2 + 2.3H_2O = Ca^{2+} + 0.7Mg^{2+} + 2SiO_2 + 3.4HCO_3^- + 0.3H^+ + 0.3Fe(OH)_3$
7	$Ca_2Mg_5Si_8O_{22}(OH)_2(Ampibole) + 14CO_2 + 22H_2O = 2Ca^{2+} + 5Mg^{2+} + 14HCO_3^- + 8H_4SiO_4$
8	$2K(Mg_2Fe)(AlSi_3)O_{10}(OH)_2(Biotite) + 5H_2CO_3 + 7H_2CO_3 + 7H_2O = Al_2Si_2O_5(OH)_4 + 2K^+ + 4Mg^{2+} + 2Fe(OH)_3 + 4H_4SiO_4 + 5HCO_3^-$
9	$2KAlSi_3O_8(K\text{-}feldspar) + 9H_2O + 2H_2CO_3 = Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_4$
10	$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$
11	$CaMg(CO_3)_2 + 2CO_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 4HCO_3^-$

Figure 21 – Weathering of minerals reactions (Zhang *et al*, 2020)

4.6. GEOCHEMIST’S WORKBENCH ANALYSIS

Geochemist’s workbench analysis has been applied to analyze the water chemistry data of the Three Hill flowback water samples. Particularly the saturation index of the minerals in the water solutions was calculated for each water sample. The saturation index is a widely used indicator in hydrogeochemical studies. It describes the saturation status of minerals in the groundwater and can usually suggest the trend of water and mineral chemical equilibrium and water–rock interaction. When saturation index is 0, the minerals in the aqueous solution are in equilibrium status; when it is negative, the minerals in the aqueous solution have not reached saturation, and bear on a dissolution trend; when a supersaturated status of minerals in the aqueous solution is indicated, mineral deposition may occur (Li *et al*, 2010).

As shown in Figure 22, the saturation index for five commonly seen minerals in the formation and barite is calculated based on the flowback water chemistry. At room temperature, the mineral that will precipitate out is quartz, while the other four minerals will continue dissolve in the water phase in the formation. There seems to be a gradual change to the saturation index of the calcite and dolomite. It is well-know that barite is used in the drilling process during the HF operations. This mineral could likely be added during the stimulation process. The trend of modeling results are similar at both room temperature and formation temperature 80°C (Figure 23), although quartz is no longer at saturation. The gradual change of the SI is likely due to the delayed mixing of the formation water with the fracking chemicals, which confirmed the findings from PCA analysis.

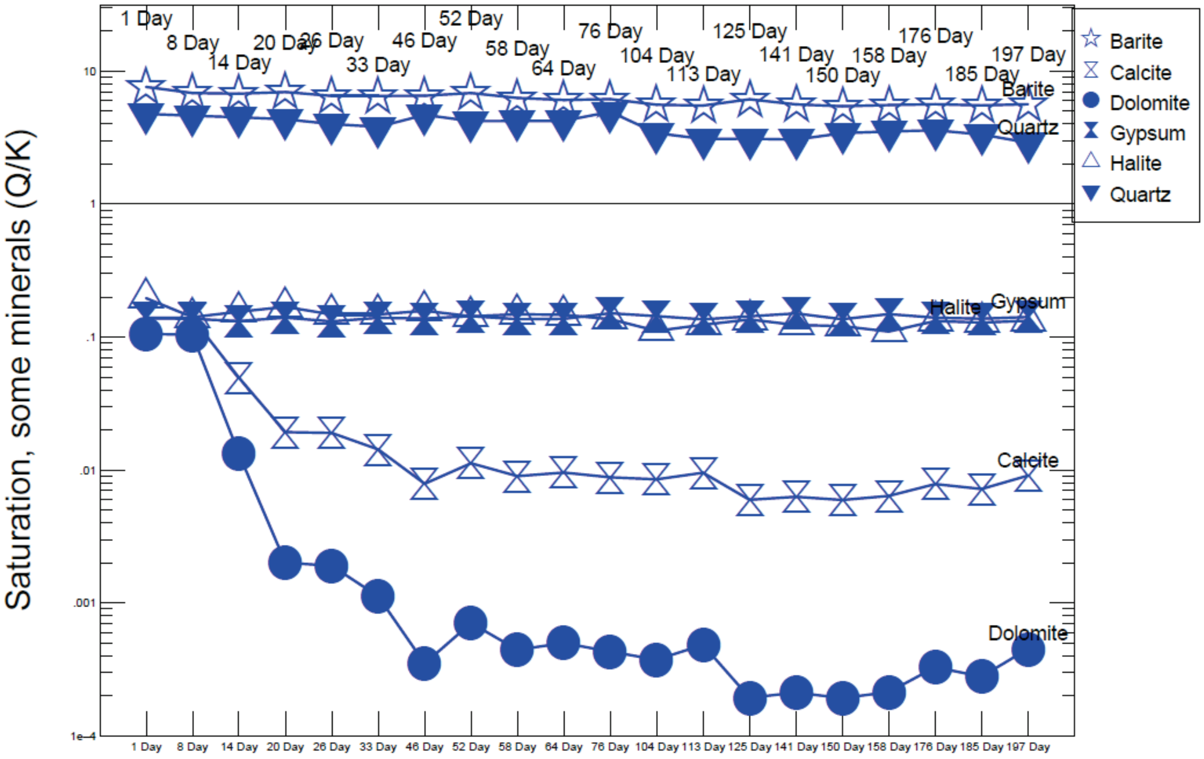


Figure 22 – Time profiles of saturation index of common minerals calculated at room temperature from the flowback water chemistry at Three Hills region. Y-axis is the saturation index for the minerals at log scale.

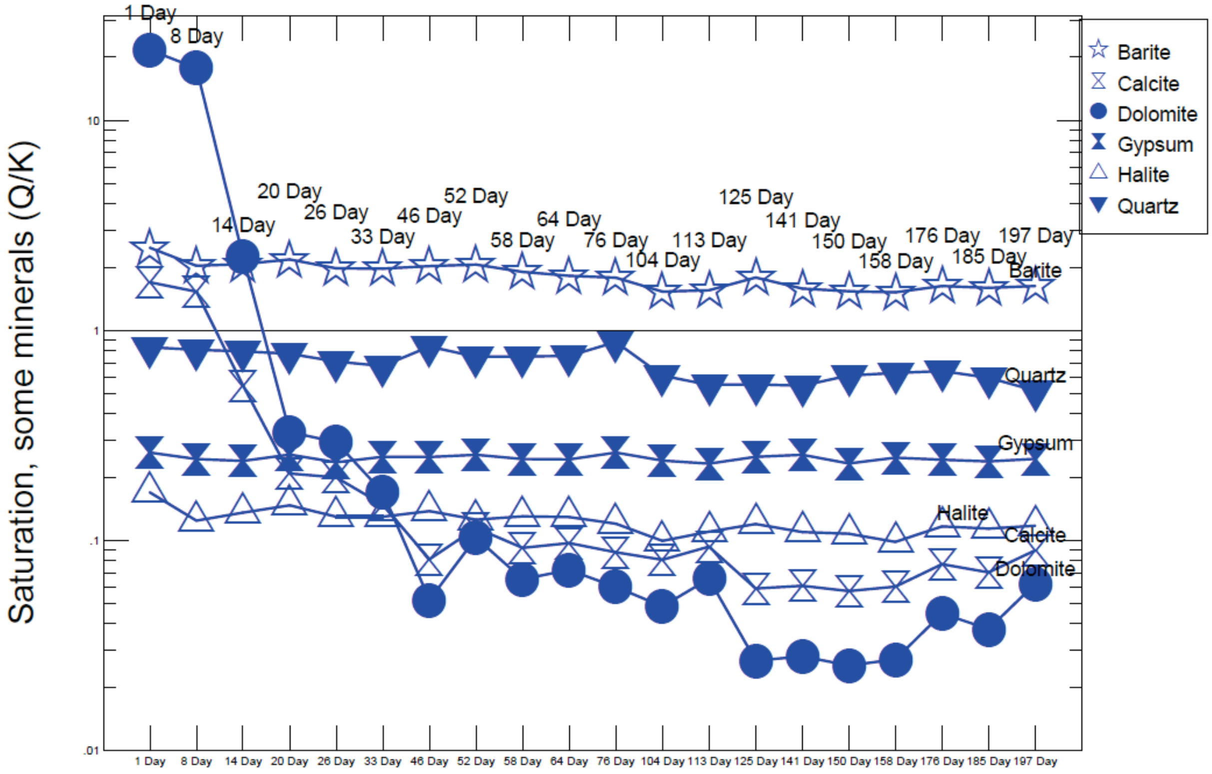


Figure 23 – Time profiles of saturation index of common minerals calculated at 80°C formation temperature from the flowback water chemistry at Three Hills region. Y-axis is the saturation index for the minerals at log scale.

4.7. ISOTOPES

Isotopes of hydrogen and oxygen were measured to gain further information on source of produced waters. Results are presented in Figure 24. Produced water samples from Fox Creek and Three Hills tend to fall below the local meteoric water line for Edmonton (the closest station with isotope precipitation monitoring). The δ^2H of samples ranges from -113.2 to -30.2 ‰ and δ^{18}O ranges from -9.9 to 3.7 ‰. Fox Creek samples show a smaller ranges of values, presumably related to being later produced waters dominated by formation fluids. Samples from the Three Hills well show a greater variation over time, and this is interpreted to be the result of change in the water source over time. Water produced from the well soon after completion is presumed to be a mix of injected water and formation water, and the proportion of injected fracking fluid/water is expected to decrease over time. If injected water is sourced from surface water or shallow groundwater it is expected to have an isotopic signature that falls along the local meteoric water line. Early produced water samples will have a depleted (more negative) isotopic signature compared to later produced waters.

