ECF-100HR3-19-0105
Revision 0

ION BALANCE CALCULATIONS FOR GROUNDWATER AT THE 100-HR-3 OPERABLE UNIT

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

CH2MHILL
Plateau Remediation Company

P.O. Box 1600
Richland, Washington 99352

Approved for Public Release;
Further Dissemination Unlimited

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ENVIRONMENTAL CALCULATION COVER PAGE

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Terms

ECF	environmental calculation file
HEIS	Hanford Environmental Information System
OU	operable unit
P&T	pump and treat
RUM	Ringold Formation upper mud (unit)

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1 Background and Purpose

The uppermost confined or semiconfined aquifer unit in the 100-HR-3 Groundwater Operable Unit (OU) at the Hanford Site is referred to as the Ringold Formation upper mud (RUM) unit aquifer. The RUM aquifer is considered a separate aquifer that lies below the unconfined aquifer. The lateral and vertical extent of the RUM aquifer, its degree of leakage or confinement by the overlying fine-grained RUM unit, and its hydraulic interconnection with the overlying unconfined aquifer and the Columbia River have been a subject of uncertainty (Chapter 3 of DOE/RL-2010-95, *Remedial Investigation/Feasibility Study for the 100-DR-1, 100-DR-2, 100-HR-1, 100-HR-2, and 100-HR-3 Operable Units*). Available data are lacking for sufficiently defining the lateral extent and nature of the RUM aquifer across the 100-HR-3 OU. Contamination found in the uppermost RUM aquifer indicates that the overlying RUM confining or semiconfining unit may be thin, permeable, or absent, which provides a pathway for contaminants to migrate from the unconfined aquifer to the RUM aquifer.

Groundwater in deeper confined aquifers typically have longer residence times and more evolved groundwater chemistries compared to shallower unconfined groundwater. This is due to various processes within the flow system, including residence time for geochemical processes to take place, chemical reactions between the groundwater and the aquifer matrix, and length of groundwater flow paths. With increased residence time, more chemical interaction with the aquifer matrix, and longer groundwater flow paths groundwater in deeper confined aquifers evolves to a predominantly sodium character and has a chemical composition distinctly different than shallower unconfined groundwater. A similar chemical composition between deep and shallow groundwater indicates mixing and suggests hydraulic interconnection between aquifers. One method for evaluating whether mixing of unconfined aquifer groundwater occurs within the RUM aquifer is to compare the general chemical composition of groundwater within these aquifers. Columbia River water is connected to unconfined aquifer groundwater, so river water chemistry must be considered in the evaluation. Because the 100-HR-3 OU pump and treat (P&T) system has impacted the unconfined aquifer, the chemistry of the treated effluent injected into the unconfined aquifer must also be considered in the evaluation.

Standard and widely accepted methods for comparing and evaluating the general chemical composition of groundwater between aquifers is to display results of major ion charge balance calculations onto Stiff (Stiff, 1951, “The Interpretation of Chemical Water Analysis by Means of Patterns”; Hem, 1985, *Study and Interpretation of the Chemical Characteristics of Natural Water*) and Piper (Piper, 1944, “A graphical procedure in the geochemical interpretation of water analyses”) (or trilinear) diagrams. These graphical methods are useful for determining similarities and/or differences in the general chemical composition of groundwater from the unconfined and RUM aquifers and Columbia River water. The diagrams can be used to show whether the aquifer units and river water are hydraulically separate or interconnected. The Stiff diagrams (or variations of the Stiff diagram such as radial plots) show differences in water composition patterns from individual water samples and are useful for displaying the patterns spatially on a map or over time. Piper diagrams visually show the distribution or trends of many water samples to indicate the effects of mixing of waters from different sources. These graphical methods require that major ion charge balance calculations are performed using complete major ion datasets for each of the aquifers and river water.

This environmental calculation file (ECF) presents the methodology, hydrochemical data input, and results of major ion charge balance calculations for groundwater within the unconfined aquifer and the RUM aquifer in the 100-HR-3 Groundwater OU at the Hanford Site. These calculation results and the graphical methods presented here provide supporting information for evaluating the inter-connection between the RUM aquifer and the overlying unconfined aquifer and Columbia River. The interpretation and evaluation of these calculation results and a map of the Stiff (or radial) diagrams are to be documented in a technical memorandum to follow.

2 Methodology

Before the chemical ion charge balance is calculated, chemistry data must be compiled from the database, lab and review qualifiers must be reviewed for data quality, and wells with complete analytical datasets must be identified. Each of these steps are necessary before the major ion balance calculation steps can be initiated. The calculation methodology includes steps to estimate bicarbonate concentrations from alkalinity data, calculate equivalent concentrations for each dissolved ionic species, and determine the major ion balance by comparing the sum of the major cations and anions. Following the calculation steps, the data are displayed graphically for comparing the chemistries between wells and between aquifers.

2.1 Chemistry Data Acquisition

Hydrochemistry data used for the major ion balance calculations and graphical analysis were exported from the Hanford Environmental Information System (HEIS) database using the Environmental Dashboard Application and imported into a Microsoft® Excel® spreadsheet. As an initial step, available major ion chemistry data from approximately 2010 through June 2019 from wells completed within the RUM aquifer and the overlying unconfined aquifer at the 100-HR-3 OU were queried from the database in July 2019. After reviewing these data, subsets of the most recent data containing all the major anions and cations for each sampling event were selected for the hydrochemistry charge balance calculations. The sample dates of the most recent complete datasets available collectively ranged from 2015 to 2019. All ions in each complete dataset have the same sample date. For multiple subsets from an individual well, the most recent sample set was typically used. Where available, filtered analyses were used for the ion balance calculations. Data indicate that the difference in the analytical results between filtered and unfiltered samples was negligible and does not change the outcome of the ion balance evaluation.

The major ion concentrations in the Environmental Dashboard Application are expressed in units of microgram per liter (µg/L), which are converted to milligram per liter (mg/L) in the spreadsheet. The compiled data, calculations, and diagram plots were generated in Microsoft Excel spreadsheets.

2.2 Chemistry Data Qualifiers

Estimated data (lab qualifier = B) were considered as detected values. The only B flagged data included in this ECF were potassium ion for a few samples. Results not valid (review qualifier = R) and suspect results (review qualifier = Y) in the HEIS database were not included in the ion balance calculations.

2.3 Wells and Constituents

A list of unconfined aquifer and RUM aquifer wells in the 100-HR-3 Groundwater OU and constituents for the major ion balance calculations are provided in Table 1. Carbonate alkalinity and fluoride were at nondetectable or low concentrations and were not included in the ion chemistry calculations. A subset of unconfined aquifer wells was selected for the major ion calculations where complete datasets are available (Figure 1). Because some areas of the OU (e.g., 100-D and 100-H Areas) have a large density of unconfined aquifer wells with at least one complete major ion dataset, only a few representative wells for these areas were arbitrarily selected for the evaluation to reduce redundancy (i.e., well datasets indicate similar chemical character). For the 2010 to 2019 period, all available datasets for unconfined aquifer wells in the Horn outside these large well density areas were included in the major ion calculations. The subset of unconfined aquifer wells spatially cover the same general area as the RUM aquifer wells.

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Table 1. List of Unconfined Aquifer Wells, RUM Aquifer Wells, and Major Ions

Unconfined Aquifer Well Name	RUM Aquifer Well Name	Major Ions
199-D3-5	199-D5-134	Bicarbonate*
199-D4-102	199-D5-141	Calcium
199-D4-103	199-H1-50	Chloride
199-D5-152	199-H2-1	Magnesium
199-D5-160	199-H3-2C	Nitrate
199-D6-3	199-H3-9	Potassium
199-D8-101	199-H3-10	Sodium
199-D8-102	199-H3-12	Sulfate
199-H1-7	199-H3-13	
199-H1-46	199-H3-22	
199-H1-47	199-H3-28	
199-H3-6	199-H3-29	
199-H3-7	199-H3-30	
199-H3-21	199-H3-32	
199-H4-5	199-H4-12C	
199-H4-85	199-H4-15CS	
199-H4-87	199-H4-90	
199-H4-88	199-H4-91	
199-H4-92	199-H7-1	
199-H6-1	699-95-45C	
199-H6-7	699-97-43C	
199-H6-8	699-97-45B	
699-88-41A	699-97-48C	
699-95-45	699-97-60	
699-95-48	699-97-61	
699-95-51		
699-96-43		
699-96-52B		
699-97-41		
699-97-45		
699-97-51A		
699-98-43		
699-98-46		
699-98-51		

*Bicarbonate is estimated from the alkalinity measured concentration.

RUM = Ringold Formation upper mud (unit)

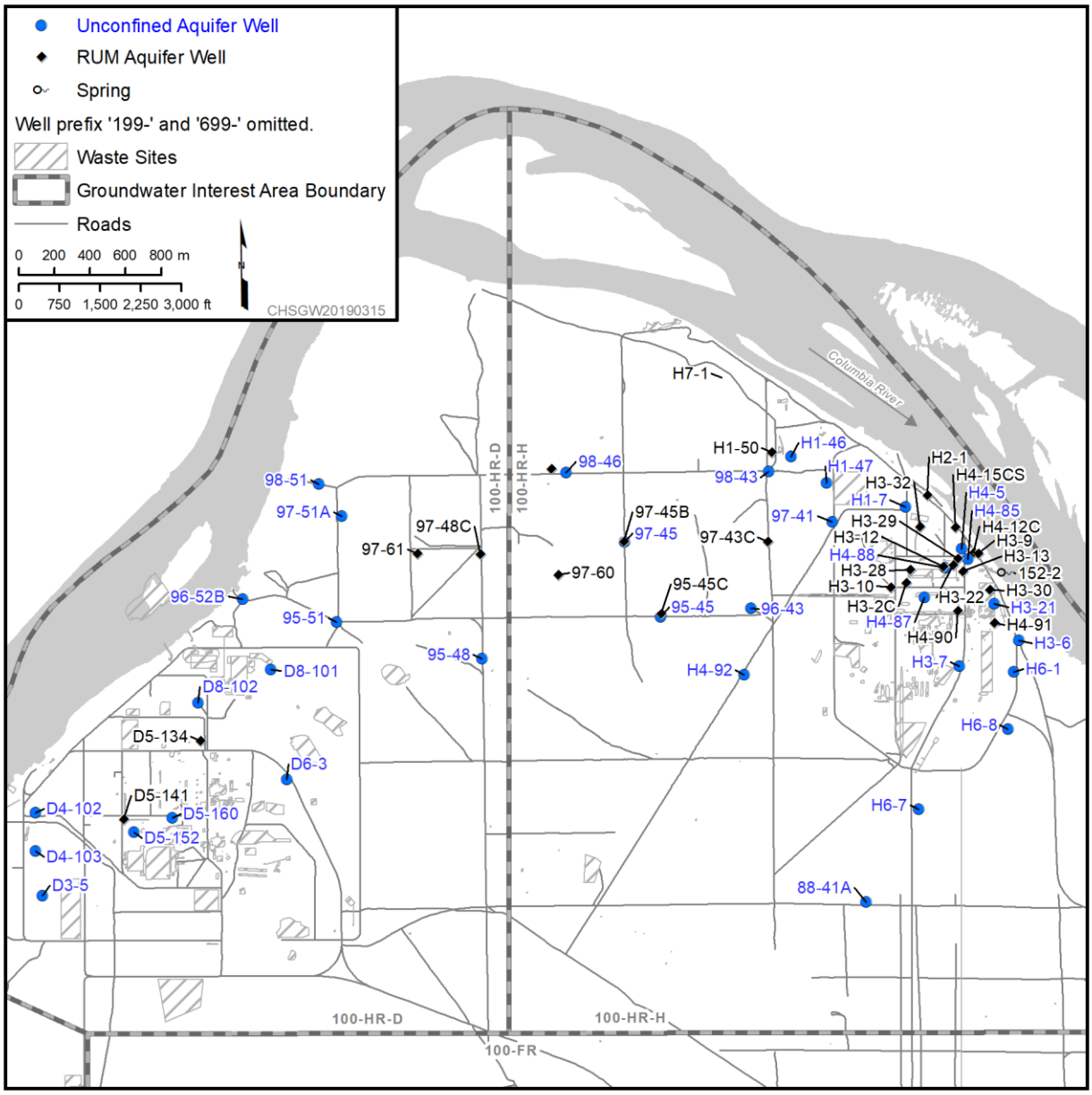

Figure 1. Map of Unconfined and RUM Aquifer Well Locations, 100-HR-3 Groundwater OU

At least one complete subset of the downloaded data was available for each RUM aquifer well in the 100-HR-3 OU except for well 199-D8-54B. No recent alkalinity data were available for estimating the bicarbonate anion concentration for RUM aquifer well 199-D8-54B, and therefore the ion balance could not be calculated for this well.

2.4 Major Ion Balance Calculation

The major ion charge-balance calculation includes estimating the concentration of bicarbonate from alkalinity concentration data, calculating the equivalent concentrations for each ion species, and calculating the total sum of cations and total sum of anions. The equivalent concentrations and percent equivalent concentrations for the cations and anions are used to graphically display the data.

2.4.1 Bicarbonate Estimate

It is common practice to estimate the concentration of bicarbonate (HCO_3) in terms of an equivalent amount of calcium carbonate ($CaCO_3$). Alkalinity concentration expressed as $CaCO_3$ is typically multiplied by 1.22 to convert to an estimate for the HCO_3 concentration, calculated as follows:

$$Alkalinity\left(\frac{mg}{L} as\ HCO_3\right)$$
$$= Alkalinity\left(\frac{mg}{L} as\ CaCO_3\right) x \left(\frac{1\ mole\ CaCO_3}{100\ g\ CaCO3}\right) x \left(\frac{2\ equivalents\ CaCO_3}{1\ mole\ CaCO3}\right) x$$
$$\left(\frac{1\ mole\ HCO_3}{1\ equivalent\ HCO_3}\right) x \left(\frac{61\ g\ HCO_3}{1\ mole\ HCO_3}\right)$$
$$= Alkalinity\left(\frac{mg}{L} as\ CaCO_3\right) x\ 1.22$$

The 1.22 multiplier above provides a good estimate for the HCO_3 concentration at pH values ranging from 4 to 9 (Deutsch, 1997, *Groundwater Geochemistry: Fundamentals and Applications to Contamination*). An equivalent is the valence (or charge) on the dissolved species. A mole is the number of atoms or molecules of a dissolved species in solution and has a mass equal to the formula weight of the constituent.

2.4.2 Equivalent Calculation Method

Major dissolved constituents in groundwater must be electrically balanced because the solutes are positively and negatively charged species. Analytical laboratory data for these species can be evaluated to determine if the measured concentrations result in an electrically neutral solution. To do this evaluation, the measured concentrations in mg/L is converted to an equivalent unit concentration for each major constituent. Equivalent unit concentrations are typically reported in milliequivalents per liter (meq/L), which is calculated using the following equation:

$$\frac{\text{Milliequivalents}}{\text{Liter}} = Measured\ concentration\left(\frac{mg}{L}\right) x \frac{1\ mole}{formula\ weight\ in\ grams} x \frac{1\ equivalent}{1\ mole} x \left(\frac{1\ gram}{1000\ mg}\right) x \left(\frac{1000\ milliequivalents}{1\ equivalent}\right)$$

Table 2 shows the molecular weight and valence (or charge) for each major cation and anion species included in this major ion balance calculation procedure.