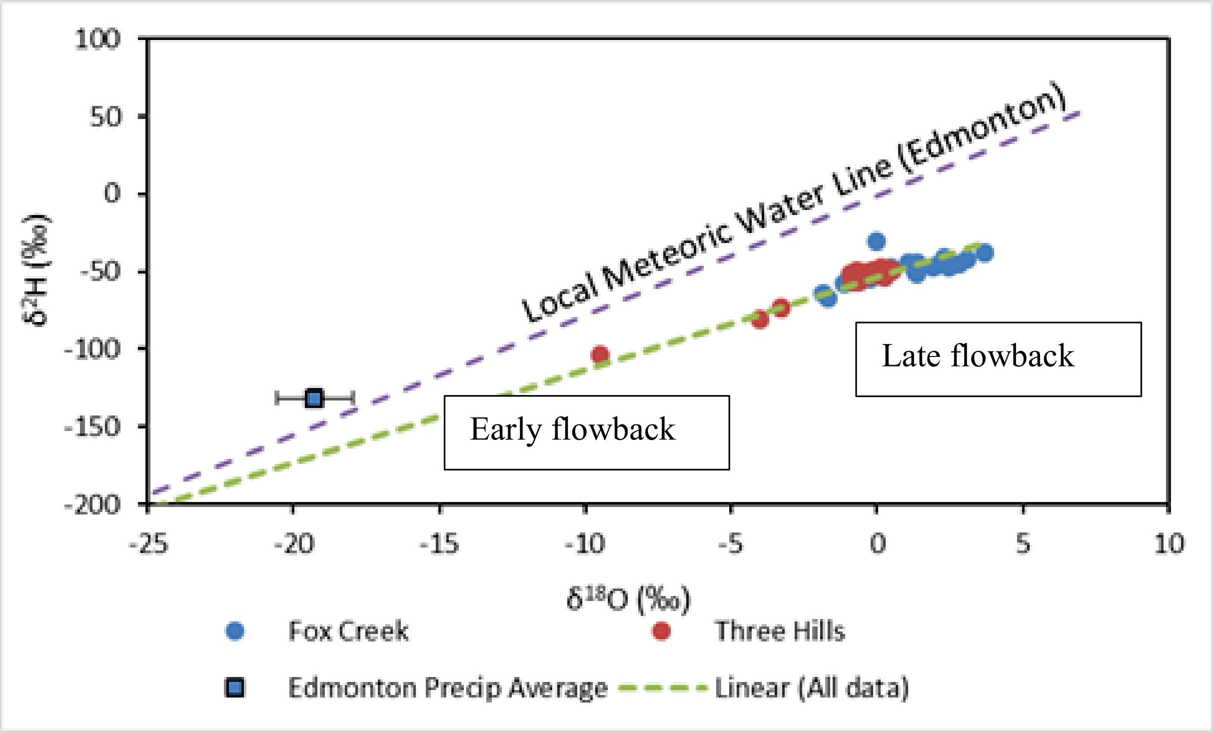


Figure 24 – δ^2H vs. δ^{18}O of flowback water samples, plotted with average value for Edmonton, Alberta and Local Meteoric Water Line for Edmonton (IAEA/WMO, 2021)

5.0 DISCUSSION

Generally speaking, FPW samples from the Fox Creek and Three Hills regions have similar water chemistry. FPW is a mixture of hydraulic fracturing fluid and formation water, and the percentage of formation water in FPW generally increases over time during flowback and production stage. This, combined with the large similarities in measured water chemistry between the two regions and isotope data, indicates that the FPW from both regions is mainly composed of Duvernay formation water. While there was little difference in the major ions (Cl, Na, Ca), trace ions showed differences between the two sample sets. The Fox Creek region had lower concentrations of K, Mg, HCO_3, and SO_4 (Figure 4) which may represent regional differences in the formation waters. However, these differences account for less than 1.5% of the overall TDS. Both sample sets showed very low bicarbonate concentrations. Previous studies report comparable values of Na, Ca, K, and Cl in FPW from the Duvernay formation (He *et al*, 2017), which may suggest that fracking fluids do not influence water chemistry much. Trace elemental composition was also very similar between the two regions.

To better characterize the water chemistry in FPW samples, statistical analysis has been applied to the flowback water samples. This analysis has obviously distinguished the flowback water samples from the two regions. This difference appears to be driven by conductivity, Fe, Ba, K, S and Sulfate.

In addition, we performed ion correlation analysis. There was a strong correlation between Mg and Ca in both sample sets, which represents the formation water mixing. Several other correlations were found, however, many of these were only seen in the Fox Creek region samples. These correlations may not have been as evident in the Three Hills samples because these samples were from a single well over a period of time. This has created different mixing ratio between the fracking fluids and the formation water and therefore affects the correlation among different elements.

The second aspect of this study evaluated the change in FPW water chemistry over time, post-fracturing. 23 FPW samples were collected from a single well in the Three Hills region over the course of 7 months after four months of shut-in. Increases in Ca and Mg, and a decrease in SO_4 was seen over the sampling period. Additionally, the majority of trace elements showed small gradual changes in concentration, except for Cu, Zn, Tl, and Pb which showed large decreases within the first two weeks post-shut-in and Si which showed a large decrease at week 11. A four month shut-in time was used, allowing more complete mixing via diffusion of HF fluid and formation water, resulting in less changes in FPW compared to shorter shut-in time fracturing operations. Many previous studies analyzing FPW often have a shorter sampling time (<4 months) after fracturing (Barbot *et al*, 2013; He *et al*, 2017; Oetjen *et al*, 2018; Sun *et al*, 2019). However, the longer 7-month post-shut-in samples give new insight into changes of FPW over a longer timeline that may better relate to the lifetime FPW of a well.

Geochemical modeling has also been applied in this study to calculated the SI of the minerals in flowback water samples. The results indicate the likelihood of some operational change after Day 64 post fracturing, which warrants further study.

Stable isotope analysis of HPW samples from the Three Hills confirmed the mixing of injection water and the formation water and may be used to identify the potential source water for injection water in a future study.

6.0 CONCLUSIONS

We analyzed and compared the water chemistry between 17 Fox Creek region samples, each from a different well, and 23 Three Hills region samples from a single well. The results allowed us to compare regional differences in FPW composition from the same formation. Overall, the two regions were similar in chemical composition but showed small differences in some lower abundance dissolved elements. Additionally, we investigated changes in water chemistry of FPW over time from a single well. The majority of water quality parameters and water chemistry remained constant over the 7-month sampling time. Major ion chemistry showed increasing concentrations of Ca and Mg, and a decreasing concentration of SO_4. Several trace elements also showed small trends of both increasing and decreasing concentrations over time.

There was a strong correlation between Ca and Mg concentrations in both the Fox Creek region samples and Three Hills region samples, which is an indication of the mixing of formation water. However, the correlation between B and Sr was different among two region samples, which is likely due to the delayed mixing of formation water with the fracturing fluids during the flowback at different time periods of post fracturing. Likewise, Fox Creek region samples showed correlations between concentrations of Cl and Ca, Na and Ca, and Na and Mg, but these correlations were not seen in the Three Hills region samples.

Geochemical modeling demonstrates that there are potential scales formed in the flowback water, but most of the minerals are still in the dissolution state in the formation. Stable isotopic analysis confirmed the mixing of injection water and the formation water.

7.0 ACKNOWLEDGMENTS

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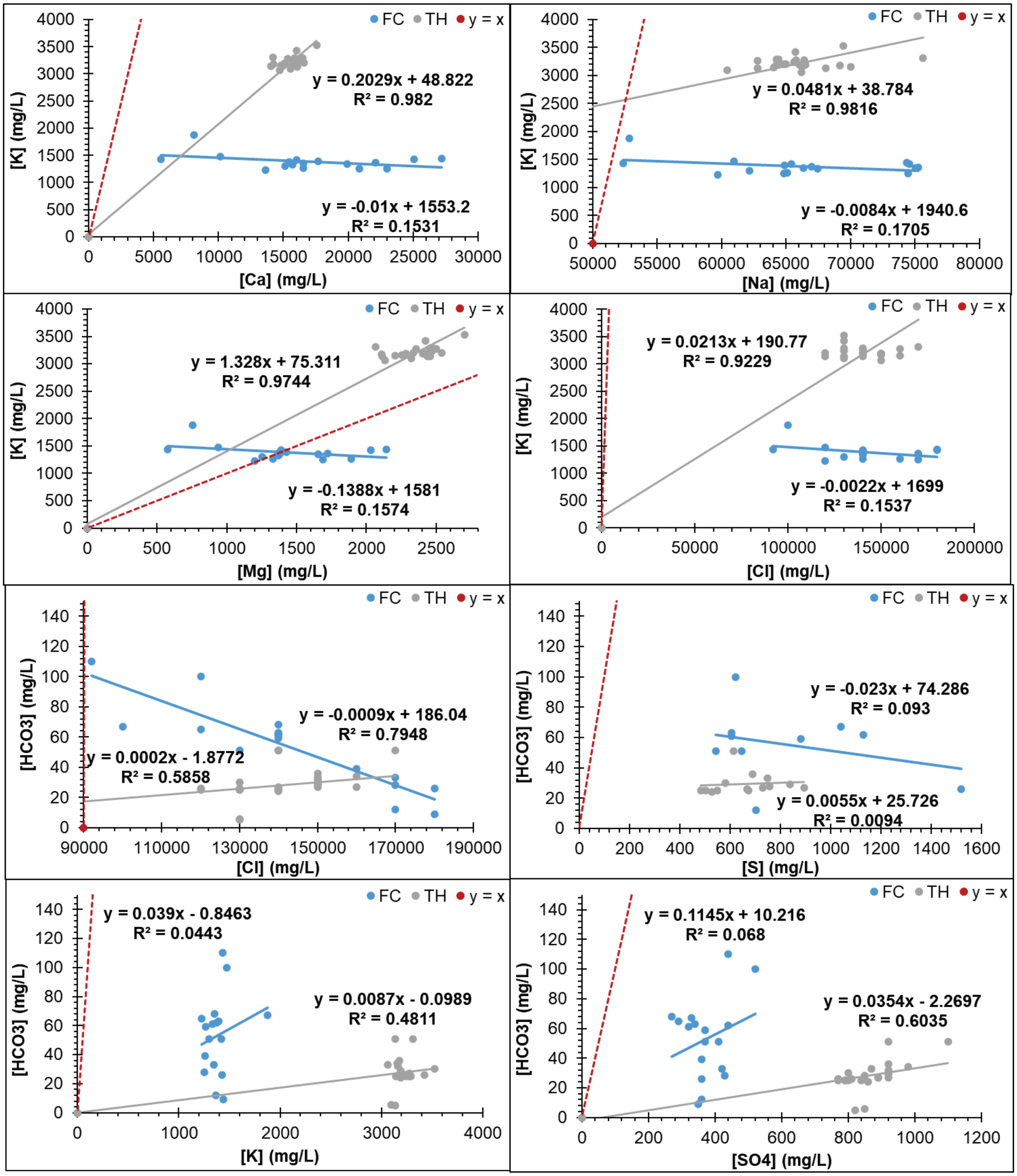
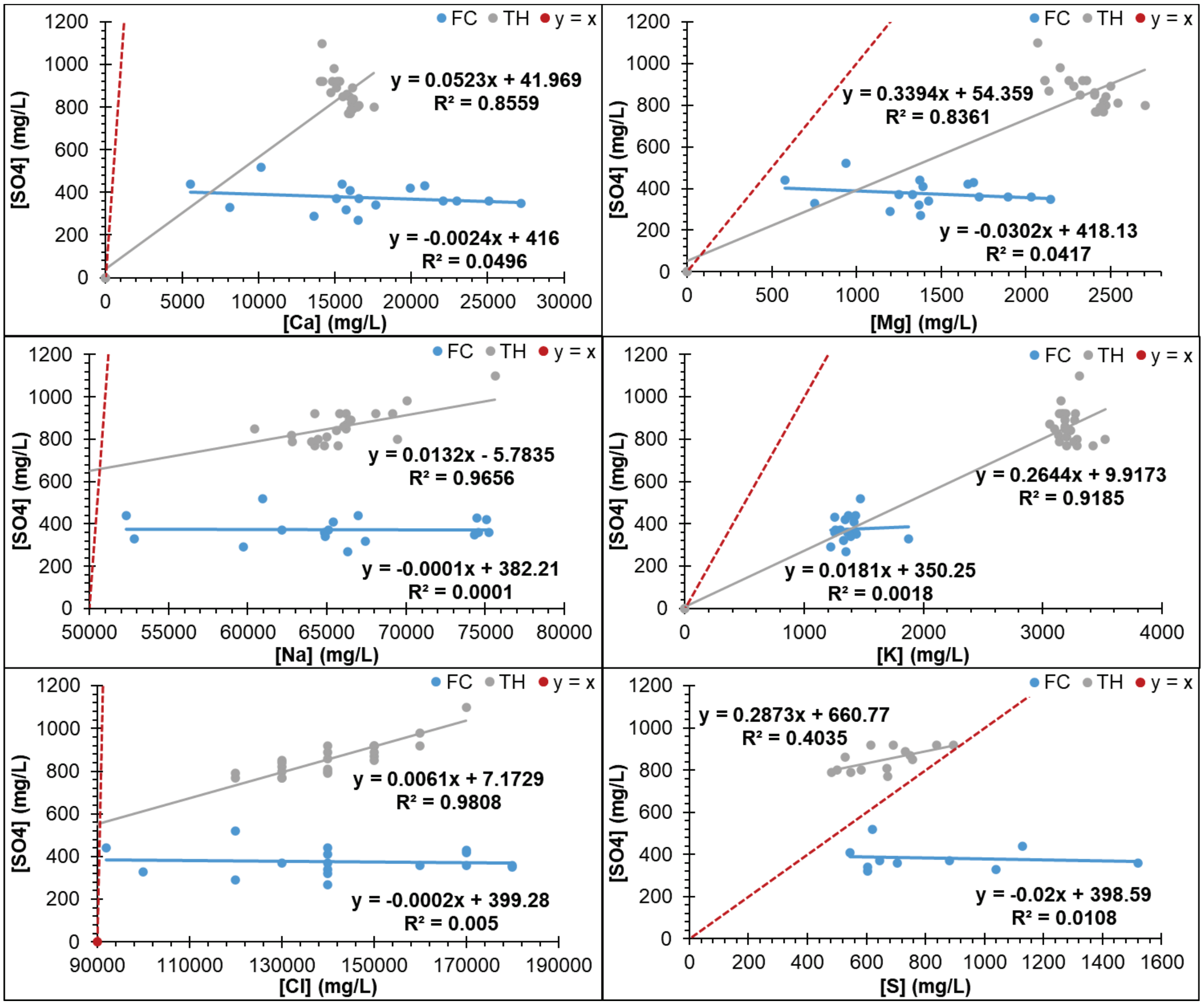
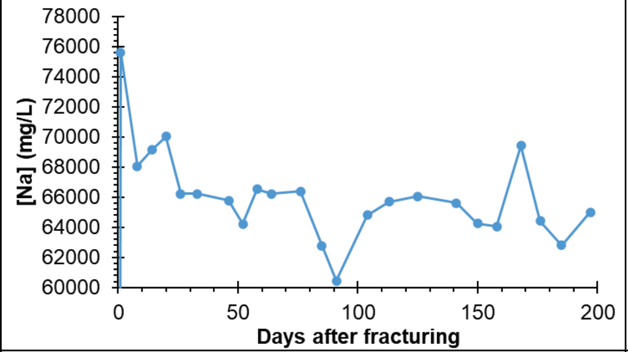
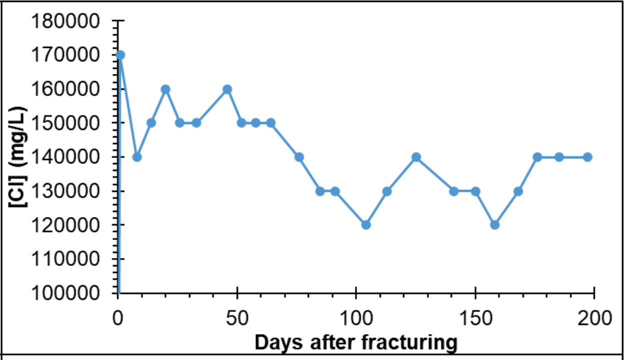
APPENDIX A: WATER CHEMISTRY CORRELATIONS

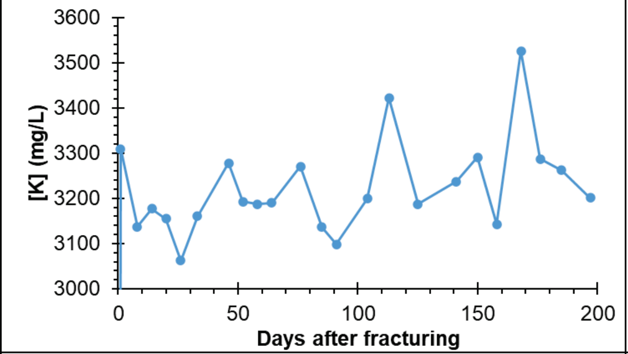


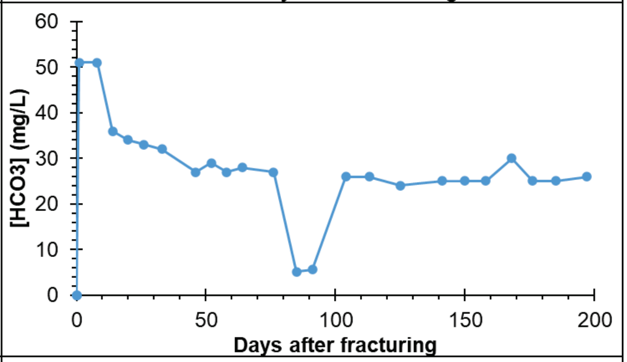

FC
TH
y = x
[SO4] (mg/L)
[Ca] (mg/L)
0
5000
10000
15000
20000
25000
30000
0
200
400
600
800
1000
1200
y = 0.0523x + 41.969
R² = 0.8559
y = -0.0024x + 416
R² = 0.0496
[Mg] (mg/L)
0
500
1000
1500
2000
2500
y = 0.3394x + 54.359
R² = 0.8361
y = -0.0302x + 418.13
R² = 0.0417
[Na] (mg/L)
50000
55000
60000
65000
70000
75000
80000
y = 0.0132x - 5.7835
R² = 0.9656
y = -0.0001x + 382.21
R² = 0.0001
[K] (mg/L)
0
1000
2000
3000
4000
y = 0.2644x + 9.9173
R² = 0.9185
y = 0.0181x + 350.25
R² = 0.0018
[Cl] (mg/L)
90000
110000
130000
150000
170000
190000
y = 0.0061x + 7.1729
R² = 0.9808
y = -0.0002x + 399.28
R² = 0.005
[S] (mg/L)
0
200
400
600
800
1000
1200
1400
1600
y = 0.2873x + 660.77
R² = 0.4035
y = -0.02x + 398.59
R² = 0.0108