Table 2. Formula Weight and Valence for Each Major Ion

Major Ion	Formula Weight (g)	Valence (or Charge)
Ca^{2+}	40.08	+2
Mg^{2+}	24.31	+2
Na^{+}	23.00	+1
K^{+}	39.10	+1
HCO_3^{-}	61.02	-1
Cl^{-}	35.45	-1
NO_3^{-}	62.00	-1
SO_4^{2-}	96.06	-2

2.4.3 Major Ion Balance

When all the major anions and cations have been analyzed for a sample, the total sum of the anions in meq/L should equal the total sum of the cations in meq/L. The electrical balance of the groundwater sample solution is calculated by comparing the sum of cation equivalents with the sum of anion equivalents. The following equation is used to make the cation equivalent and anion equivalent comparison:

$$Cation\ anion\ balance = \frac{\Sigma\left(\text{cations}, \frac{\text{meq}}{\text{L}}\right) - \Sigma\left(\text{anions}, \frac{\text{meq}}{\text{L}}\right)}{\Sigma\left(\text{cations}, \frac{\text{meq}}{\text{L}}\right) + \Sigma\left(\text{anions}, \frac{\text{meq}}{\text{L}}\right)}\ x\ 100\%$$

The anion-cation balance in a water sample can serve as a check on the accuracy of the major ion concentration values. The difference between the anion and cation sums should generally not exceed 5% of the total sum of anions and cations (Deutsch, 1997). The most common source of anion-cation charge balance errors for water samples are associated with the alkalinity measurement used to determine bicarbonate concentration (Fritz, 1994, “A survey of charge-balance errors on published analyses of potable ground and surface waters”).

2.4.4 Graphical Methods

A variety of graphical methods are available for representing the analyses to provide a visual means for comparing the major cations and anions between well locations and between aquifers. These graphical methods are useful for detecting and identifying mixing of waters of different composition and identifying chemical processes as groundwater evolves. Stiff diagrams and Piper (Piper, 1944) (or trilinear) diagrams were used to graphically display the data analysis conducted in this ECF. Radial diagrams are an alternative graphical method to the Stiff diagrams to compare major cations and anions (Lloyd and Heathcote, 1985, *Natural Inorganic Hydrochemistry in Relation to Groundwater*). The radial diagrams are not included in this ECF but are available in the supporting calculation files.

A Stiff diagram is a simple graphical method for plotting the major anion and cation analyses from individual water samples (Stiff, 1951; Hem, 1985). The Stiff plotting method uses parallel horizontal axes extending as units of meq/L on either side of a zero vertical axis (Figure 2). Cations Na+K, Ca, and Mg are typically plotted on the left side of the zero vertical axis, and anions Cl, HCO_3, and SO_4 are typically plotted on the right side of the axis. Because nitrate is considered a major anion in groundwater at some well locations within the 100-HR-3 OU area, this anion must be included in the ion balance calculations. Nitrate is typically plotted with chloride on the Cl horizontal axis (i.e., Cl+NO_3). The resulting data points on the diagram are connected to provide an irregular polygonal shape. The Stiff diagrams can be used to show differences in water composition patterns and make visual comparisons between chemical analyses, such as displaying the Stiff diagrams on a map. When comparing Stiff diagrams between water samples, each diagram must have the same ionic species and plotted in the same order and on the same horizontal axes.

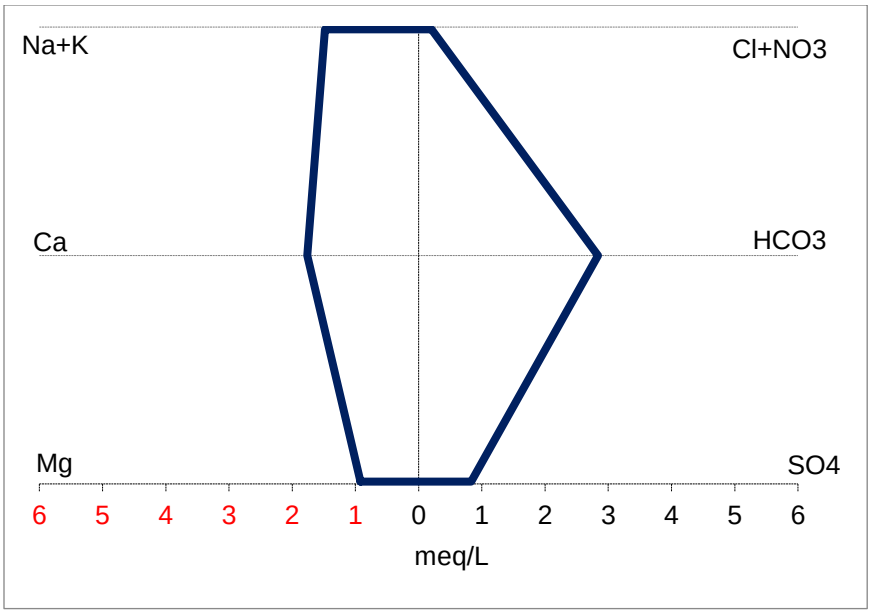

Figure 2. Example Stiff Diagram

For graphically representing a large number of analyses, the Piper or trilinear diagram is used to display major anion and cation compositions (Piper, 1944). On this diagram, the major ions are plotted on separate cation and anion triangles as relative concentrations in percent meq/L for each respective triangle (Figure 3). The three axes on the cation triangle include Ca, Mg, and Na+K. For the anion triangular plot, the percent meq/L axes are $Cl+NO_3$, SO_4, and CO_3+HCO_3. The plots on the cation and anion triangles are projected to an intersecting point on a diamond-shaped diagram, which represents both cations and anions. The opposing axes on the diamond plot are grouped as Na+K and Ca+Mg for the cations and the opposing axes for the anions are grouped as $SO_4+Cl+NO_3$ and CO_3+HCO_3. The Na+K and CO_3+HCO_3 axes on the diamond plot correspond to the same axes on the respective cation and anion triangular plots. The trilinear diagram can visually show groupings or trends in the data and conveniently show the effects of mixing of waters from different sources. These diagrams can also be used to classify groundwater into different water types based on the major ion composition.

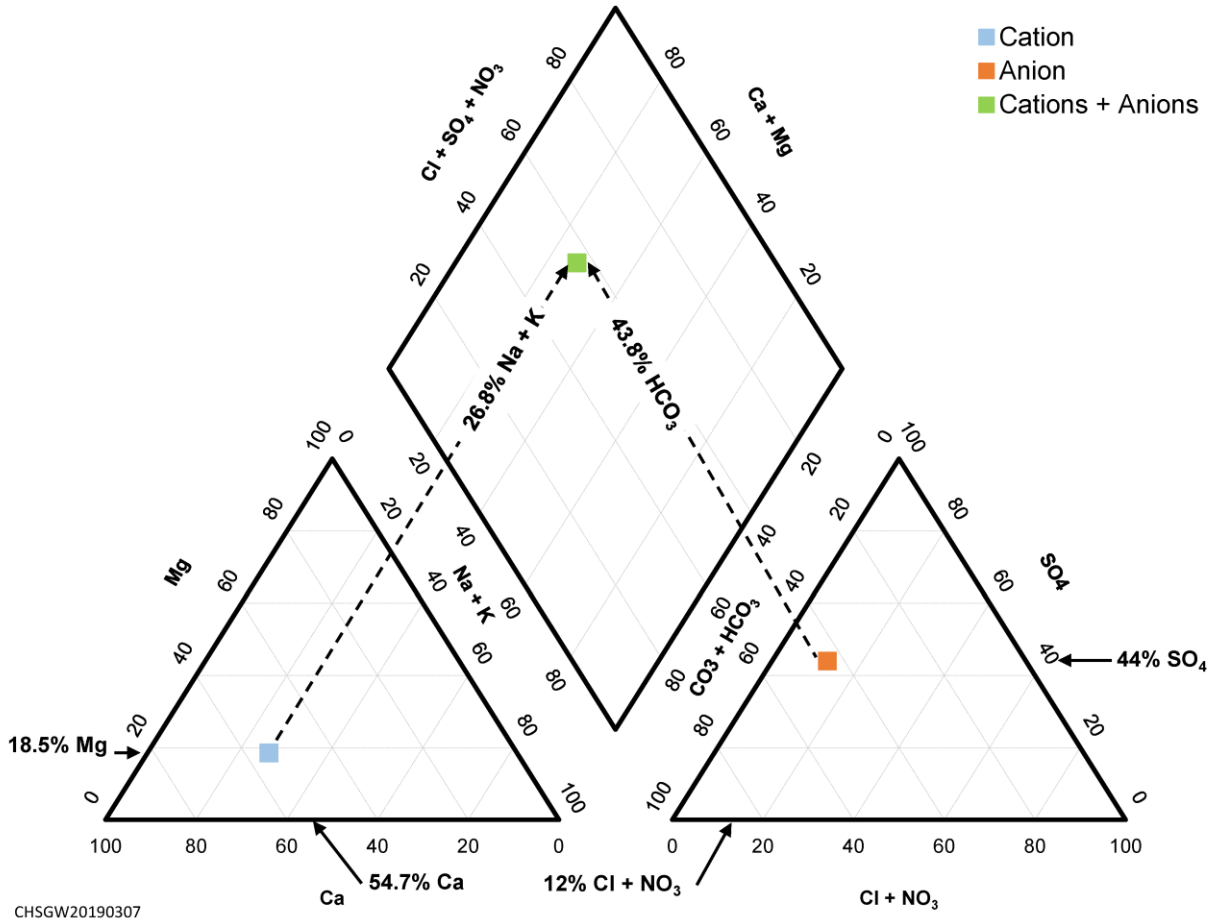

Figure 3. Example Piper (or Trilinear) Diagram

3 Assumptions and Inputs

3.1 Alkalinity

Alkalinity is the capacity of an aqueous solution to react with and neutralize an acid. It is assumed that all alkalinity in the sample solution is present as HCO_3. Bicarbonate is the most dominant component of alkalinity in shallow groundwater with pH ranging up to about 9 (Deutsch, 1997). The pH of unconfined aquifer groundwater samples used in this ECF ranged from 6.9 to 8.1 and the pH of RUM aquifer samples ranged from 7.4 to 8.9.

Higher values of pH within the pH range of 4 to 9 affect the estimate for HCO_3 concentration only slightly. At a pH of 9 the estimate for HCO_3 concentration using the 1.22 multiplier is about 10% lower than the estimate calculated using equations that incorporate the equilibrium constant for the speciation reaction and the pH measurement (refer to Equations 1-8 and 1-13 in Deutsch, 1997). This difference in how the HCO_3 concentration is estimated at high pH values does not significantly affect the ion balance calculation results.

Carbonate alkalinity (i.e., alkalinity present as CO_3) was negligible and therefore was not included in the ion balance calculations. Carbonate alkalinity was not detected in any of the unconfined aquifer samples and was not detected in most of the RUM aquifer well samples. For one RUM aquifer well (199-H3-30), carbonate alkalinity was estimated by the analytical lab to be 1.6 mg/L (lab qualifier = B). Recent analyses of carbonate alkalinity were not available for several of the RUM aquifer wells; however, historical data show nondetections of carbonate alkalinity for many of these wells.

When the alkalinity analysis is used to estimate the bicarbonate concentration in solution, it is assumed that all other possible titratable species contributing to alkalinity in the solution are present in minor concentrations. This is a good assumption at pH values less than about 9 (Deutsch, 1997). The pH measurements for all analyses used in this ECF were less than 9.

3.2 Analytical Data

A summary of the analytical cation, anion, and alkalinity data for the unconfined and RUM aquifer datasets are presented in Tables 3 and 4, respectively. A summary of the Columbia River sample analytical data is presented in Table 5. These data were exported from the HEIS database and used for performing the calculation steps presented in Chapter 5. Complete datasets for performing the ion balance calculations for the treated effluent water injected into the unconfined aquifer are not available for the DX and HX P&T systems.

Table 3. Unconfined Aquifer Analytical Data

Unconfined Aquifer Well Name	Sample Date	Ca	Mg	K	Na	Cl	NO_3	SO_4	Alkalinity
199-D3-5	10/30/2015	73.0	13.0	4.5*	14.8	20.0	35.4	97.0	110
199-D4-102	5/17/2019	74.0	18.0	4.8	13.2	14.1	1.1	165	120
199-D4-103	5/17/2019	83.0	16.7	4.9	19.3	15.0	10.6	160	122
199-D5-152	8/10/2017	82.0	19.0	5.4	31.0	14.7	23.7	183	126
199-D5-160	5/10/2019	71.6	22.0	5.3	17.0	17.0	31.4	150	95.9
199-D6-3	11/8/2015	68.2	19.1	6.6	39.5	16.0	25.2	190	98
199-D8-101	10/28/2015	89.9	13.8	5.7	30.9	17.0	26.6	200	126
199-D8-102	10/11/2016	91.0	22.4	6.6	18.9	18.0	20.8	190	142
199-H1-7	12/1/2015	56.4	11.6	5.8	28.3	9.0	23.5	110	114
199-H1-46	12/11/2017	47.0	10.0	4.2	13.0	8.9	20.4	51	120
199-H1-47	6/19/2019	40.3	9.5	4.3	15.8	9.6	14.2	49.5	109
199-H3-6	5/11/2016	60.0	7.9	3.5	21.0	8.3	13.7	95	114
199-H3-7	5/20/2019	47.4	11.1	5.6	30.9	11.0	14.2	94	115
199-H3-21	5/20/2019	53.0	9.3	3.9	21.0	10.0	26.3	57.9	116
199-H4-5	12/1/2015	60.2	11.8	5.1	13.1	8.0	13.7	94	113

Table 3. Unconfined Aquifer Analytical Data

Unconfined Aquifer Well Name	Sample Date	Ca	Mg	K	Na	Cl	NO_3	SO_4	Alkalinity
199-H4-85	2/10/2016	51.6	9.4	4.4	25.5	6.5	20.8	86	117
199-H4-87	11/1/2018	74.2	15.6	5.6	21.8	24.0	39.0	110	145
199-H4-88	5/1/2019	92.9	19.2	7.0	29.3	25.6	47.8	116	188
199-H4-92	4/16/2019	44.0	15.0	5.5	25.0	9.5	15.9	81.1	120
199-H6-1	11/13/2015	61.9	10.9	3.7	23.6	11.0	22.6	120	112
199-H6-7	6/26/2015	45.0	15.5	5.6	25.3	18.4	20.9	59.1	136
199-H6-8	6/26/2015	71.5	17.1	6.4	24.4	31.4	23.5	126	124
699-88-41A	11/30/2018	46.5	17.0	5.7	30.1	21.0	21.7	73	126
699-95-45	11/4/2015	51.6	14.0	5.4	27.7	8.8	13.1	110	112
699-95-48	11/5/2015	49.4	13.1	5.5	24.2	15.0	15.5	77	108
699-95-51	11/5/2015	86.3	18.0	6.4	22.5	16.0	25.2	190	102
699-96-43	10/29/2015	55.0	13.3	5.6	24.0	19.0	22.1	69	124
699-96-52B	11/30/2015	91.3	14.4	6.0	17.9	14.5	23.0	193	97.2
699-97-41	11/4/2015	49.4	12.1	5.2	20.8	16.0	21.7	65	114
699-97-45	10/28/2015	47.1	11.5	4.4	22.3	15.0	20.4	66	113
699-97-51A	11/4/2015	78.4	17.0	4.3	15.9	14.1	22.0	174	92
699-98-43	10/30/2015	51.4	10.3	4.9*	17.1	12.0	20.8	55	112
699-98-46	11/1/2015	49.6	11.2	4.2	16.4	15.0	21.2	70	104
699-98-51	11/1/2015	74.1	18.3	3.4	17.0	13.7	21.6	180	85.2

Note: All values recorded in mg/L.

*Detected at less than the analyzing laboratory's estimated quantitation limit but greater than the method detection limit.

Table 4. RUM Aquifer Analytical Data

RUM Aquifer Well Name	Sample Date	Ca	Mg	K	Na	Cl	NO_3	SO_4	Alkalinity
199-D5-134	10/28/2015	35.3	11.2	6.3	30.4	7.0	0.4	40.0	142
199-D5-141	10/26/2017	15.0	3.3	6.1	33.6	9.6	0.1	45.0	62.2
199-H1-50	6/14/2019	22.8	7.6	4.5	7.7	1.0	1.2	11.0	106
199-H2-1	11/16/2016	32.7	7.7	4.4	20.1	10.0	2.6	33.0	116
199-H3-2C	12/11/2018	32.4	12.2	5.0	13.2	5.6	8.9	40.0	108
199-H3-9	9/13/2018	24.3	9.0	3.7	6.1	1.9	4.9	18.0	98.2
199-H3-10	11/8/2015	22.7	6.9	6.4	26.0	1.5	2.1	21.0	122
199-H3-12	3/6/2019	35.6	14.0	4.5	5.1	3.9	11.1	29.5	125
199-H3-13	3/7/2019	39.4	14.3	4.3	4.5	2.2	60.6	23.7	101
199-H3-22	2/20/2019	41.6	15.1	5.0	6.0	4.1	48.7	29.0	114
199-H3-28	6/19/2019	38.0	14.0	5.1	9.4	9.6	15.2	45.0	108
199-H3-29	6/26/2019	53.5	19.6	5.5	5.7	4.8	100	31.9	103
199-H3-30	4/9/2019	29.3	9.9	3.8	5.8	3.8	3.5	34.6	98.8
199-H3-32	2/20/2019	52.5	11.2	4.3	13.7	11.0	16.4	65.0	119
199-H4-12C	9/13/2018	29.6	10.7	4.2	5.9	2.8	20.4	24.0	93.8
199-H4-15CS	10/20/2017	28.2	10.0	4.2*	4.8	2.9	5.8	19.6	102
199-H4-90	12/8/2015	41.0	13.0	5.2	12.0	17.0	18.1	44.0	100
199-H4-91	12/8/2015	35.7	11.0	4.8	9.1	11.0	17.3	38.0	92.5
199-H7-1	6/21/2019	33.5	9.8	4.1	20.5	26.2	5.3	39.5	82.5
699-95-45C	5/1/2019	27.1	10.5	4.8	18.3	1.2	1.7	24.1	123
699-97-43C	11/9/2016	24.3	8.1	4.3*	4.8	4.4	3.7	15.0	88.0
699-97-45B	11/8/2016	24.0	9.2	3.7	3.3	5.0	2.8	12.0	86.0
699-97-48C	11/8/2016	31.7	10.6	4.1	3.4	5.0	3.7	37.0	94
699-97-60	5/15/2019	25.8	11.6	4.9*	13.3	5.2	2.2	44.0	82.8
699-97-61	5/23/2019	29.0	11.0	4.0	4.0	4.9	4.4	31.0	100

Note: All values recorded in mg/L.

*Detected at less than the analyzing laboratory's estimated quantitation limit but greater than the method detection limit.

RUM = Ringold Formation upper mud (unit)

Table 5. Columbia River Sample Analytical Data

Sampling Location Name	Sample Date	Ca	Mg	K	Na	Cl	NO_3	SO_4	Alkalinity
Spring 152-2	9/27/2018	21.7	4.5	1.2	2.9	2.6	2.2	11.0	67.8
100-N River	9/28/2005	19.0	4.6	0.7	2.0	0.9	0.3	8.1	60.0

Note: All values recorded in mg/L.

4 Software Applications

Microsoft Office 2016 Excel was used to perform the calculations and plot the data. All supporting calculations, Stiff diagram plots, and radial diagram plots are included in files *Rum_aquifer_balance_calculations.xlsx*, *Unconfined_aquifer_balance_calculations.xlsx* and *100-N Area_River_balance_calculations.xlsx*. A Microsoft Office spreadsheet tool developed by the United States Geological Survey, Nevada District, was used to prepare the Piper plot (USGS, 2004, *Excel for Hydrology*). The Piper plot was generated in the file *PiperPlot_HR-3.xls*.

5 Calculations

This section shows the calculation procedure for estimating bicarbonate, for calculating the equivalent for each ion species, and for determining the cation-anion balance. One dataset is used here as an example (i.e., RUM aquifer well 199-D5-134) for each of the calculation steps. A summary of the calculations for the unconfined aquifer wells, RUM aquifer wells, and Columbia River spring samples are presented. Diagrams for displaying the analyses are presented in Appendices A, B, and C.

5.1 Bicarbonate Estimates

The first step in the calculation procedure is to estimate the bicarbonate concentration from the alkalinity data. The concentration of bicarbonate was estimated from measured alkalinity concentration data for each unconfined and RUM aquifer dataset by using the equation presented in the Section 2.4.1. An example estimate of bicarbonate concentration in terms of an equivalent amount of $CaCO_3$ from the measured alkalinity concentration at well 199-D5-134 is calculated as follows:

$$Alkalinity\ \left(\frac{mg}{L} as\ HCO_3\right) = Alkalinity\ \left(\frac{mg}{L} as\ CaCO_3\right)\ x\ 1.22$$
$$= 142\frac{mg}{L}x\ 1.22 = 173\ mg/L$$

5.2 Equivalent Calculations

The equivalent calculation method introduced in Section 2.4.2 was used to calculate the meq/L of each major cation and anion species for each dataset. An example summary of the equivalents calculation procedure for one dataset (RUM aquifer well 199-D5-134) is shown in Table 6. An example for calculating the equivalents for one of the constituents within the dataset, Ca, is as follows:

$$Ca\left(\frac{\text{meq}}{\text{L}}\right) = \left(\frac{35.3\ mg}{L}\right) x \left(\frac{1\ mole}{40.08\ g}\right) x \left(\frac{2\ equivalents}{1\ mole}\right) x \left(\frac{1\ g}{1000\ mg}\right) x \left(\frac{1000\ milliequivalents}{1\ equivalent}\right) = 1.76\frac{meq}{L}$$

All other constituents listed in Table 6 are calculated in a similar manner to determine relative concentrations in units of meq/L. These relative concentrations are then plotted on a Stiff diagram for each dataset.

Table 6. Example of Equivalent Calculation Procedure for One Dataset

Major Ion	Measured Concentration (mg/L)	Formula Weight (g)	Valence (or Charge)	Calculated (meq/L)
Ca^{2+}	35.3	40.08	+2	1.76
Mg^{2+}	11.2	24.31	+2	0.93
Na^{+}	30.4	23.00	+1	1.32
K^{+}	6.3	39.10	+1	0.16
			Sum of Cation Equivalents	**4.16**
HCO_3^-	173*	61.02	-1	2.84
Cl^-	7.0	35.45	-1	0.20
NO_3^-	0.42	62.00	-1	0.01
SO_4^{2-}	40.0	96.06	-2	0.83
			Sum of Anion Equivalents	**3.88**

*Bicarbonate is estimated from the alkalinity measured concentration of 142 mg/L, which is expressed as $CaCO_3$.

5.3 Major Ion Balance Calculations

The cation-anion balance was calculated for each unconfined and RUM aquifer dataset to compare the sum of cation equivalents with the sum of anion equivalents. From the example, in Table 6 the sum of the cation equivalents is 4.16 meq/L and the sum of the anion equivalents is 3.88 meq/L. The cation-anion balance calculation for RUM aquifer well 199-D5-134 is as follows:

$$Cation\ anion\ balance = \frac{\left(4.16\frac{\text{meq}}{\text{L}} - 3.88\ \frac{\text{meq}}{\text{L}}\right)}{\left(4.16\frac{\text{meq}}{\text{L}} + 3.88\ \frac{\text{meq}}{\text{L}}\right)}\ x\ 100\% = 3.6\%$$

A balance calculation of 3.6% is considered reasonable because it does not exceed 5% and suggests there are no significant errors in the concentrations reported for the major ions.

6 Results

A summary of the ion balance calculations for the unconfined and RUM aquifer wells is presented in Tables 7 and 8, respectively. A summary of the ion balance calculations for a spring sampling location along the Columbia River shore and a river water sample is presented in Table 9. These calculations include estimates of bicarbonate concentration, equivalent calculations, and the percent difference between the sum of cation and anion equivalents. The results and graphical diagrams indicate that calcium and bicarbonate dominate the chemical composition of groundwater within the RUM aquifer at the 100 HR-3 OU and Columbia River water. The chemical composition of groundwater within the unconfined aquifer is dominated by calcium and a mix of bicarbonate and sulfate. An evaluation of this dissimilar groundwater will be discussed in a technical memorandum to follow.

The cation, anion, and total sum of equivalent concentration ranges for the unconfined aquifer are generally higher than equivalent ranges calculated for the RUM aquifer (Table 10). The largest contributions to the higher equivalent ranges for the unconfined aquifer are Ca and SO_4 ion.

The cation anion balance calculations indicate that the percent differences between the sum of cation and anion equivalents did not exceed 5%, suggesting the concentrations reported for the major ions have no significant analytical errors.

The equivalent calculation results in Tables 7, 8, and 9 are used to graphically display the analyses on Stiff diagrams. Because of the large number of plots, the Stiff diagrams for the 100-HR-3 OU unconfined and RUM aquifer wells are provided in Appendices A and B. Stiff diagrams for the Columbia River water samples are provided in Appendix C. The Stiff diagrams, alternative radial plots for the same datasets, and supporting data and calculations are provided in a link to the Microsoft spreadsheet data calculation files in Appendix D.

A Piper plot showing a comparison of the chemical composition between the unconfined aquifer, the RUM aquifer, and spring and river water representing Columbia River water is presented in Figure 4. The equivalent calculations in Tables 7, 8, and 9 are used to calculate the relative concentrations as percent meq/L for each of the cation and anion triangles. The plots on the cation and anion triangles are projected to an intersecting point on the diamond-shaped portion of the diagram, which represents both cations and anions. The relative concentrations as percent meq/L for each of the unconfined and RUM aquifer wells and Columbia River water samples are provided in Table 11.

Table 7. Unconfined Aquifer Major Ion Balance Calculation Results

Unconfined Aquifer Well Name	HCO_3 Estimate (mg/L)	Ca (meq/L)	Mg (meq/L)	K (meq/L)	Na (meq/L)	Total Cations (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	NO_3 (meq/L)	SO_4 (meq/L)	Total Anions (meq/L)	Cation Anion Balance (% Difference)
199-D3-5	134.1	3.65	1.08	0.12	0.64	5.47	2.20	0.56	0.57	2.02	5.35	1.1
199-D4-102	146.3	3.70	1.50	0.12	0.57	5.87	2.40	0.40	0.02	3.44	6.25	-3.1
199-D4-103	148.7	4.15	1.39	0.12	0.84	6.48	2.44	0.42	0.17	3.33	6.36	0.9
199-D5-152	153.6	4.10	1.58	0.14	1.35	7.14	2.52	0.41	0.38	3.81	7.12	0.1
199-D5-160	116.9	3.58	1.83	0.13	0.74	6.26	1.92	0.48	0.51	3.12	6.03	1.9
199-D6-3	119.5	3.41	1.59	0.17	1.72	6.86	1.96	0.45	0.41	3.96	6.77	0.7
199-D8-101	153.6	4.49	1.15	0.15	1.34	7.11	2.52	0.48	0.43	4.16	7.59	-3.3
199-D8-102	173.1	4.54	1.86	0.17	0.82	7.37	2.84	0.51	0.34	3.96	7.64	-1.8
199-H1-7	139.0	2.82	0.97	0.15	1.23	5.15	2.28	0.25	0.38	2.29	5.20	-0.5
199-H1-46	146.3	2.35	0.83	0.11	0.57	3.84	2.40	0.25	0.33	1.06	4.04	-2.6
199-H1-47	132.9	2.01	0.79	0.11	0.69	3.59	2.18	0.27	0.23	1.03	3.71	-1.7
199-H3-6	139.0	3.00	0.66	0.09	0.91	4.65	2.28	0.23	0.22	1.98	4.71	-0.7
199-H3-7	140.2	2.37	0.92	0.14	1.34	4.76	2.30	0.31	0.23	1.96	4.80	-0.3
199-H3-21	141.4	2.65	0.77	0.10	0.91	4.42	2.32	0.28	0.42	1.21	4.23	2.2
199-H4-5	137.8	3.01	0.98	0.13	0.57	4.67	2.26	0.23	0.22	1.96	4.66	0.1
199-H4-85	142.6	2.58	0.79	0.11	1.11	4.57	2.34	0.18	0.34	1.79	4.65	-0.8
199-H4-87	176.8	3.71	1.30	0.14	0.95	6.08	2.90	0.68	0.63	2.29	6.49	-3.3
199-H4-88	229.2	4.64	1.60	0.18	1.27	7.67	3.76	0.72	0.77	2.42	7.67	0.01
199-H4-92	146.3	2.20	1.25	0.14	1.09	4.66	2.40	0.27	0.26	1.69	4.61	0.5

Table 7. Unconfined Aquifer Major Ion Balance Calculation Results

Unconfined Aquifer Well Name	HCO_3 Estimate (mg/L)	Ca (meq/L)	Mg (meq/L)	K (meq/L)	Na (meq/L)	Total Cations (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	NO_3 (meq/L)	SO_4 (meq/L)	Total Anions (meq/L)	Cation Anion Balance (% Difference)
199-H6-1	136.6	3.09	0.91	0.10	1.03	5.11	2.24	0.31	0.36	2.50	5.41	-2.9
199-H6-7	165.8	2.25	1.29	0.14	1.10	4.76	2.72	0.52	0.34	1.23	4.81	-0.5
199-H6-8	151.2	3.57	1.42	0.16	1.06	6.20	2.48	0.89	0.38	2.62	6.37	-1.3
699-88-41A	153.6	2.32	1.41	0.15	1.31	5.17	2.52	0.59	0.35	1.52	4.98	1.9
699-95-45	136.6	2.58	1.16	0.14	1.20	5.07	2.24	0.25	0.21	2.29	4.99	0.8
699-95-48	131.7	2.47	1.09	0.14	1.05	4.73	2.16	0.42	0.25	1.60	4.44	3.3
699-95-51	124.4	4.31	1.50	0.16	0.98	6.93	2.04	0.45	0.41	3.96	6.85	0.6
699-96-43	151.2	2.75	1.11	0.14	1.04	5.03	2.48	0.54	0.36	1.44	4.81	2.2
699-96-52B	118.5	4.56	1.20	0.15	0.78	6.67	1.94	0.41	0.37	4.02	6.74	-0.5
699-97-41	139.0	2.47	1.01	0.13	0.90	4.50	2.28	0.45	0.35	1.35	4.43	0.7
699-97-45	137.8	2.35	0.96	0.11	0.97	4.38	2.26	0.42	0.33	1.37	4.39	-0.1
699-97-51A	112.2	3.92	1.41	0.11	0.69	6.11	1.84	0.40	0.35	3.62	6.21	-0.8
699-98-43	136.6	2.57	0.86	0.13	0.74	4.28	2.24	0.34	0.34	1.15	4.06	2.7
699-98-46	126.8	2.48	0.93	0.11	0.71	4.22	2.08	0.42	0.34	1.46	4.30	-1.0
699-98-51	103.9	3.70	1.52	0.09	0.74	6.03	1.70	0.39	0.35	3.75	6.18	-1.3
Average	***142.4***	***3.18***	***1.19***	***0.13***	***0.97***	***5.46***	***2.33***	***0.42***	***0.35***	***2.39***	***5.50***	***-0.21***
Minimum	***103.9***	***2.01***	***0.66***	***0.09***	***0.57***	***3.59***	***1.70***	***0.18***	***0.02***	***1.03***	***3.71***	***-3.3***
Maximum	***229.2***	***4.64***	***1.86***	***0.18***	***1.72***	***7.67***	***3.76***	***0.89***	***0.77***	***4.16***	***7.67***	***3.3***