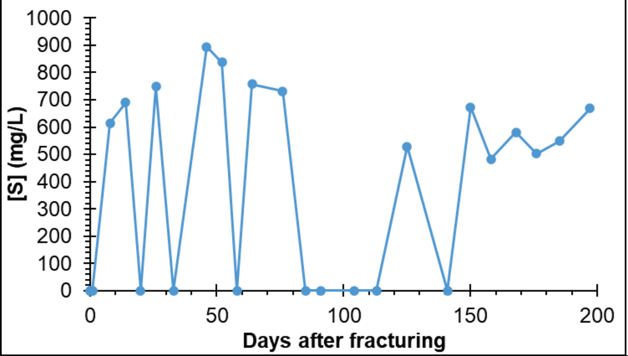
APPENDIX B: CHANGE IN WATER CHEMISTRY OVER TIME

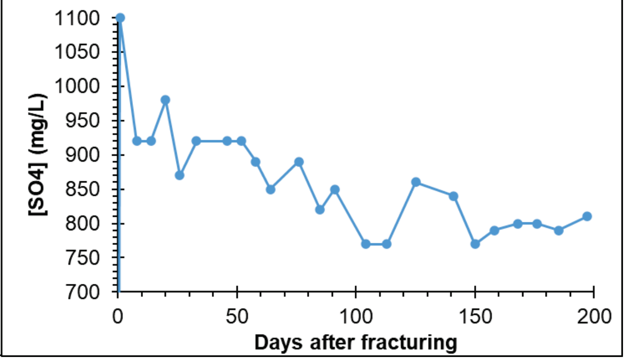




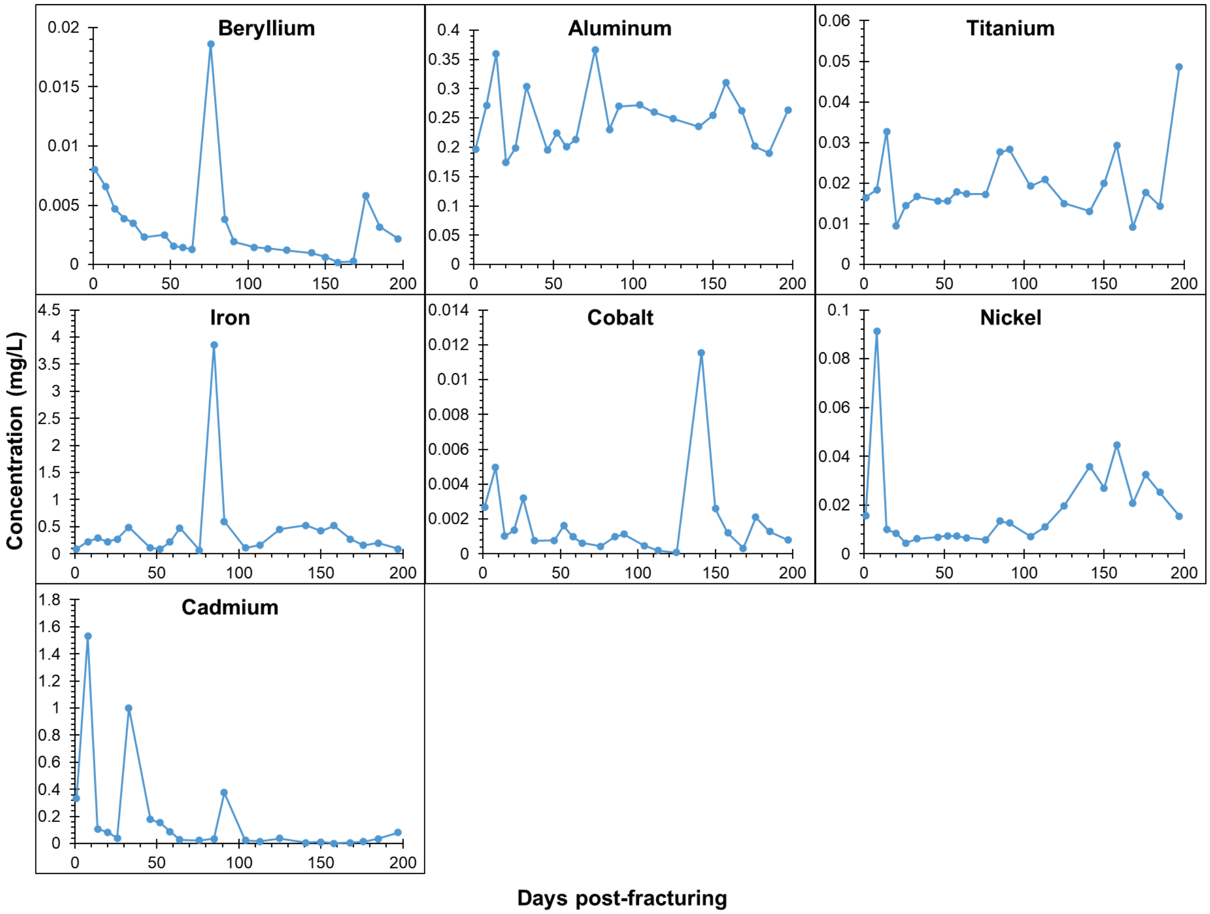




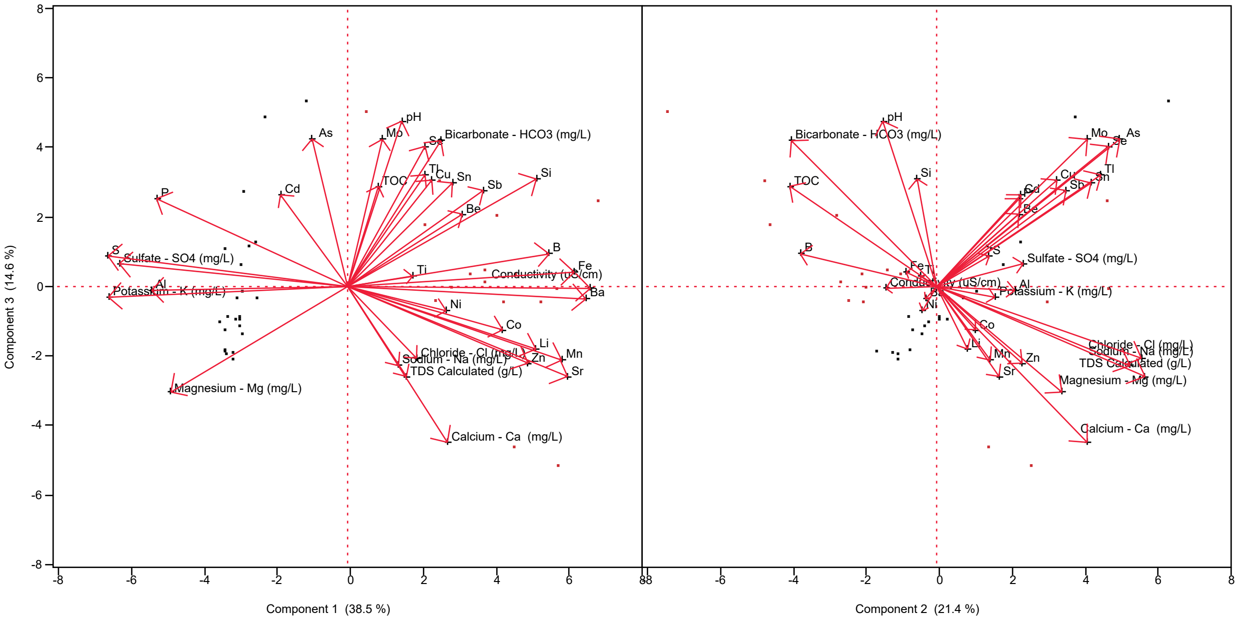




APPENDIX C: CHANGES IN TRACE ELEMENTS OVER TIME



APPENDIX D: BIPLOTS FOR PRINCIPAL COMPONENT ANALYSIS



APPENDIX E: MULTIVARIATE ANALYSIS FOR WATER CHEMISTRY DATA OF HF FLOWBACK WATER

Three Hills:

	Li	Be	B	Al	Si	P	Ti	S	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Sn	Sb	Ba	Tl	Pb	Conductivit	pH	TDS Calcu	Chloride - (	Sodium - N	Calcium - (	Potassium	Magnesiun	Sulfate - S(	Bicarbonat	TOC
Li	1	0.0494	0.818	-0.0311	-0.8288	-0.7581	0.0128	-0.6268	0.382	0.5359	-0.5758	-0.0092	-0.0667	0.1326	-0.2848	-0.2394	-0.5693	-0.6071	0.7544	-0.0507	-0.4054	-0.378	-0.8582	-0.5666	-0.0891	-0.8735	0.3119	-0.3768	-0.4687	-0.523	-0.2735	0.8059	0.5165	0.7657	-0.58	-0.3196	0.1343
Be	0.0494	1	-0.3243	0.3332	0.0797	0.2661	-0.0592	0.3424	-0.5705	-0.5325	0.1468	-0.0742	-0.0386	0.0125	0.5258	0.3161	0.5307	0.4136	-0.357	0.6792	0.1446	0.5109	0.1348	0.1357	0.5985	-0.4392	-0.2695	0.2863	0.2856	0.2643	0.2852	-0.1892	0.0077	-0.1675	0.3876	0.2622	-0.1042
B	0.818	-0.3243	1	-0.062	-0.8464	-0.8417	0.1581	-0.8537	0.6788	0.7552	-0.6794	0.1053	-0.0542	0.0351	-0.6942	-0.5293	-0.8432	-0.8805	0.9615	-0.5185	-0.5217	-0.7561	-0.9494	-0.7603	-0.5583	-0.9064	0.2023	-0.668	-0.6594	-0.6682	-0.5833	0.904	0.3438	0.8881	-0.8354	-0.5866	0.0162
Al	-0.0311	0.3332	-0.062	1	-0.1763	0.1406	0.4097	0.0076	0.1642	-0.0471	-0.0713	-0.0365	-0.1478	0.0923	-0.0328	-0.1214	-0.0222	0.0452	-0.011	-0.0397	0.1684	-0.0271	-0.1153	-0.0976	-0.1304	-0.3426	-0.1104	0.0207	-0.3757	-0.4044	-0.0763	0.033	-0.0101	0.1041	-0.1641	-0.0247	0.0698
Si	-0.8288	0.0797	-0.8464	-0.1763	1	0.7814	-0.2137	0.8146	-0.6528	-0.7159	0.4832	-0.1957	0.007	-0.0943	0.4697	0.3712	0.7422	0.7141	-0.7938	0.3251	0.4254	0.5567	0.9011	0.7509	0.3124	0.9874	-0.2624	0.6383	0.7603	0.7878	0.5229	-0.7996	-0.3541	-0.7915	0.7312	0.6051	0.0106
P	-0.7581	0.2661	-0.8417	0.1406	0.7814	1	-0.0791	0.8112	-0.6227	-0.6757	0.6777	-0.1012	0.1696	0.1473	0.632	0.5415	0.7962	0.8261	-0.7859	0.4328	0.6418	0.6584	0.8181	0.7401	0.3509	0.8295	-0.1824	0.6803	0.4687	0.4815	0.4451	-0.8065	-0.3539	-0.798	0.5984	0.6029	0.0229
Ti	0.0128	-0.0592	0.1581	0.4097	-0.2137	-0.0791	1	-0.0632	0.5111	0.0405	-0.0492	0.1942	-0.2016	0.0121	-0.1028	0.0234	-0.0597	-0.0209	0.1617	-0.0415	-0.0355	-0.0053	-0.2299	-0.0807	-0.0842	-0.0995	-0.2017	-0.1801	-0.2816	-0.2485	-0.2867	0.062	-0.278	0.0706	-0.2314	-0.2665	-0.3027
S	-0.6268	0.3424	-0.8537	0.0076	0.8146	0.8112	-0.0632	1	-0.719	-0.8063	0.6697	-0.1266	-0.0669	0.0841	0.737	0.5407	0.8887	0.9005	-0.8322	0.6283	0.43	0.8192	0.8191	0.8958	0.5623	0.9809	-0.1856	0.7374	0.6334	0.6307	0.5908	-0.8105	-0.2901	-0.8299	0.7299	0.6211	0.0448
V	0.382	-0.5705	0.6788	0.1642	-0.6528	-0.6227	0.5111	-0.719	1	0.7699	-0.4337	0.0722	-0.0674	-0.0459	-0.6591	-0.4388	-0.8112	-0.6767	0.6784	-0.7089	-0.3725	-0.6899	-0.639	-0.5346	-0.6032	-0.9928	0.1389	-0.5846	-0.6754	-0.6781	-0.5187	0.6175	0.0944	0.6289	-0.6839	-0.5365	-0.0421
Cr	0.5359	-0.5325	0.7552	-0.0471	-0.7159	-0.6757	0.0405	-0.8063	0.7699	1	-0.454	0.0982	0.1285	-0.0254	-0.6382	-0.4989	-0.8747	-0.7589	0.6973	-0.6696	-0.4432	-0.7778	-0.6607	-0.6342	-0.534	-0.7452	0.3001	-0.56	-0.5535	-0.5834	-0.37	0.6736	0.3184	0.6835	-0.6115	-0.4706	0.0028
Mn	-0.5758	0.1468	-0.6794	-0.0713	0.4832	0.6777	-0.0492	0.6697	-0.4337	-0.454	1	0.3198	-0.0578	-0.0277	0.5152	0.4026	0.5951	0.6631	-0.6304	0.3411	0.4467	0.5689	0.6923	0.6735	0.3673	0.9711	-0.2267	0.2497	0.2579	0.2949	0.1908	-0.6566	-0.3432	-0.6618	0.4816	0.1179	-0.1439
Fe	-0.0092	-0.0742	0.1053	-0.0365	-0.1957	-0.1012	0.1942	-0.1266	0.0722	0.0982	0.3198	1	-0.017	-0.0272	-0.0213	-0.1862	-0.1113	-0.0908	0.1172	-0.1132	-0.0677	-0.082	-0.035	-0.1561	-0.092	0.346	-0.4435	-0.455	-0.2877	-0.2583	-0.2997	0.132	-0.2444	0.1391	-0.1629	-0.5494	-0.1125
Co	-0.0667	-0.0386	-0.0542	-0.1478	0.007	0.1696	-0.2016	-0.0669	-0.0674	0.1285	-0.0578	-0.017	1	0.4722	0.1825	0.2371	0.0349	0.0958	-0.1206	0.0767	0.17	0.015	0.0579	-0.2354	0.0547	0.7614	0.1958	0.141	-0.0586	-0.0731	0.0722	-0.1159	-0.1083	-0.1223	0.0861	0.1953	-0.0999
Ni	0.1326	0.0125	0.0351	0.0923	-0.0943	0.1473	0.0121	0.0841	-0.0459	-0.0254	-0.0277	-0.0272	0.4722	1	0.3436	0.5701	0.0857	0.2223	-0.0064	0.2193	0.5626	0.1369	-0.055	-0.073	0.036	0.4893	0.2281	0.3031	-0.2699	-0.2975	0.0134	-0.0888	-0.0447	-0.0633	-0.0955	0.3378	0.073
Cu	-0.2848	0.5258	-0.6942	-0.0328	0.4697	0.632	-0.1028	0.737	-0.6591	-0.6382	0.5152	-0.0213	0.1825	0.3436	1	0.821	0.8241	0.8876	-0.774	0.8605	0.5175	0.9005	0.6275	0.6022	0.8538	0.9837	-0.0668	0.7832	0.5386	0.4843	0.6873	-0.6088	-0.0391	-0.631	0.6924	0.6929	0.1419
Zn	-0.2394	0.3161	-0.5293	-0.1214	0.3712	0.5415	0.0234	0.5407	-0.4388	-0.4989	0.4026	-0.1862	0.2371	0.5701	0.821	1	0.6792	0.761	-0.6021	0.7212	0.7464	0.726	0.4969	0.4231	0.6776	0.9731	0.1218	0.7156	0.4148	0.3954	0.4709	-0.5829	-0.0721	-0.5679	0.5635	0.6746	0.0202
As	-0.5693	0.5307	-0.8432	-0.0222	0.7422	0.7962	-0.0597	0.8887	-0.8112	-0.8747	0.5951	-0.1113	0.0349	0.0857	0.8241	0.6792	1	0.9427	-0.8714	0.823	0.5128	0.9299	0.7651	0.7179	0.7456	0.9875	-0.1604	0.7506	0.7022	0.7013	0.6158	-0.8095	-0.2846	-0.8353	0.796	0.6492	-0.0661
Se	-0.6071	0.4136	-0.8805	0.0452	0.7141	0.8261	-0.0209	0.9005	-0.6767	-0.7589	0.6631	-0.0908	0.0958	0.2223	0.8876	0.761	0.9427	1	-0.9191	0.7553	0.5867	0.9248	0.8154	0.7725	0.728	0.9917	-0.103	0.8196	0.6168	0.5948	0.672	-0.843	-0.2584	-0.8531	0.788	0.7117	0.0102