Table 8. RUM Aquifer Major Ion Balance Calculation Results

RUM Aquifer Well Name	HCO_3 Estimate (mg/L)	Ca (meq/L)	Mg (meq/L)	K (meq/L)	Na (meq/L)	Total Cations (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	NO_3 (meq/L)	SO_4 (meq/L)	Total Anions (meq/L)	Cation Anion Balance (% Difference)
199-D5-134	173.1	1.76	0.93	0.16	1.32	4.17	2.84	0.20	0.01	0.83	3.87	3.6
199-D5-141	75.8	0.75	0.27	0.16	1.46	2.63	1.24	0.27	0.002	0.94	2.45	3.6
199-H1-50	129.2	1.14	0.63	0.12	0.33	2.21	2.12	0.03	0.02	0.23	2.39	-4.0
199-H2-1	141.4	1.63	0.64	0.11	0.87	3.25	2.32	0.28	0.04	0.69	3.33	-1.2
199-H3-2C	131.7	1.62	1.02	0.13	0.57	3.32	2.16	0.16	0.14	0.83	3.29	0.5
199-H3-9	119.7	1.21	0.75	0.10	0.27	2.32	1.96	0.05	0.08	0.37	2.47	-3.2
199-H3-10	148.7	1.13	0.58	0.16	1.13	3.00	2.44	0.04	0.03	0.44	2.95	0.8
199-H3-12	152.4	1.78	1.16	0.12	0.22	3.27	2.50	0.11	0.18	0.61	3.40	-2.0
199-H3-13	123.1	1.97	1.19	0.11	0.20	3.45	2.02	0.06	0.98	0.49	3.55	-1.5
199-H3-22	139.0	2.08	1.26	0.13	0.26	3.71	2.28	0.12	0.79	0.60	3.78	-1.0
199-H3-28	131.7	1.90	1.16	0.13	0.41	3.59	2.16	0.27	0.25	0.94	3.61	-0.3
199-H3-29	125.6	2.67	1.63	0.14	0.25	4.67	2.06	0.14	1.61	0.66	4.47	2.2
199-H3-30	120.5	1.46	0.83	0.10	0.25	2.63	1.97	0.11	0.06	0.72	2.86	-4.2
199-H3-32	145.1	2.62	0.93	0.11	0.60	4.25	2.38	0.31	0.26	1.35	4.31	-0.7
199-H4-12C	114.4	1.48	0.89	0.11	0.26	2.72	1.87	0.08	0.33	0.50	2.78	-1.1
199-H4-15CS	124.4	1.41	0.83	0.11	0.21	2.55	2.04	0.08	0.09	0.41	2.62	-1.5
199-H4-90	121.9	2.05	1.08	0.13	0.52	3.77	2.00	0.48	0.29	0.92	3.69	1.1
199-H4-91	112.8	1.78	0.92	0.12	0.39	3.20	1.85	0.31	0.28	0.79	3.23	-0.4
199-H7-1	100.6	1.67	0.82	0.11	0.89	3.48	1.65	0.74	0.08	0.82	3.29	2.7

Table 8. RUM Aquifer Major Ion Balance Calculation Results

RUM Aquifer Well Name	HCO_3 Estimate (mg/L)	Ca (meq/L)	Mg (meq/L)	K (meq/L)	Na (meq/L)	Total Cations (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	NO_3 (meq/L)	SO_4 (meq/L)	Total Anions (meq/L)	Cation Anion Balance (% Difference)
699-95-45C	150.0	1.35	0.87	0.12	0.80	3.14	2.46	0.03	0.03	0.50	2.99	2.3
699-97-43C	107.3	1.21	0.68	0.11	0.21	2.20	1.76	0.12	0.06	0.31	2.19	0.1
699-97-45B	104.9	1.20	0.77	0.09	0.14	2.19	1.72	0.14	0.04	0.25	2.15	0.9
699-97-48C	114.6	1.58	0.88	0.11	0.15	2.71	1.88	0.17	0.06	0.77	2.88	-3.1
699-97-60	100.9	1.29	0.97	0.12	0.58	2.94	1.65	0.15	0.03	0.92	2.75	3.4
699-97-61	121.9	1.45	0.92	0.10	0.17	2.63	2.00	0.14	0.07	0.65	2.85	-4.1
Average	***125.2***	***1.61***	***0.90***	***0.12***	***0.50***	***3.12***	***2.05***	***0.18***	***0.23***	***0.66***	***3.13***	***-0.3***
Minimum	***75.8***	***0.75***	***0.27***	***0.09***	***0.14***	***2.19***	***1.24***	***0.03***	***0.002***	***0.23***	***2.15***	***-4.2***
Maximum	***173.1***	***2.67***	***1.63***	***0.16***	***1.46***	***4.67***	***2.84***	***0.74***	***1.61***	***1.35***	***4.47***	***3.6***

RUM = Ringold Formation upper mud (unit)

Table 9. Columbia River Major Ion Balance Calculation Results

Sample Location Name	HCO_3 Estimate (mg/L)	Ca (meq/L)	Mg (meq/L)	K (meq/L)	Na (meq/L)	Total Cations (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	NO_3 (meq/L)	SO_4 (meq/L)	Total Anions (meq/L)	Cation Anion Balance (% Difference)
Spring 152-2	82.7	1.08	0.37	0.03	0.13	1.61	1.35	0.07	0.04	0.23	1.69	-2.6
100-N River	73.2	0.95	0.38	0.02	0.09	1.43	1.20	0.02	0.004	0.17	1.40	1.2

Table 10. Equivalent Concentration Ranges for the Unconfined and RUM Aquifers

	Cation Concentration Equivalent Range (meq/L)	Anion Concentration Equivalent Range (meq/L)	Total Sum Equivalent Range (meq/L)
Unconfined Aquifer	3.6 to 7.7	3.7 to 7.7	7.3 to 15.4
RUM Aquifer	2.2 to 4.7	2.2 to 4.5	4.4 to 9.2

RUM = Ringold Formation upper mud (unit)

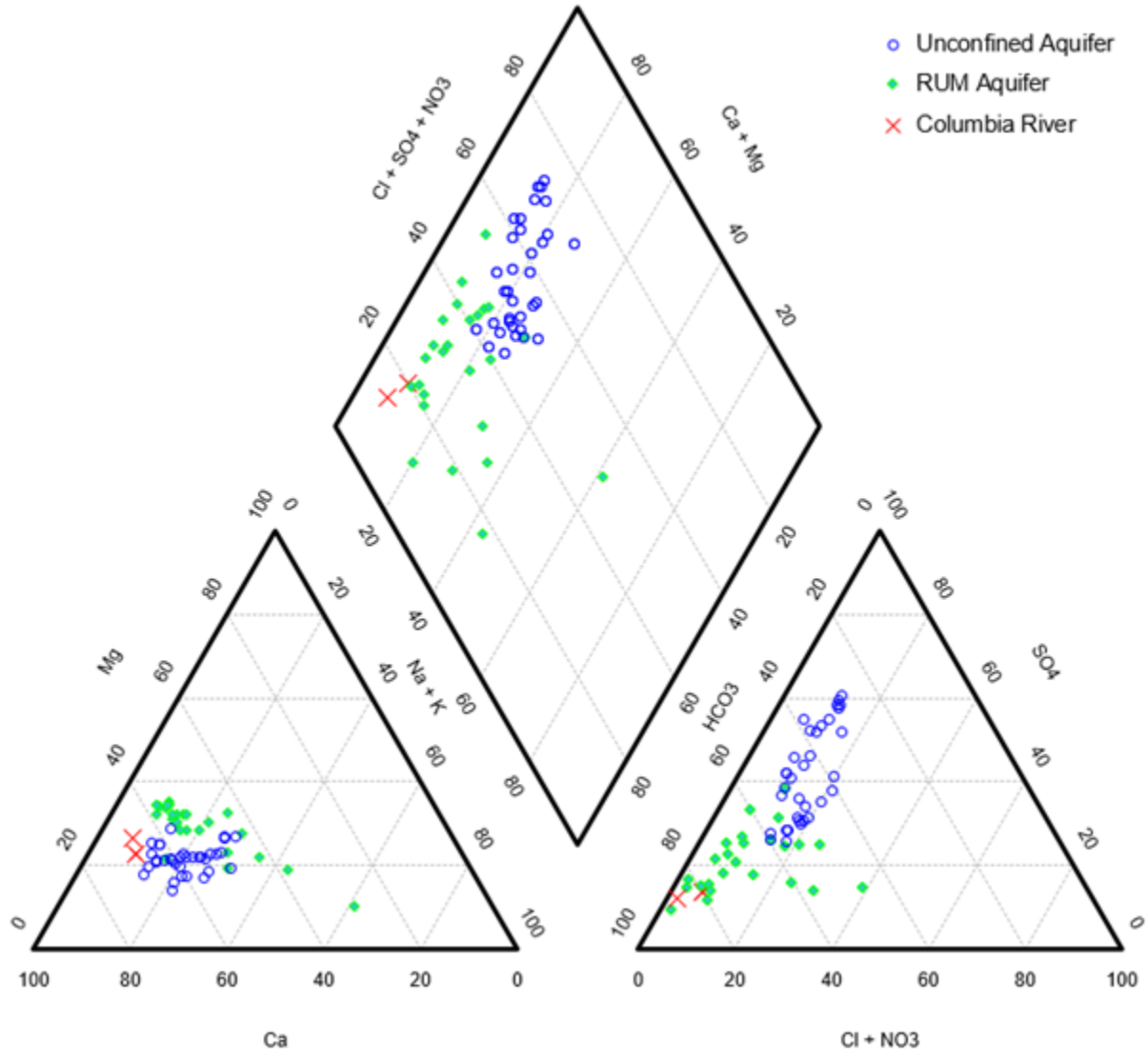

Figure 4. Piper Diagram for the Unconfined Aquifer, RUM Aquifer, and Columbia River Samples

Table 11. Relative Concentrations as Percent meq/L for Each Respective Cation and Anion

Well Name	Ca	Mg	Na+K	Cl+NO_3	SO_4	HCO_3
Unconfined Aquifer Wells						
199-D3-5	66.5	19.7	13.8	21.2	37.7	41.1
199-D4-102	62.7	25.4	11.9	6.7	55.0	38.4
199-D4-103	63.8	21.4	14.8	9.3	52.4	38.3
199-D5-152	57.2	22.1	20.8	11.2	53.5	35.3
199-D5-160	56.9	29.2	13.9	16.4	51.8	31.8
199-D6-3	49.5	23.1	27.4	12.7	58.4	28.9
199-D8-101	63.0	16.1	20.9	12.0	54.9	33.2
199-D8-102	61.4	25.2	13.4	11.0	51.8	37.2
199-H1-7	54.6	18.7	26.7	12.2	44.0	43.8
199-H1-46	60.9	21.6	17.5	14.4	26.3	59.4
199-H1-47	55.9	222.0	22.1	13.5	27.8	58.8
199-H3-6	64.4	14.1	21.5	9.7	42.0	48.4
199-H3-7	49.5	19.3	31.1	11.3	40.8	47.9
199-H3-21	59.7	17.5	22.9	16.7	28.5	54.8
199-H4-5	64.1	21.0	14.9	9.6	42.0	48.4
199-H4-85	56.2	17.1	26.7	11.2	38.5	50.3
199-H4-87	60.8	21.3	17.9	20.1	35.3	44.6
199-H4-88	60.3	20.8	18.9	19.5	31.5	49.0
199-H4-92	47.0	26.7	26.3	11.4	36.6	52.0
199-H6-1	60.4	17.7	21.9	12.5	46.2	41.4
199-H6-7	47.0	27.0	26.0	17.8	25.6	56.6
199-H6-8	57.4	22.9	19.7	19.9	41.2	38.9
699-88-41A	44.7	27.3	28.0	18.9	30.5	50.6
699-95-45	50.7	22.9	26.4	9.2	45.9	44.9
699-95-48	52.0	23.0	25.1	15.2	36.1	48.7
699-95-51	62.0	21.6	16.4	12.5	57.7	29.8
699-96-43	54.5	22.0	23.6	18.6	29.9	51.6

Table 11. Relative Concentrations as Percent meq/L for Each Respective Cation and Anion

Well Name	Ca	Mg	Na+K	Cl+NO_3	SO_4	HCO_3
699-96-52B	68.2	17.9	13.9	11.6	59.6	28.8
699-97-41	54.7	22.3	23.0	18.1	30.5	51.4
699-97-45	53.6	21.8	24.7	17.2	31.3	51.5
699-97-51A	63.9	23.1	13.1	12.1	58.3	29.6
699-98-43	59.8	20.0	20.2	16.6	28.2	55.2
699-98-46	58.6	22.0	19.4	17.8	33.9	48.3
699-98-51	61.2	25.2	13.7	11.9	60.6	27.5
RUM Aquifer Wells						
199-D5-134	42.2	22.3	35.5	5.3	21.5	73.2
199-D5-141	28.4	10.3	61.3	11.1	38.2	50.7
199-H1-50	51.3	28.5	20.2	1.9	9.6	88.5
199-H2-1	50.1	19.6	30.3	9.7	20.6	69.6
199-H3-10	37.8	19.2	43.1	2.6	14.8	82.6
199-H3-12	54.2	35.5	10.3	8.5	18.1	73.5
199-H3-13	56.8	34.4	8.9	29.3	13.9	56.8
199-H3-22	55.8	33.8	10.4	23.8	16.0	60.2
199-H3-28	52.7	32.3	15.0	14.3	26.0	59.8
199-H3-29	57.0	34.8	8.3	39.1	14.9	46.0
199-H3-2C	48.5	30.4	21.1	9.1	25.3	65.6
199-H3-30	55.5	31.3	13.2	5.7	25.2	69.1
199-H3-32	61.6	21.9	16.6	13.4	31.4	55.2
199-H3-9	52.2	32.3	15.5	5.4	15.2	79.5
199-H4-12C	54.1	32.6	13.4	14.7	18.0	67.4
199-H4-15CS	55.1	32.6	12.4	6.7	15.6	77.7
199-H4-90	54.1	28.6	17.3	20.9	24.9	54.2
199-H4-91	55.5	28.5	16.0	18.3	24.5	57.2
199-H7-1	48.0	23.5	28.6	25.0	25.0	50.0
699-95-45C	43.0	27.8	29.2	2.0	16.6	81.4

Table 11. Relative Concentrations as Percent meq/L for Each Respective Cation and Anion

Well Name	Ca	Mg	Na+K	Cl+NO_3	SO_4	HCO_3
699-97-43C	55.0	30.6	14.4	8.1	13.9	78.0
699-97-45B	54.4	34.8	10.8	8.6	11.6	79.8
699-97-48C	58.2	32.4	9.4	8.0	26.8	65.2
699-97-60	43.6	32.7	23.8	6.6	33.3	60.1
699-97-61	54.9	34.7	10.5	7.4	22.6	70.0
Columbia River Water						
Spring 152-2	67.2	23.0	9.8	6.4	13.5	80.0
100-N River	66.2	26.5	7.4	2.1	12.1	85.8

RUM = Ringold Formation upper mud (unit)

7 Conclusions

The hydraulic interconnection relationship between the uppermost RUM aquifer and the unconfined aquifer in the 100-HR-3 OU at the Hanford Site and the relationship to Columbia River water is not fully understood. Because contamination exists in the RUM aquifer, hypotheses for this contamination are the confining or semiconfining unit separating the RUM aquifer and the overlying unconfined aquifer may be thin, permeable, or absent, which provides a pathway for contaminants to migrate from the unconfined aquifer downward to the RUM aquifer.

A method for evaluating whether hydraulic interconnection relationships occur between the aquifers and between the aquifers and the adjacent Columbia River is to compare and evaluate the general chemical composition of groundwater and river water using graphical methods, including the Stiff diagram and the Piper (or trilinear) diagram. These graphical methods require that major ion charge-balance calculations are performed using complete major ion datasets for each of the aquifers and river water. This ECF presents the methodology, hydrochemistry datasets, and results of the major ion balance calculations for groundwater within the unconfined and RUM aquifers and for Columbia River water. The calculation results were used to generate Stiff diagrams and a Piper plot, which graphically display the major ion charge balance calculations.

The Stiff diagrams and Piper plot indicate that groundwater within the RUM aquifer is dominated by calcium and bicarbonate, similar to the Columbia River composition. The chemical composition of groundwater within the unconfined aquifer is dominated by calcium and a mix of bicarbonate and sulfate. The interpretation and evaluation of these calculation results and diagrams are to be documented in a technical memorandum to follow.

Because of the potential impact of the DX and HX P&T systems on the unconfined aquifer within the 100-HR-3 OU, the chemical composition of treated effluent water injected into the unconfined aquifer must be considered for the evaluation of the calculation results. Complete major ion hydrochemistry datasets were not available for the treated effluent water injected into the unconfined aquifer at the

100-HR-3 OU. Because these datasets are not available, it is not possible to compare the chemical composition of the effluent water to the composition of groundwater in the unconfined and RUM aquifers using the methods described in this ECF. At least one treated effluent water sample from each of the DX and HX P&T systems needs to be collected and analyzed for the major cations and anions for the purpose of calculating the ion charge balance and comparing its composition with the chemistry of the unconfined and RUM aquifers.