Sr	0.7544	-0.357	0.9615	-0.011	-0.7938	-0.7859	0.1617	-0.8322	0.6784	0.6973	-0.6304	0.1172	-0.1206	-0.0064	-0.774	-0.6021	-0.8714	-0.9191	1	-0.6156	-0.488	-0.8187	-0.9238	-0.7082	-0.68	-0.9103	0.1192	-0.7417	-0.7089	-0.6937	-0.7037	0.8925	0.2832	0.8853	-0.8834	-0.6693	0.0368
Mo	-0.0507	0.6792	-0.5185	-0.0397	0.3251	0.4328	-0.0415	0.6283	-0.7089	-0.6696	0.3411	-0.1132	0.0767	0.2193	0.8605	0.7212	0.823	0.7553	-0.6156	1	0.3751	0.8929	0.3939	0.4423	0.9258	0.6483	0.0199	0.6525	0.5403	0.5084	0.5611	-0.5059	-0.0244	-0.5474	0.6306	0.5777	-0.0855
Cd	-0.4054	0.1446	-0.5217	0.1684	0.4254	0.6418	-0.0355	0.43	-0.3725	-0.4432	0.4467	-0.0677	0.17	0.5626	0.5175	0.7464	0.5128	0.5867	-0.488	0.3751	1	0.4262	0.5184	0.3197	0.2527	0.7185	-0.0034	0.4875	0.1625	0.1834	0.1752	-0.5621	-0.2698	-0.4984	0.381	0.4718	0.0486
Sn	-0.378	0.5109	-0.7561	-0.0271	0.5567	0.6584	-0.0053	0.8192	-0.6899	-0.7778	0.5689	-0.082	0.015	0.1369	0.9005	0.726	0.9299	0.9248	-0.8187	0.8929	0.4262	1	0.6629	0.6933	0.8601	0.9142	0.0154	0.7596	0.6052	0.5705	0.6727	-0.7048	-0.1286	-0.7484	0.736	0.654	-0.0073
Sb	-0.8582	0.1348	-0.9494	-0.1153	0.9011	0.8181	-0.2299	0.8191	-0.639	-0.6607	0.6923	-0.035	0.0579	-0.055	0.6275	0.4969	0.7651	0.8154	-0.9238	0.3939	0.5184	0.6629	1	0.7654	0.4595	0.9779	-0.1821	0.6399	0.7025	0.7141	0.5837	-0.8783	-0.325	-0.8499	0.8303	0.5776	0.0322
Ba	-0.5666	0.1357	-0.7603	-0.0976	0.7509	0.7401	-0.0807	0.8958	-0.5346	-0.6342	0.6735	-0.1561	-0.2354	-0.073	0.6022	0.4231	0.7179	0.7725	-0.7082	0.4423	0.3197	0.6933	0.7654	1	0.438	0.9929	-0.1085	0.6532	0.5613	0.564	0.5105	-0.7388	-0.2664	-0.7655	0.5944	0.5576	0.0677
Tl	-0.0891	0.5985	-0.5583	-0.1304	0.3124	0.3509	-0.0842	0.5623	-0.6032	-0.534	0.3673	-0.092	0.0547	0.036	0.8538	0.6776	0.7456	0.728	-0.68	0.9258	0.2527	0.8601	0.4595	0.438	1	0.5695	0.0031	0.6238	0.6231	0.576	0.6587	-0.4946	0.0393	-0.5385	0.7326	0.5505	-0.0558
Pb	-0.8735	-0.4392	-0.9064	-0.3426	0.9874	0.8295	-0.0995	0.9809	-0.9928	-0.7452	0.9711	0.346	0.7614	0.4893	0.9837	0.9731	0.9875	0.9917	-0.9103	0.6483	0.7185	0.9142	0.9779	0.9929	0.5695	1	0.3835	0.999	0.5955	0.595	0.7785	-0.9952	-0.3961	-0.9946	0.78	0.9995	0.9635
Conductivit	0.3119	-0.2695	0.2023	-0.1104	-0.2624	-0.1824	-0.2017	-0.1856	0.1389	0.3001	-0.2267	-0.4435	0.1958	0.2281	-0.0668	0.1218	-0.1604	-0.103	0.1192	0.0199	-0.0034	0.0154	-0.1821	-0.1085	0.0031	0.3835	1	0.2011	-0.0928	-0.1611	0.2082	0.0689	0.4328	0.0583	-0.0951	0.271	0.1438
pH	-0.3768	0.2863	-0.668	0.0207	0.6383	0.6803	-0.1801	0.7374	-0.5846	-0.56	0.2497	-0.455	0.141	0.3031	0.7832	0.7156	0.7506	0.8196	-0.7417	0.6525	0.4875	0.7596	0.6399	0.6532	0.6238	0.999	0.2011	1	0.6483	0.5684	0.8492	-0.6202	0.1197	-0.6311	0.6623	0.964	0.3
TDS Calcu	-0.4687	0.2856	-0.6594	-0.3757	0.7603	0.4687	-0.2816	0.6334	-0.6754	-0.5535	0.2579	-0.2877	-0.0586	-0.2699	0.5386	0.4148	0.7022	0.6168	-0.7089	0.5403	0.1625	0.6052	0.7025	0.5613	0.6231	0.5955	-0.0928	0.6483	1	0.9843	0.737	-0.5764	0.0136	-0.5821	0.8651	0.6208	0.067
Chloride - (	-0.523	0.2643	-0.6682	-0.4044	0.7878	0.4815	-0.2485	0.6307	-0.6781	-0.5834	0.2949	-0.2583	-0.0731	-0.2975	0.4843	0.3954	0.7013	0.5948	-0.6937	0.5084	0.1834	0.5705	0.7141	0.564	0.576	0.595	-0.1611	0.5684	0.9843	1	0.6151	-0.6227	-0.1019	-0.6204	0.8511	0.542	-0.0468
Sodium - N	-0.2735	0.2852	-0.5833	-0.0763	0.5229	0.4451	-0.2867	0.5908	-0.5187	-0.37	0.1908	-0.2997	0.0722	0.0134	0.6873	0.4709	0.6158	0.672	-0.7037	0.5611	0.1752	0.6727	0.5837	0.5105	0.6587	0.7785	0.2082	0.8492	0.737	0.6151	1	-0.4224	0.2952	-0.4551	0.7215	0.8125	0.4005
Calcium - (	0.8059	-0.1892	0.904	0.033	-0.7996	-0.8065	0.062	-0.8105	0.6175	0.6736	-0.6566	0.132	-0.1159	-0.0888	-0.6088	-0.5829	-0.8095	-0.843	0.8925	-0.5059	-0.5621	-0.7048	-0.8783	-0.7388	-0.4946	-0.9952	0.0689	-0.6202	-0.5764	-0.6227	-0.4224	1	0.5174	0.9776	-0.747	-0.5635	0.291
Potassium	0.5165	0.0077	0.3438	-0.0101	-0.3541	-0.3539	-0.278	-0.2901	0.0944	0.3184	-0.3432	-0.2444	-0.1083	-0.0447	-0.0391	-0.0721	-0.2846	-0.2584	0.2832	-0.0244	-0.2698	-0.1286	-0.325	-0.2664	0.0393	-0.3961	0.4328	0.1197	0.0136	-0.1019	0.2952	0.5174	1	0.5277	-0.1899	0.1288	0.5841
Magnesiun	0.7657	-0.1675	0.8881	0.1041	-0.7915	-0.798	0.0706	-0.8299	0.6289	0.6835	-0.6618	0.1391	-0.1223	-0.0633	-0.631	-0.5679	-0.8353	-0.8531	0.8853	-0.5474	-0.4984	-0.7484	-0.8499	-0.7655	-0.5385	-0.9946	0.0583	-0.6311	-0.5821	-0.6204	-0.4551	0.9776	0.5277	1	-0.734	-0.5614	0.2728
Sulfate - S(	-0.58	0.3876	-0.8354	-0.1641	0.7312	0.5984	-0.2314	0.7299	-0.6839	-0.6115	0.4816	-0.1629	0.0861	-0.0955	0.6924	0.5635	0.796	0.788	-0.8834	0.6306	0.381	0.736	0.8303	0.5944	0.7326	0.78	-0.0951	0.6623	0.8651	0.8511	0.7215	-0.747	-0.1899	-0.734	1	0.6029	0.0146
Bicarbonat	-0.3196	0.2622	-0.5866	-0.0247	0.6051	0.6029	-0.2665	0.6211	-0.5365	-0.4706	0.1179	-0.5494	0.1953	0.3378	0.6929	0.6746	0.6492	0.7117	-0.6693	0.5777	0.4718	0.654	0.5776	0.5576	0.5505	0.9995	0.271	0.964	0.6208	0.542	0.8125	-0.5635	0.1288	-0.5614	0.6029	1	0.2255
TOC	0.1343	-0.1042	0.0162	0.0698	0.0106	0.0229	-0.3027	0.0448	-0.0421	0.0028	-0.1439	-0.1125	-0.0999	0.073	0.1419	0.0202	-0.0661	0.0102	0.0368	-0.0855	0.0486	-0.0073	0.0322	0.0677	-0.0558	0.9635	0.1438	0.3	0.067	-0.0468	0.4005	0.291	0.5841	0.2728	0.0146	0.2255	1