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Appendix A

Unconfined Aquifer Stiff Diagrams

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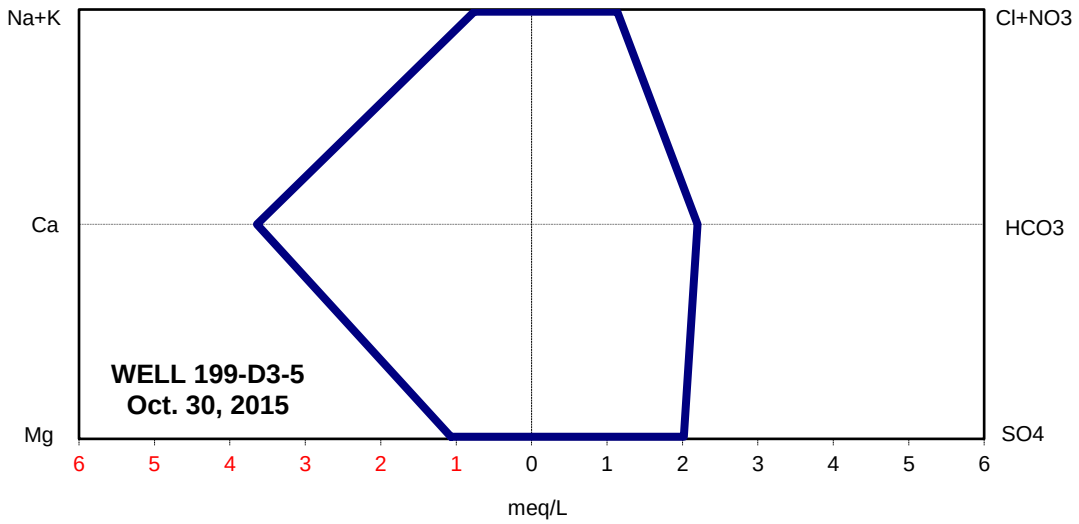
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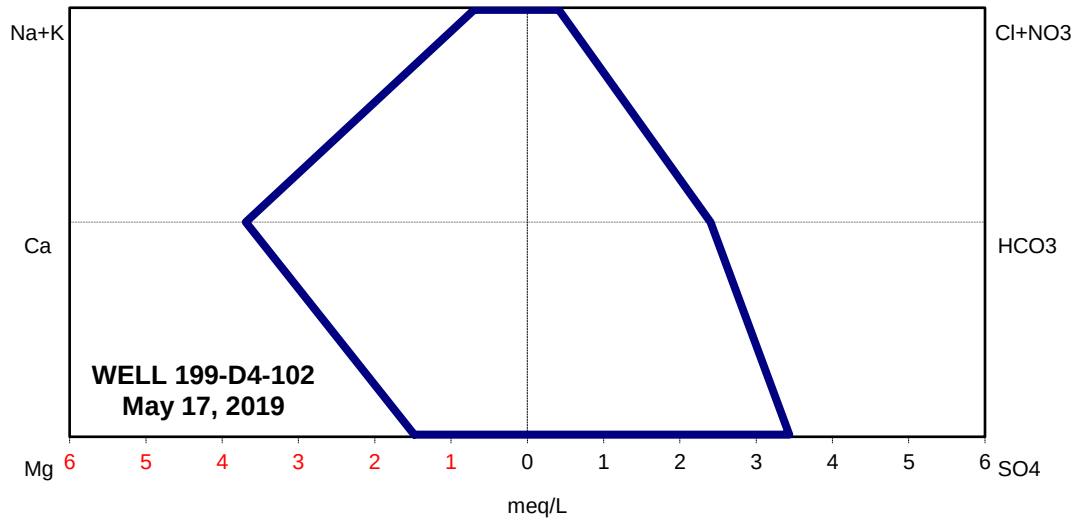
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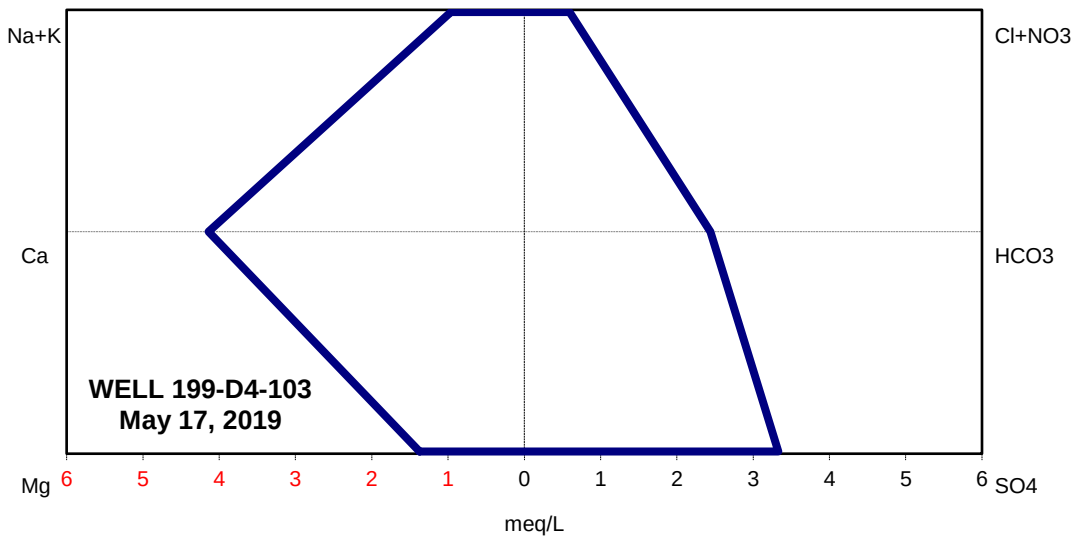
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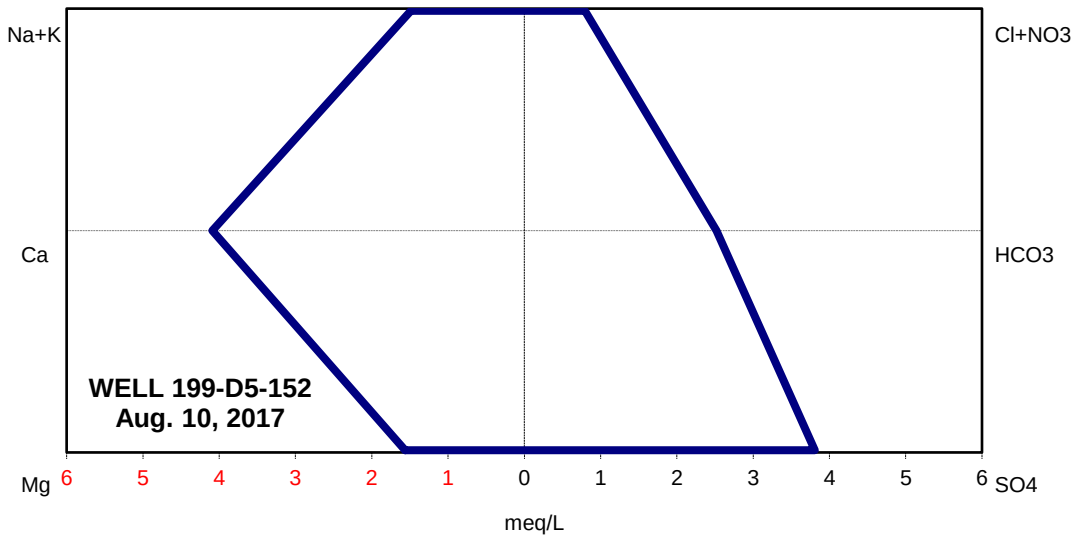
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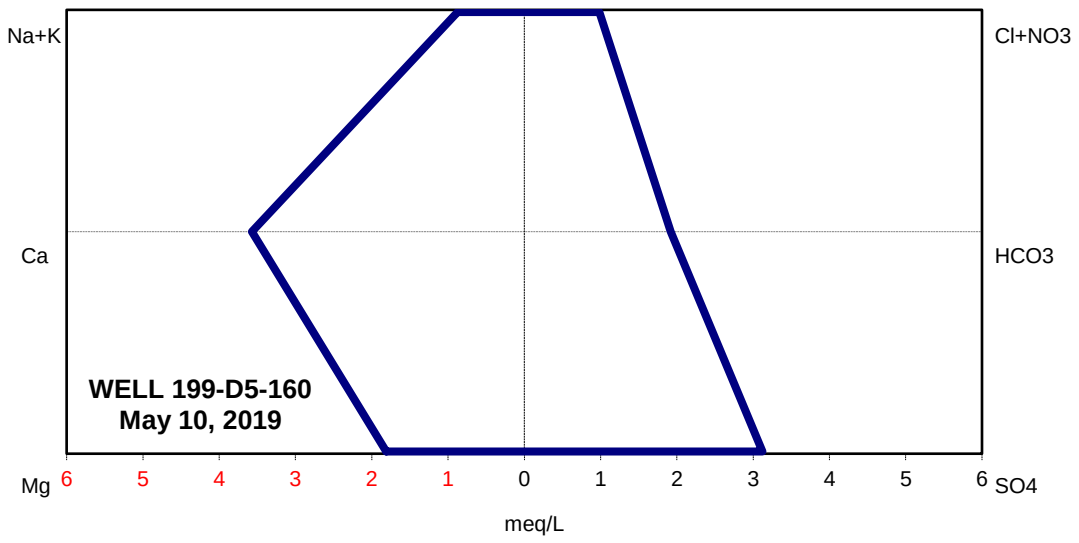
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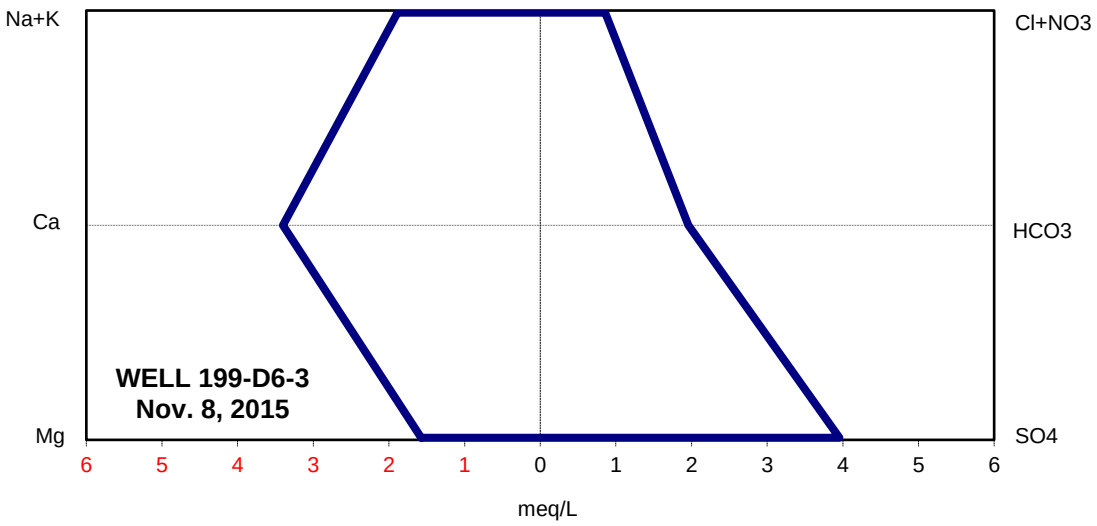
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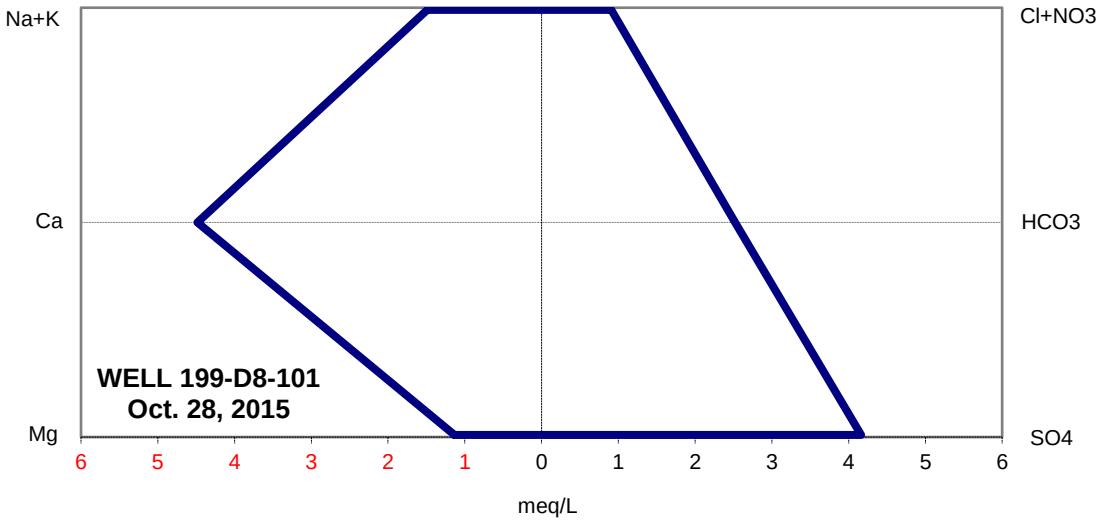
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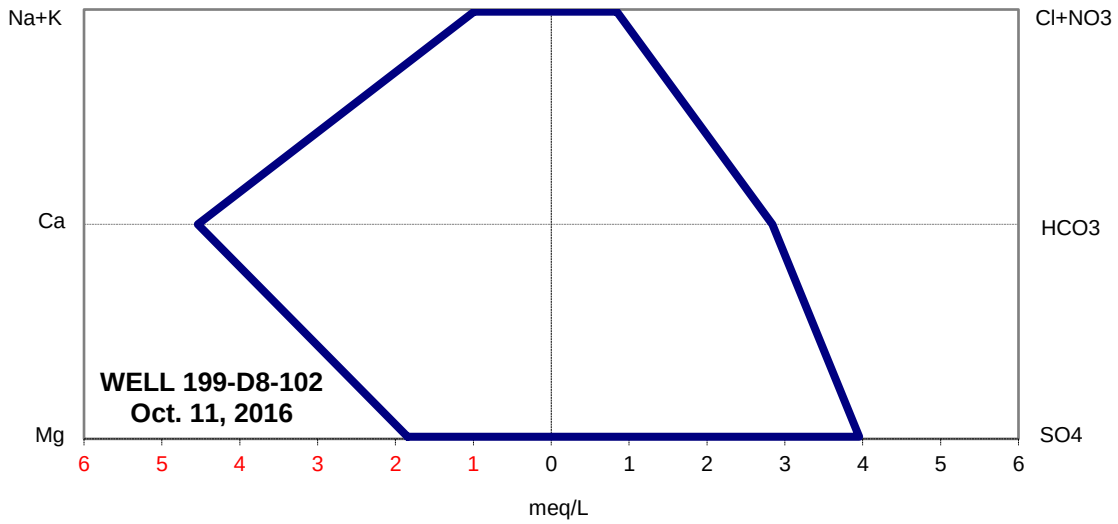
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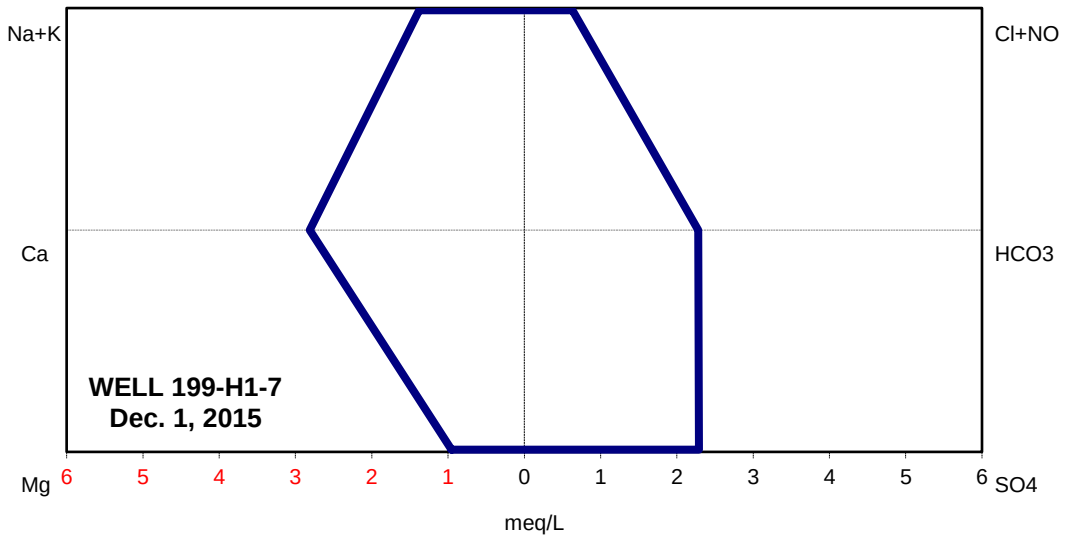
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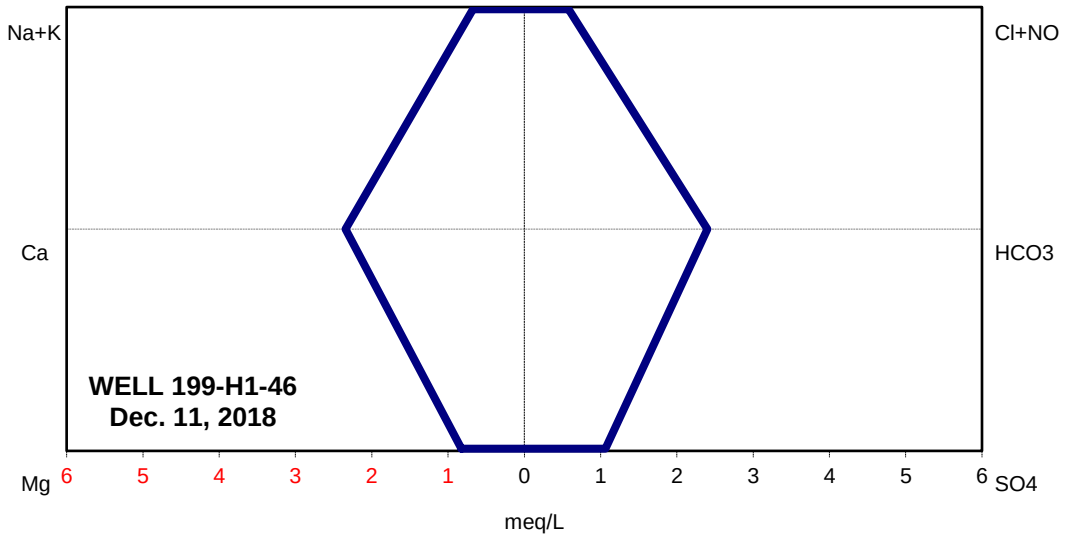
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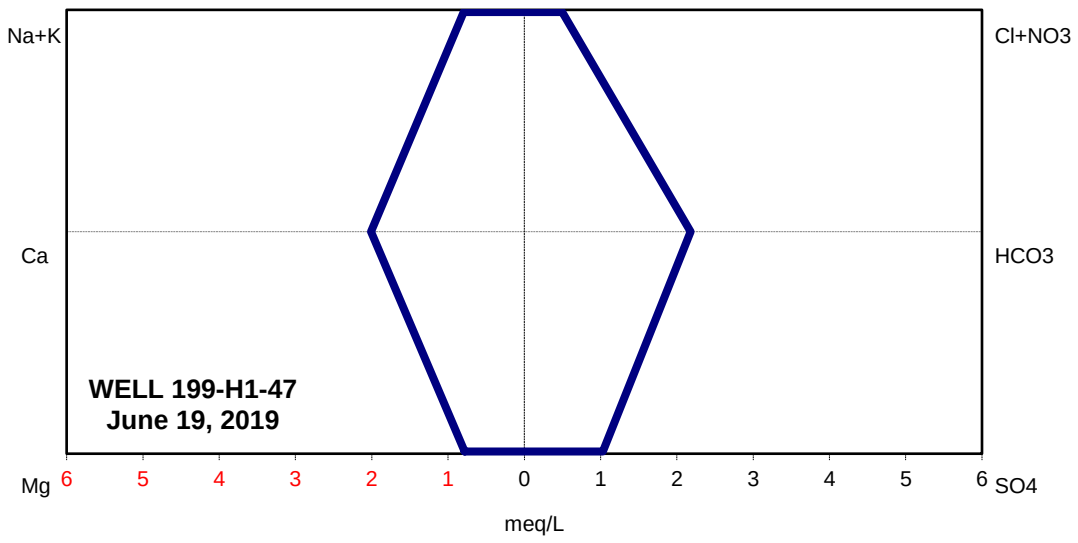
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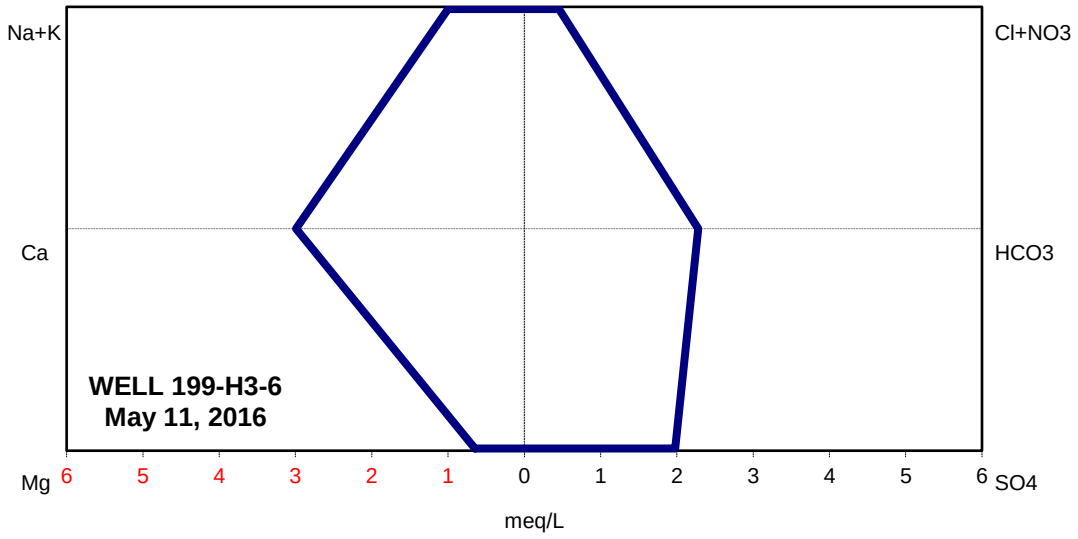
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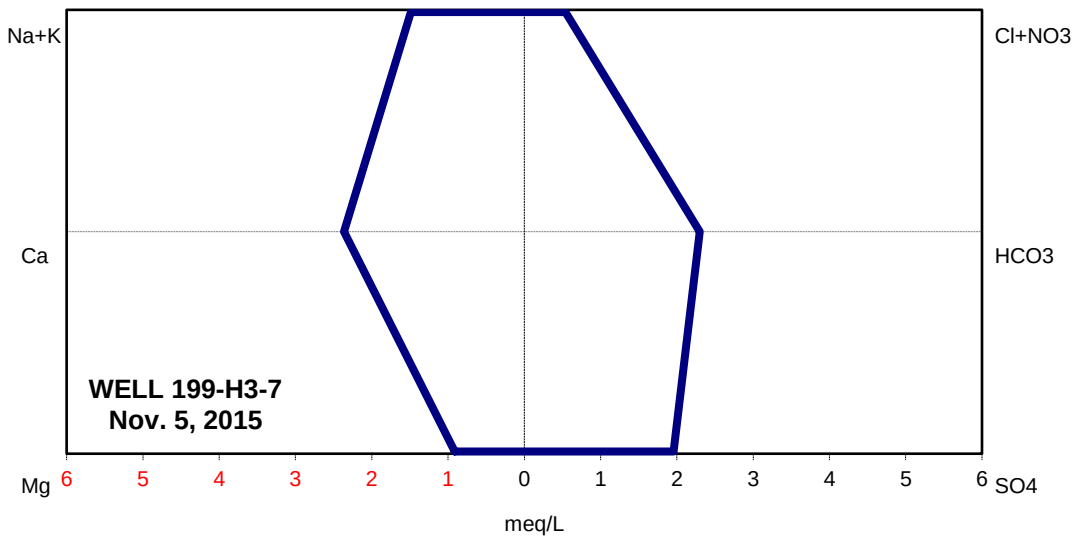
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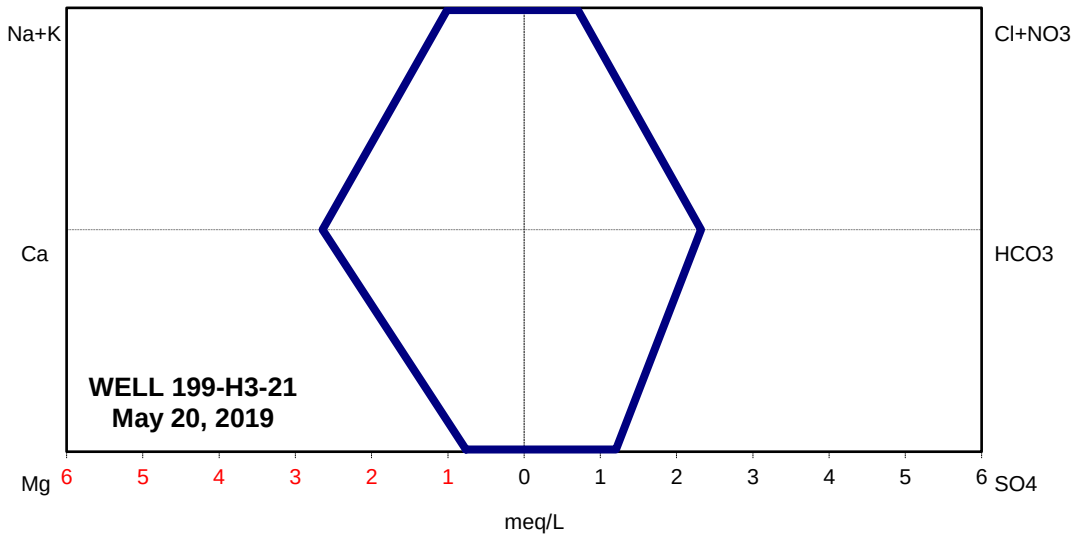
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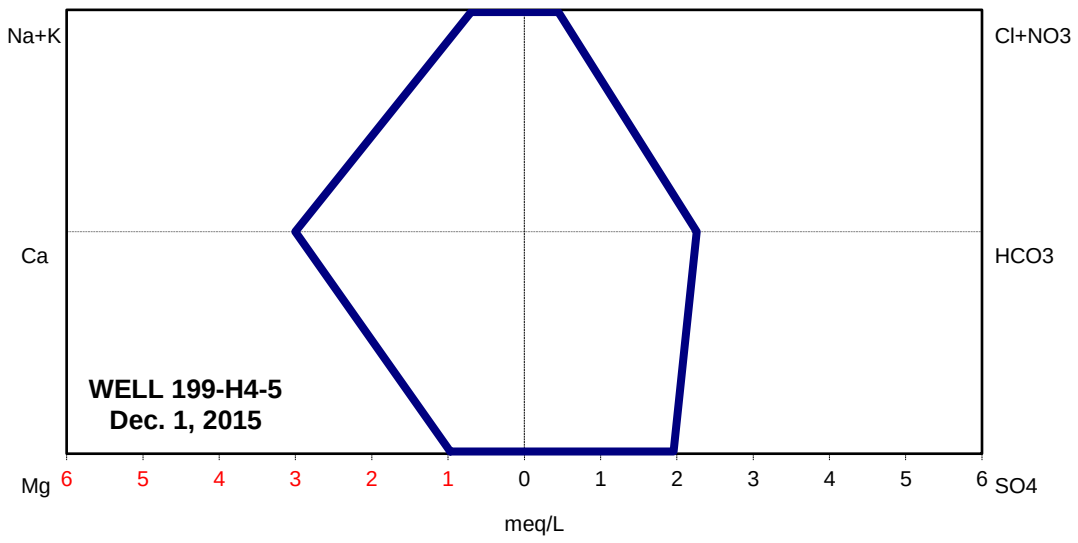
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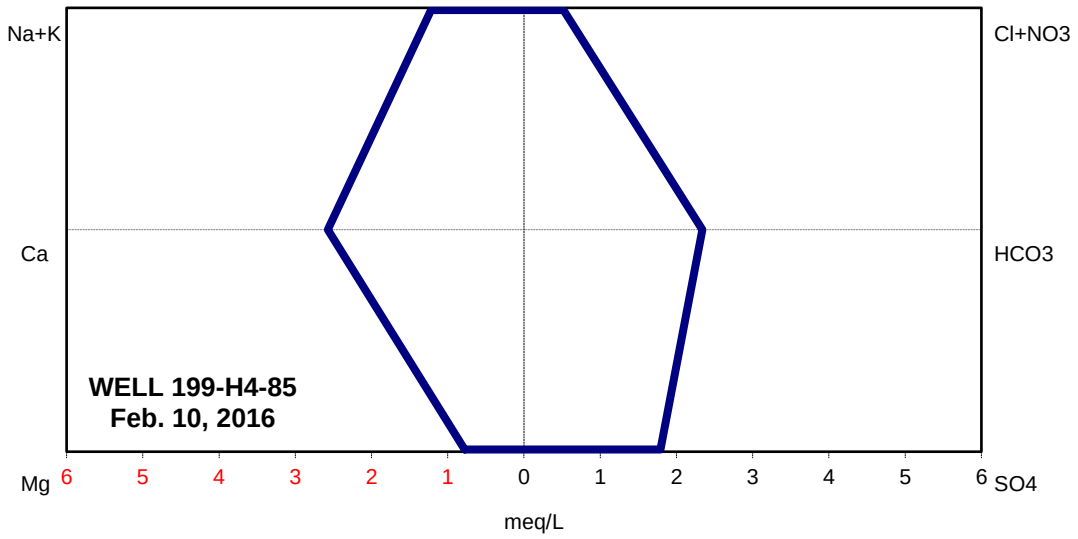
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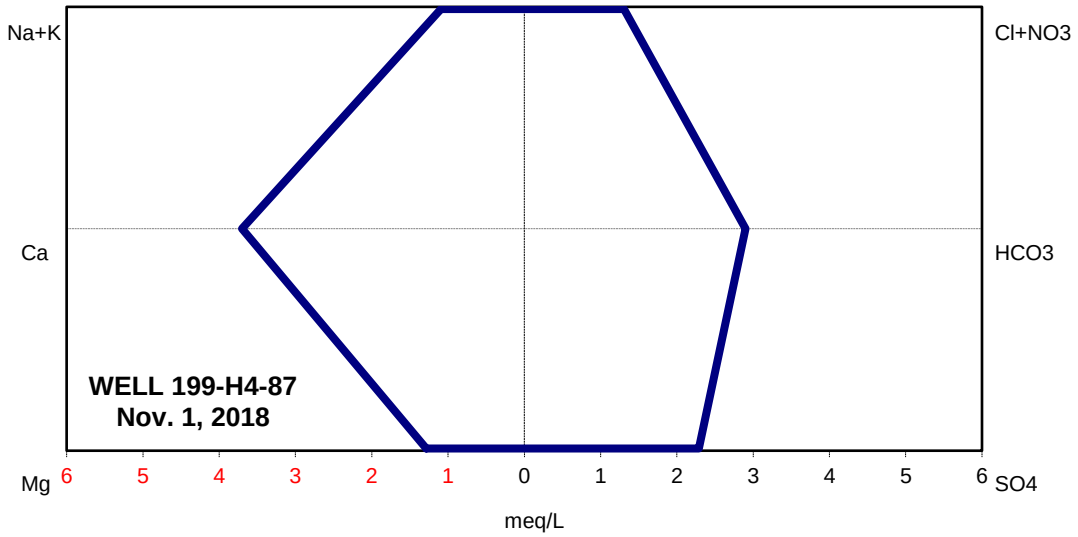
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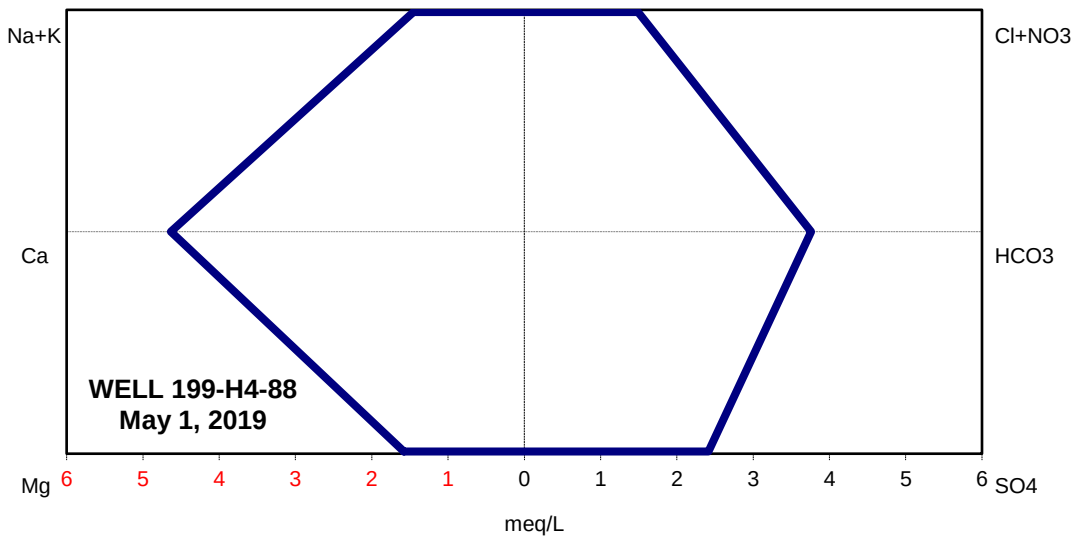
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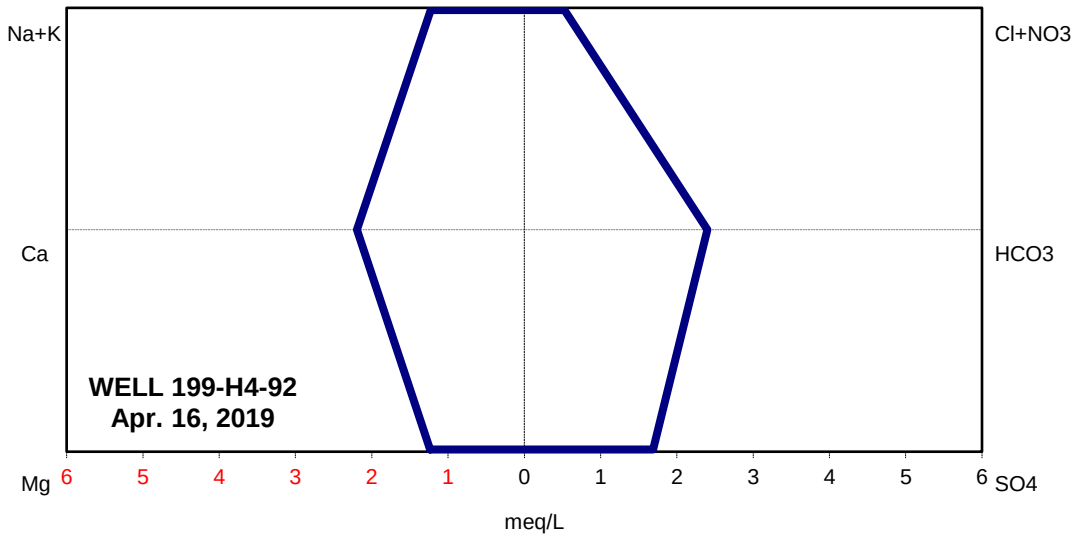
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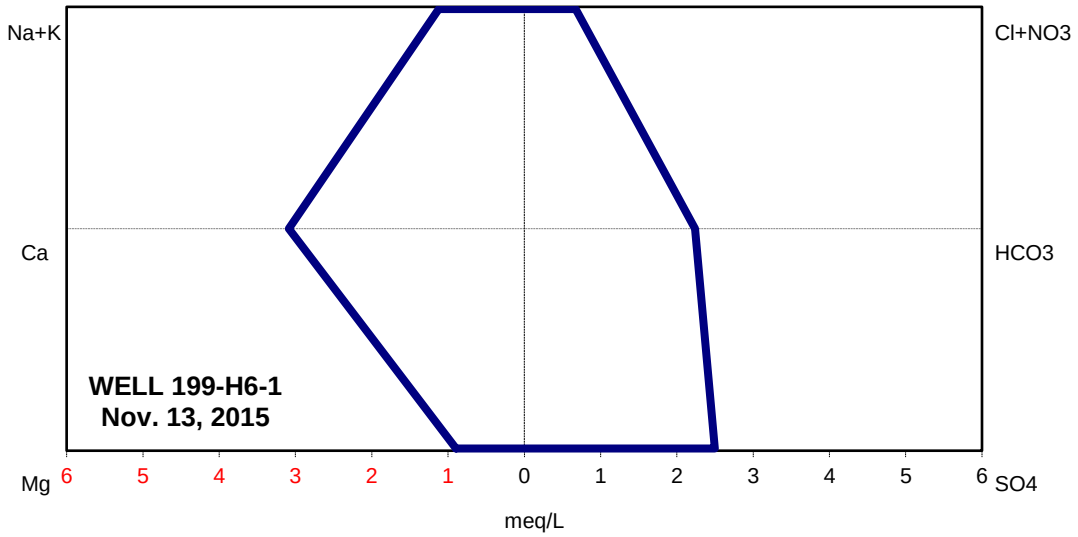
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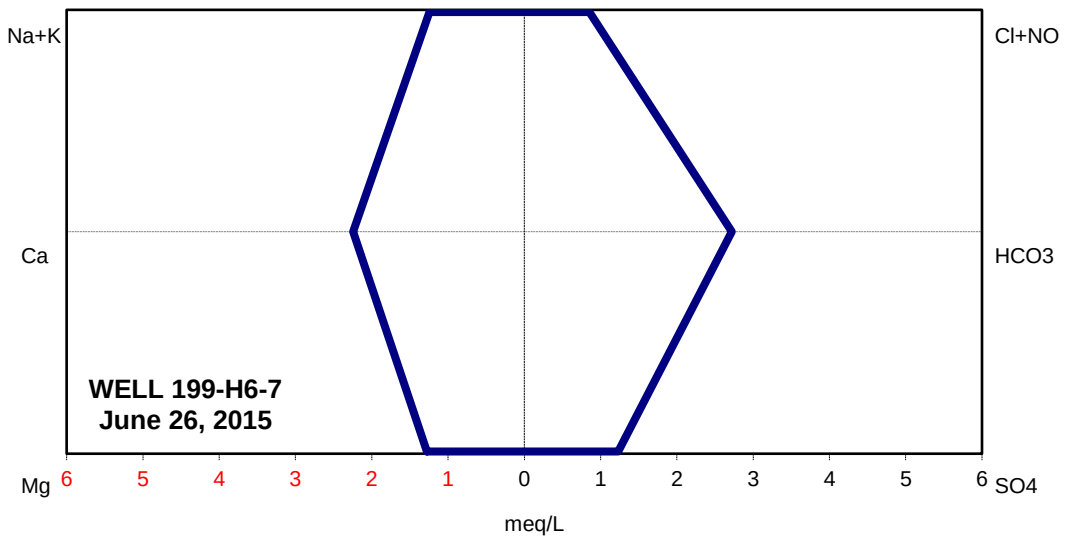
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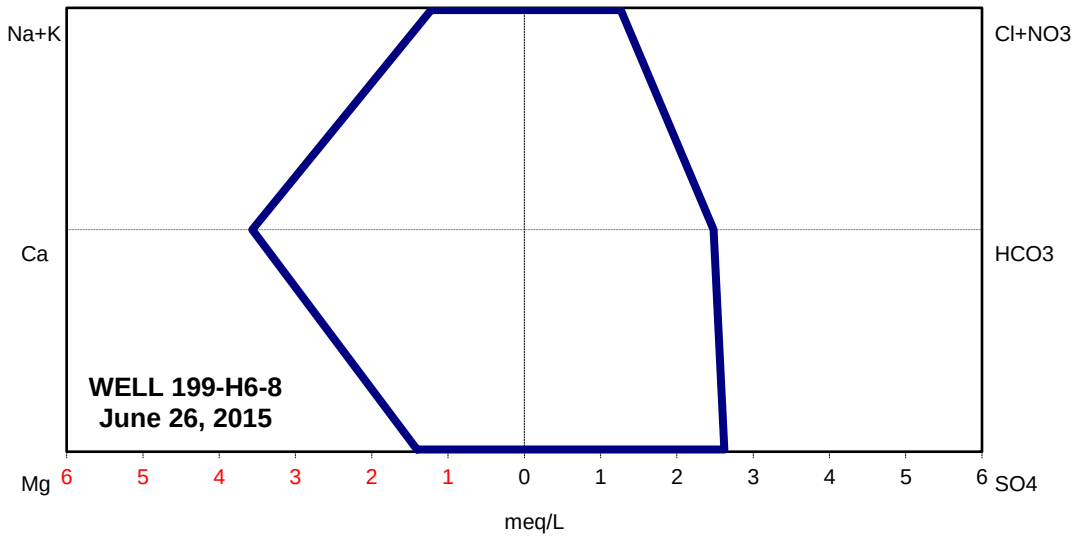
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Cl+NO3
Ca
HCO3
WELL 199-H6-8
June 26, 2015
Mg
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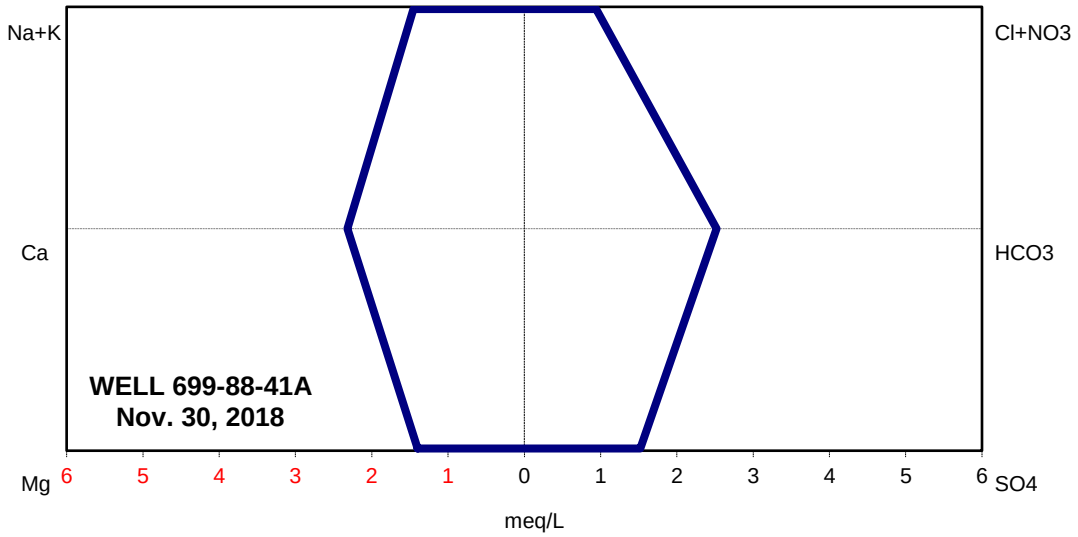
SO4
meq/L