Fox Creek:

	Li	Be	B	Na	Mg	Al	Si	P	K	Ca	Ti	S	V	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Sn	Sb	Ba	Tl	Pb	Conductivit	pH	TDS Calcu	Chloride - (	Sodium - N	Calcium - (	Potassium	Magnesiun	Sulfate - S(	Bicarbonat	TOC
Li	1	0.2068	-0.3437	0.6291	0.6065	-0.1176	0.1777	-0.2915	-0.5153	0.6182	-0.124	-0.6876	0.1584	0.2476	0.0975	0.0879	-0.1948	0.0093	0.2396	0.4082	0.4452	0.6536	0.299	0.1013	0.5374	0.5461	0.8421	0.548	0.1177	0.7011	-0.2987	0.6139	0.6138	0.5974	0.5992	-0.5771	0.5932	-0.2232	-0.4916	-0.7517
Be	0.2068	1	-0.232	0.2966	0.2631	0.2246	0.0601	-0.0853	-0.1685	0.2606	0.032	0.0044	0.0315	0.243	0.1922	-0.0608	-0.3289	0.1765	0.0684	0.6004	0.5601	0.2127	0.5831	0.0756	0.5727	0.426	0.2918	0.5367	0.3884	0.2823	-0.168	0.2353	0.2443	0.1998	0.2226	-0.1787	0.227	0.0833	-0.1288	-0.246
B	-0.3437	-0.232	1	-0.7704	-0.8895	-0.1832	0.4186	0.1878	0.5821	-0.8798	-0.1382	0.5336	0.0178	-0.8441	0.0367	-0.4633	-0.1263	-0.3159	-0.886	-0.236	-0.3061	-0.8545	-0.1903	-0.7672	-0.262	-0.3153	-0.4173	-0.4378	-0.2034	-0.8358	0.6647	-0.8845	-0.8845	-0.8257	-0.8908	0.4227	-0.9083	0.1289	0.8237	0.3941
Na	0.6291	0.2966	-0.7704	1	0.8809	0.1856	-0.2031	-0.1667	-0.4433	0.857	-0.2724	-0.5393	0.0908	0.7712	0.0592	0.2721	-0.0945	-0.044	0.8065	0.2878	0.3743	0.8476	0.1271	0.6189	0.3878	0.4323	0.5157	0.5168	-0.0003	0.954	-0.7176	0.9439	0.942	0.9707	0.8549	-0.4325	0.8434	0.0147	-0.7956	-0.6449
Mg	0.6065	0.2631	-0.8895	0.8809	1	0.1678	-0.3481	-0.32	-0.4976	0.9979	0.0378	-0.7156	0.1041	0.8774	0.1621	0.4749	0.1412	0.2621	0.8095	0.3162	0.4031	0.9894	0.2319	0.7132	0.3738	0.4314	0.6237	0.5537	0.2726	0.9515	-0.7833	0.9752	0.9756	0.8973	0.9968	-0.4057	0.993	-0.2031	-0.8953	-0.656
Al	-0.1176	0.2246	-0.1832	0.1856	0.1678	1	0.1815	0.1867	0.0456	0.1594	0.3643	-0.1235	0.1489	0.1627	0.258	0.3616	0.2131	0.3342	0.0773	0.3624	0.4126	0.1101	0.3789	-0.108	0.2962	0.3358	0.178	0.3139	-0.023	0.1475	-0.4391	0.1455	0.1334	0.1722	0.1605	-0.0112	0.1179	-0.2553	-0.3284	0.1113
Si	0.1777	0.0601	0.4186	-0.2031	-0.3481	0.1815	1	0.5139	0.2215	-0.3267	0.1232	-0.0211	0.1552	-0.5255	0.2418	-0.2773	-0.2585	-0.0696	-0.5197	0.4421	0.4034	-0.2996	0.3886	-0.521	0.5155	0.5276	0.0218	0.1922	-0.0771	-0.274	0.1555	-0.3396	-0.3363	-0.3098	-0.3526	-0.1705	-0.3894	-0.1094	0.253	0.1621
P	-0.2915	-0.0853	0.1878	-0.1667	-0.32	0.1867	0.5139	1	0.1728	-0.3326	-0.1863	0.4662	-0.145	-0.3368	-0.2	-0.1789	-0.2346	-0.1336	-0.2647	0.0974	0.1797	-0.3449	-0.0648	-0.3033	0.2447	0.3006	-0.3554	-0.1452	-0.1056	-0.3495	0.1819	-0.3137	-0.3106	-0.2697	-0.3479	-0.2476	-0.3634	0.2172	0.3709	0.6212
K	-0.5153	-0.1685	0.5821	-0.4433	-0.4976	0.0456	0.2215	0.1728	1	-0.4901	0.0105	0.2202	-0.0466	-0.2443	0.4895	-0.2096	0.0837	-0.0085	-0.3709	0.0477	-0.0411	-0.4674	0.0301	-0.1116	-0.0707	-0.0993	-0.5808	-0.0546	0.2465	-0.5619	-0.0098	-0.511	-0.5007	-0.5356	-0.5018	0.8197	-0.5364	0.0432	0.3222	0.1923
Ca	0.6182	0.2606	-0.8798	0.857	0.9979	0.1594	-0.3267	-0.3326	-0.4901	1	0.073	-0.7449	0.1192	0.8636	0.187	0.4859	0.16	0.292	0.7869	0.3328	0.4147	0.9939	0.2566	0.7053	0.3892	0.4474	0.6399	0.5624	0.305	0.9405	-0.7808	0.9636	0.9645	0.874	0.9979	-0.4033	0.9931	-0.2323	-0.8946	-0.6669
Ti	-0.124	0.032	-0.1382	-0.2724	0.0378	0.3643	0.1232	-0.1863	0.0105	0.073	1	-0.2865	0.1868	0.0487	0.2465	0.3088	0.3009	0.6794	-0.0423	0.3701	0.2917	0.078	0.5898	0.0421	0.1908	0.1986	0.164	0.3235	0.4323	-0.1272	-0.1438	-0.0685	-0.0629	-0.21	0.0794	0.1415	0.084	-0.3615	-0.1744	0.1947
S	-0.6876	0.0044	0.5336	-0.5393	-0.7156	-0.1235	-0.0211	0.4662	0.2202	-0.7449	-0.2865	1	-0.2354	-0.5005	-0.4419	-0.354	-0.2276	-0.338	-0.4513	-0.3898	-0.3756	-0.7806	-0.3671	-0.4372	-0.3917	-0.4378	-0.7081	-0.5772	-0.3514	-0.6897	0.6342	-0.6637	-0.6627	-0.564	-0.7426	0.1821	-0.7196	0.5863	0.7909	0.7686
V	0.1584	0.0315	0.0178	0.0908	0.1041	0.1489	0.1552	-0.145	-0.0466	0.1192	0.1868	-0.2354	1	-0.0701	-0.0638	0.0992	0.2492	-0.1656	0.0363	-0.053	-0.1692	0.1252	0.1215	-0.0037	-0.0337	-0.0381	0.2735	-0.0936	-0.2154	0.1195	-0.0553	0.0775	0.0672	0.0638	0.1316	0.0412	0.0917	-0.1947	-0.0096	-0.1235
Mn	0.2476	0.243	-0.8441	0.7712	0.8774	0.1627	-0.5255	-0.3368	-0.2443	0.8636	0.0487	-0.5005	-0.0701	1	0.2724	0.4473	0.2078	0.2822	0.8715	0.1974	0.2637	0.8497	0.1407	0.8547	0.1763	0.2275	0.2637	0.4545	0.279	0.7907	-0.8273	0.8596	0.8633	0.7839	0.8662	-0.1063	0.8687	-0.1131	-0.8363	-0.4614
Fe	0.0975	0.1922	0.0367	0.0592	0.1621	0.258	0.2418	-0.2	0.4895	0.187	0.2465	-0.4419	-0.0638	0.2724	1	0.2235	0.2838	0.4266	-0.0756	0.5563	0.513	0.2108	0.5483	0.0682	0.4526	0.4476	0.0467	0.5445	0.5145	0.0805	-0.5947	0.0796	0.0876	-0.0291	0.165	0.3446	0.1234	-0.3283	-0.3971	-0.3231
Co	0.0879	-0.0608	-0.4633	0.2721	0.4749	0.3616	-0.2773	-0.1789	-0.2096	0.4859	0.3088	-0.354	0.0992	0.4473	0.2235	1	0.8444	0.7198	0.4047	0.1262	0.1513	0.494	0.2174	0.298	0.1046	0.2952	0.147	0.1584	0.2701	0.3448	-0.6002	0.3945	0.3877	0.302	0.5069	-0.1578	0.485	-0.2606	-0.5061	-0.093
Ni	-0.1948	-0.3289	-0.1263	-0.0945	0.1412	0.2131	-0.2585	-0.2346	0.0837	0.16	0.3009	-0.2276	0.2492	0.2078	0.2838	0.8444	1	0.5585	0.1421	-0.17	-0.197	0.1776	0.0079	0.1313	-0.2458	-0.0658	-0.1143	-0.1721	0.1179	0.0024	-0.3749	0.0457	0.0342	-0.0378	0.1893	0.1959	0.1637	-0.3993	-0.2323	0.065
Cu	0.0093	0.1765	-0.3159	-0.044	0.2621	0.3342	-0.0696	-0.1336	-0.0085	0.292	0.6794	-0.338	-0.1656	0.2822	0.4266	0.7198	0.5585	1	0.1181	0.5018	0.4595	0.3062	0.6186	0.1696	0.397	0.4714	0.1717	0.4558	0.7031	0.0638	-0.4252	0.1203	0.1275	-0.0516	0.2854	-0.0242	0.2845	-0.391	-0.3373	0.0106
Zn	0.2396	0.0684	-0.886	0.8065	0.8095	0.0773	-0.5197	-0.2647	-0.3709	0.7869	-0.0423	-0.4513	0.0363	0.8715	-0.0756	0.4047	0.1421	0.1181	1	0.0109	0.0471	0.7814	-0.0543	0.906	0.0268	0.1047	0.2115	0.2758	0.0092	0.7962	-0.6718	0.8581	0.8582	0.8461	0.8066	-0.2086	0.8131	-0.0068	-0.7672	-0.4107
As	0.4082	0.6004	-0.236	0.2878	0.3162	0.3624	0.4421	0.0974	0.0477	0.3328	0.3701	-0.3898	-0.053	0.1974	0.5563	0.1262	-0.17	0.5018	0.0109	1	0.9659	0.3347	0.9301	0.0159	0.9427	0.8806	0.3982	0.9259	0.6847	0.2764	-0.4685	0.2691	0.2837	0.1764	0.299	-0.1265	0.2866	-0.1176	-0.3905	-0.2809