Na+K
Cl+NO3
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HCO3
WELL 699-88-41A
Nov. 30, 2018
Mg
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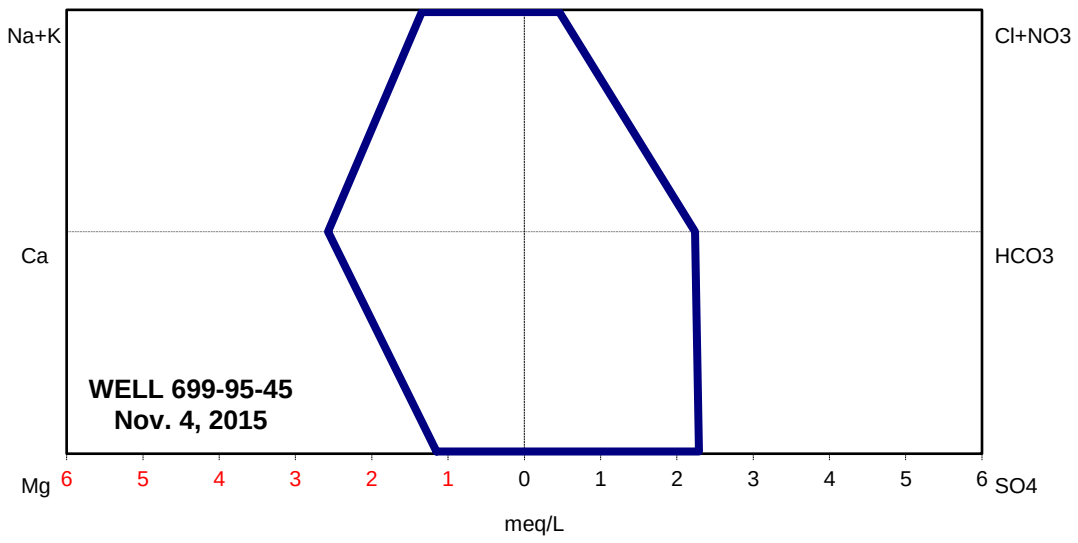
SO4
meq/L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Mg
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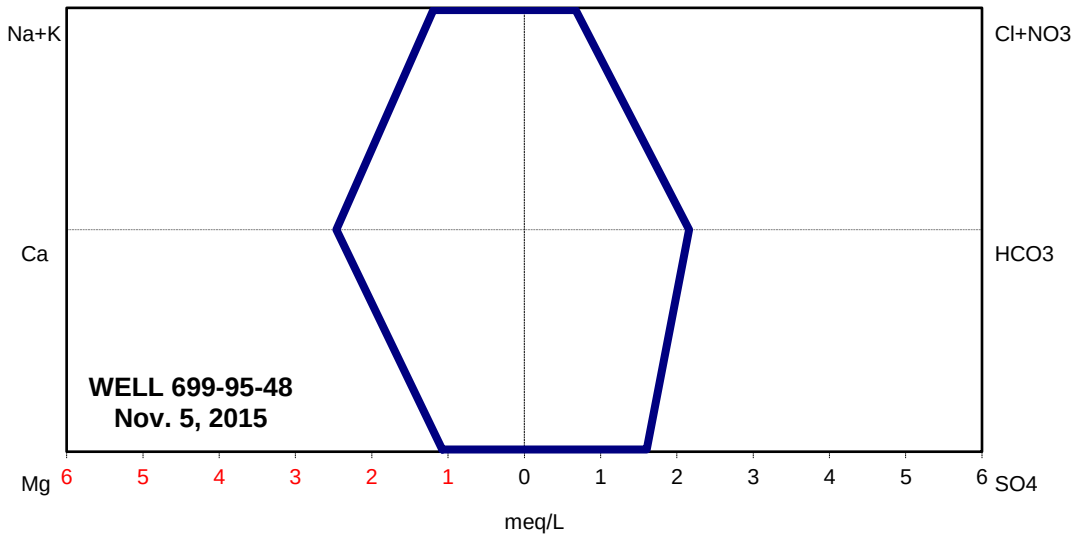
SO4
meq/L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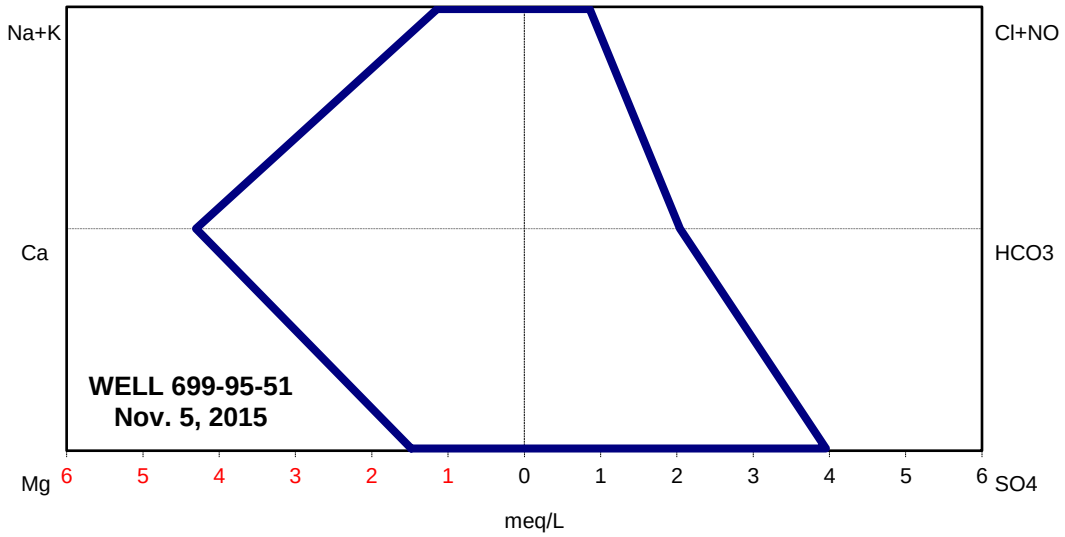
meq/L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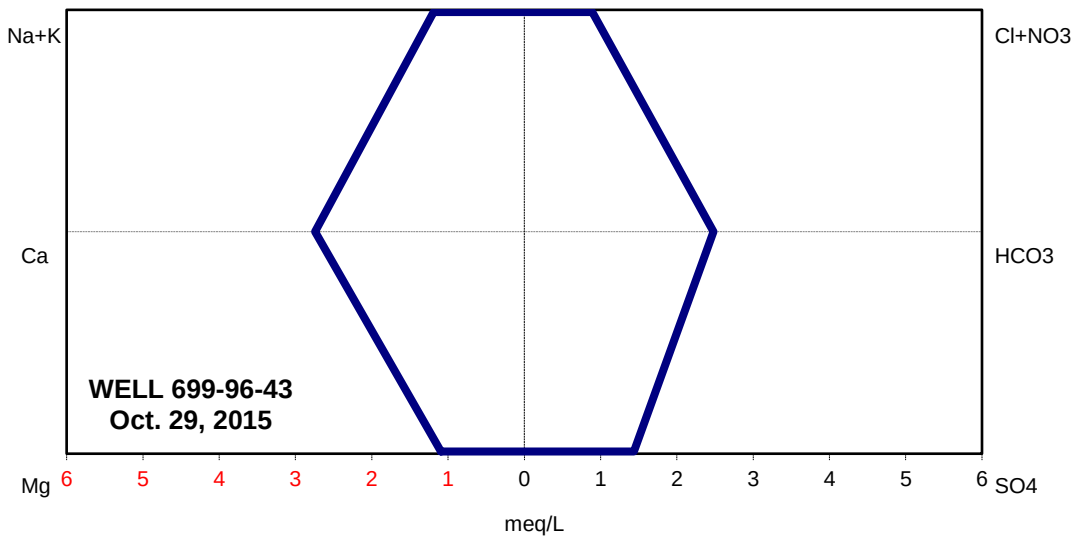
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-96-43
Oct. 29, 2015
Mg
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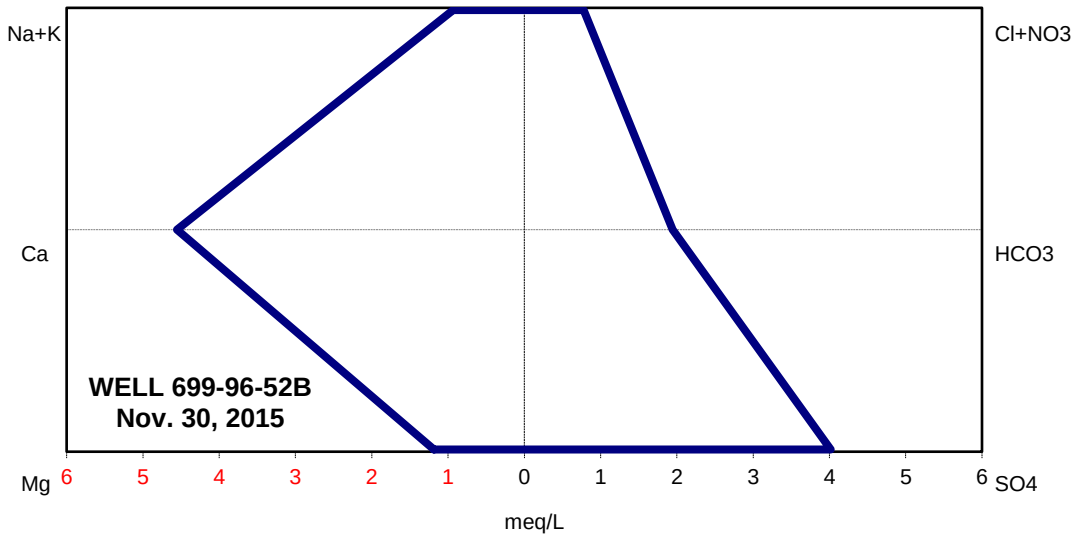
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-96-52B
Nov. 30, 2015
Mg
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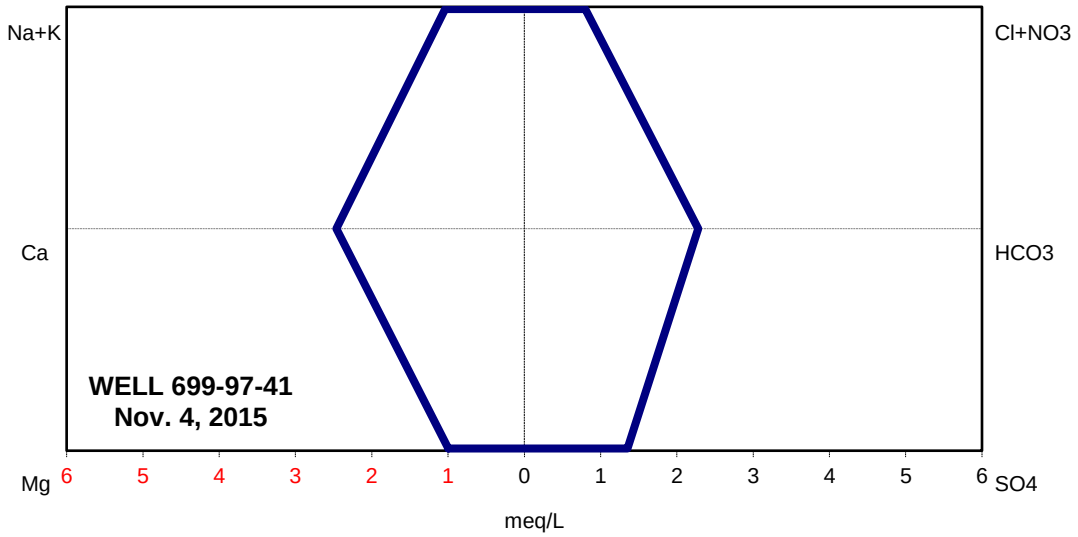
SO4
meq/L