Se	0.4452	0.5601	-0.3061	0.3743	0.4031	0.4126	0.4034	0.1797	-0.0411	0.4147	0.2917	-0.3756	-0.1692	0.2637	0.513	0.1513	-0.197	0.4595	0.0471	0.9659	1	0.4056	0.8541	0.0144	0.9522	0.9098	0.4344	0.9091	0.6497	0.3569	-0.5194	0.3576	0.3707	0.2717	0.3806	-0.2411	0.3689	-0.0587	-0.4506	-0.2743
Sr	0.6536	0.2127	-0.8545	0.8476	0.9894	0.1101	-0.2996	-0.3449	-0.4674	0.9939	0.078	-0.7806	0.1252	0.8497	0.2108	0.494	0.1776	0.3062	0.7814	0.3347	0.4056	1	0.2546	0.7109	0.3947	0.4644	0.6451	0.5687	0.3178	0.9301	-0.7813	0.953	0.9548	0.8579	0.9913	-0.4027	0.9847	-0.2606	-0.8921	-0.6824
Mo	0.299	0.5831	-0.1903	0.1271	0.2319	0.3789	0.3886	-0.0648	0.0301	0.2566	0.5898	-0.3671	0.1215	0.1407	0.5483	0.2174	0.0079	0.6186	-0.0543	0.9301	0.8541	0.2546	1	-0.04	0.8191	0.7487	0.376	0.8374	0.671	0.1711	-0.3935	0.1608	0.1725	0.0495	0.2311	-0.0226	0.2246	-0.1865	-0.3188	-0.1983
Cd	0.1013	0.0756	-0.7672	0.6189	0.7132	-0.108	-0.521	-0.3033	-0.1116	0.7053	0.0421	-0.4372	-0.0037	0.8547	0.0682	0.298	0.1313	0.1696	0.906	0.0159	0.0144	0.7109	-0.04	1	-0.0052	0.0466	0.0526	0.2554	0.2308	0.629	-0.6228	0.7244	0.734	0.6455	0.7158	0.0234	0.7241	-0.0092	-0.6612	-0.3982
Sn	0.5374	0.5727	-0.262	0.3878	0.3738	0.2962	0.5155	0.2447	-0.0707	0.3892	0.1908	-0.3917	-0.0337	0.1763	0.4526	0.1046	-0.2458	0.397	0.0268	0.9427	0.9522	0.3947	0.8191	-0.0052	1	0.9599	0.4745	0.8515	0.5781	0.3526	-0.4388	0.3274	0.3409	0.2465	0.3487	-0.3668	0.3294	-0.0703	-0.3658	-0.3105
Sb	0.5461	0.426	-0.3153	0.4323	0.4314	0.3358	0.5276	0.3006	-0.0993	0.4474	0.1986	-0.4378	-0.0381	0.2275	0.4476	0.2952	-0.0658	0.4714	0.1047	0.8806	0.9098	0.4644	0.7487	0.0466	0.9599	1	0.4353	0.7907	0.5343	0.3919	-0.5312	0.3827	0.3939	0.3003	0.414	-0.436	0.3866	-0.1243	-0.4326	-0.2644
Ba	0.8421	0.2918	-0.4173	0.5157	0.6237	0.178	0.0218	-0.3554	-0.5808	0.6399	0.164	-0.7081	0.2735	0.2637	0.0467	0.147	-0.1143	0.1717	0.2115	0.3982	0.4344	0.6451	0.376	0.0526	0.4745	0.4353	1	0.5397	0.1575	0.6525	-0.2716	0.5691	0.5632	0.5195	0.6226	-0.5324	0.6172	-0.4398	-0.5044	-0.6471
Tl	0.548	0.5367	-0.4378	0.5168	0.5537	0.3139	0.1922	-0.1452	-0.0546	0.5624	0.3235	-0.5772	-0.0936	0.4545	0.5445	0.1584	-0.1721	0.4558	0.2758	0.9259	0.9091	0.5687	0.8374	0.2554	0.8515	0.7907	0.5397	1	0.6665	0.5266	-0.6284	0.5272	0.5404	0.44	0.5356	-0.1107	0.5309	-0.1646	-0.6281	-0.5064
Pb	0.1177	0.3884	-0.2034	-0.0003	0.2726	-0.023	-0.0771	-0.1056	0.2465	0.305	0.4323	-0.3514	-0.2154	0.279	0.5145	0.2701	0.1179	0.7031	0.0092	0.6847	0.6497	0.3178	0.671	0.2308	0.5781	0.5343	0.1575	0.6665	1	0.0676	-0.3852	0.1438	0.1664	-0.0615	0.2771	0.2047	0.2883	-0.0976	-0.2708	-0.2227
Conductivit	0.7011	0.2823	-0.8358	0.954	0.9515	0.1475	-0.274	-0.3495	-0.5619	0.9405	-0.1272	-0.6897	0.1195	0.7907	0.0805	0.3448	0.0024	0.0638	0.7962	0.2764	0.3569	0.9301	0.1711	0.629	0.3526	0.3919	0.6525	0.5266	0.0676	1	-0.7055	0.9824	0.979	0.9717	0.9418	-0.4562	0.9379	-0.1321	-0.867	-0.7415
pH	-0.2987	-0.168	0.6647	-0.7176	-0.7833	-0.4391	0.1555	0.1819	-0.0098	-0.7808	-0.1438	0.6342	-0.0553	-0.8273	-0.5947	-0.6002	-0.3749	-0.4252	-0.6718	-0.4685	-0.5194	-0.7813	-0.3935	-0.6228	-0.4388	-0.5312	-0.2716	-0.6284	-0.3852	-0.7055	1	-0.7579	-0.7601	-0.6808	-0.7821	0.0144	-0.7479	0.1945	0.8901	0.483
TDS Calcu	0.6139	0.2353	-0.8845	0.9439	0.9752	0.1455	-0.3396	-0.3137	-0.511	0.9636	-0.0685	-0.6637	0.0775	0.8596	0.0796	0.3945	0.0457	0.1203	0.8581	0.2691	0.3576	0.953	0.1608	0.7244	0.3274	0.3827	0.5691	0.5272	0.1438	0.9824	-0.7579	1	0.9995	0.9683	0.968	-0.3971	0.967	-0.0828	-0.8926	-0.6737
Chloride - (	0.6138	0.2443	-0.8845	0.942	0.9756	0.1334	-0.3363	-0.3106	-0.5007	0.9645	-0.0629	-0.6627	0.0672	0.8633	0.0876	0.3877	0.0342	0.1275	0.8582	0.2837	0.3707	0.9548	0.1725	0.734	0.3409	0.3939	0.5632	0.5404	0.1664	0.979	-0.7601	0.9995	1	0.9634	0.968	-0.392	0.9675	-0.0707	-0.8915	-0.6748
Sodium - N	0.5974	0.1998	-0.8257	0.9707	0.8973	0.1722	-0.3098	-0.2697	-0.5356	0.874	-0.21	-0.564	0.0638	0.7839	-0.0291	0.302	-0.0378	-0.0516	0.8461	0.1764	0.2717	0.8579	0.0495	0.6455	0.2465	0.3003	0.5195	0.44	-0.0615	0.9717	-0.6808	0.9683	0.9634	1	0.8833	-0.4129	0.8821	-0.0121	-0.8321	-0.6425
Calcium - (	0.5992	0.2226	-0.8908	0.8549	0.9968	0.1605	-0.3526	-0.3479	-0.5018	0.9979	0.0794	-0.7426	0.1316	0.8662	0.165	0.5069	0.1893	0.2854	0.8066	0.299	0.3806	0.9913	0.2311	0.7158	0.3487	0.414	0.6226	0.5356	0.2771	0.9418	-0.7821	0.968	0.968	0.8833	1	-0.3913	0.996	-0.2228	-0.9045	-0.6561
Potassium	-0.5771	-0.1787	0.4227	-0.4325	-0.4057	-0.0112	-0.1705	-0.2476	0.8197	-0.4033	0.1415	0.1821	0.0412	-0.1063	0.3446	-0.1578	0.1959	-0.0242	-0.2086	-0.1265	-0.2411	-0.4027	-0.0226	0.0234	-0.3668	-0.436	-0.5324	-0.1107	0.2047	-0.4562	0.0144	-0.3971	-0.392	-0.4129	-0.3913	1	-0.3968	0.0428	0.2104	0.0947
Magnesiun	0.5932	0.227	-0.9083	0.8434	0.993	0.1179	-0.3894	-0.3634	-0.5364	0.9931	0.084	-0.7196	0.0917	0.8687	0.1234	0.485	0.1637	0.2845	0.8131	0.2866	0.3689	0.9847	0.2246	0.7241	0.3294	0.3866	0.6172	0.5309	0.2883	0.9379	-0.7479	0.967	0.9675	0.8821	0.996	-0.3968	1	-0.2043	-0.8908	-0.644
Sulfate - S(	-0.2232	0.0833	0.1289	0.0147	-0.2031	-0.2553	-0.1094	0.2172	0.0432	-0.2323	-0.3615	0.5863	-0.1947	-0.1131	-0.3283	-0.2606	-0.3993	-0.391	-0.0068	-0.1176	-0.0587	-0.2606	-0.1865	-0.0092	-0.0703	-0.1243	-0.4398	-0.1646	-0.0976	-0.1321	0.1945	-0.0828	-0.0707	-0.0121	-0.2228	0.0428	-0.2043	1	0.2607	0.2066
Bicarbonat	-0.4916	-0.1288	0.8237	-0.7956	-0.8953	-0.3284	0.253	0.3709	0.3222	-0.8946	-0.1744	0.7909	-0.0096	-0.8363	-0.3971	-0.5061	-0.2323	-0.3373	-0.7672	-0.3905	-0.4506	-0.8921	-0.3188	-0.6612	-0.3658	-0.4326	-0.5044	-0.6281	-0.2708	-0.867	0.8901	-0.8926	-0.8915	-0.8321	-0.9045	0.2104	-0.8908	0.2607	1	0.636
TOC	-0.7517	-0.246	0.3941	-0.6449	-0.656	0.1113	0.1621	0.6212	0.1923	-0.6669	0.1947	0.7686	-0.1235	-0.4614	-0.3231	-0.093	0.065	0.0106	-0.4107	-0.2809	-0.2743	-0.6824	-0.1983	-0.3982	-0.3105	-0.2644	-0.6471	-0.5064	-0.2227	-0.7415	0.483	-0.6737	-0.6748	-0.6425	-0.6561	0.0947	-0.644	0.2066	0.636	1