Na+K
Cl+NO3
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HCO3
WELL 699-97-41
Nov. 4, 2015
Mg
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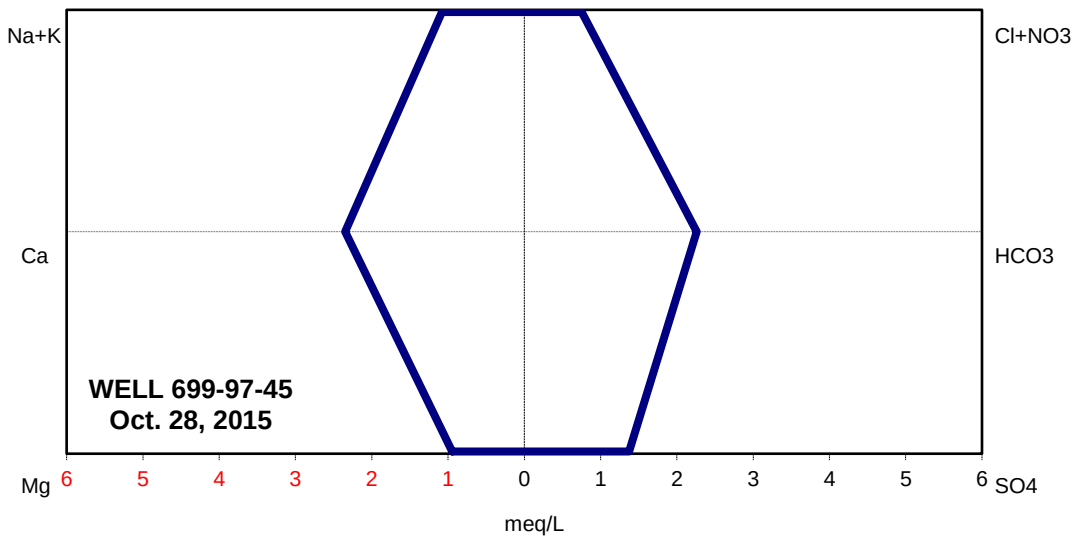
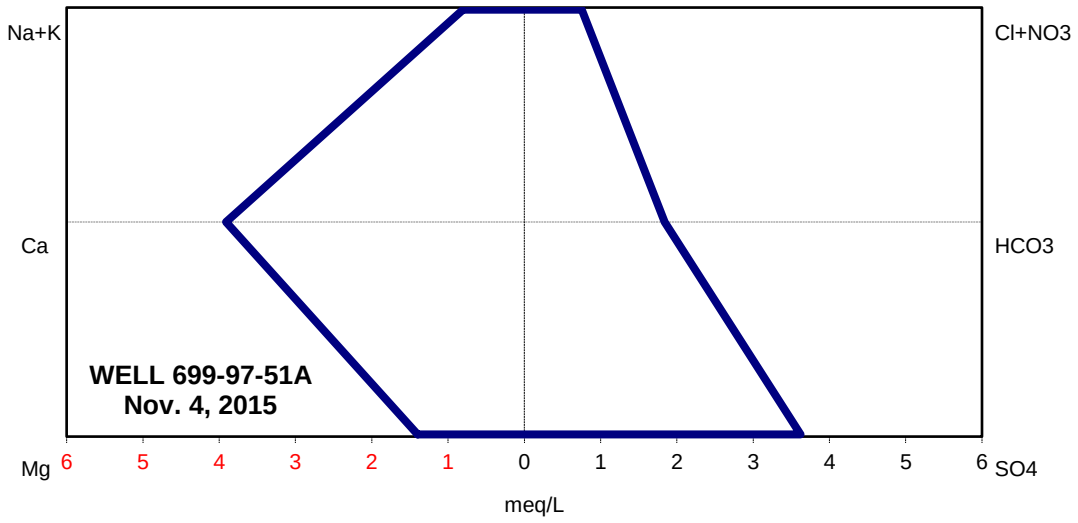
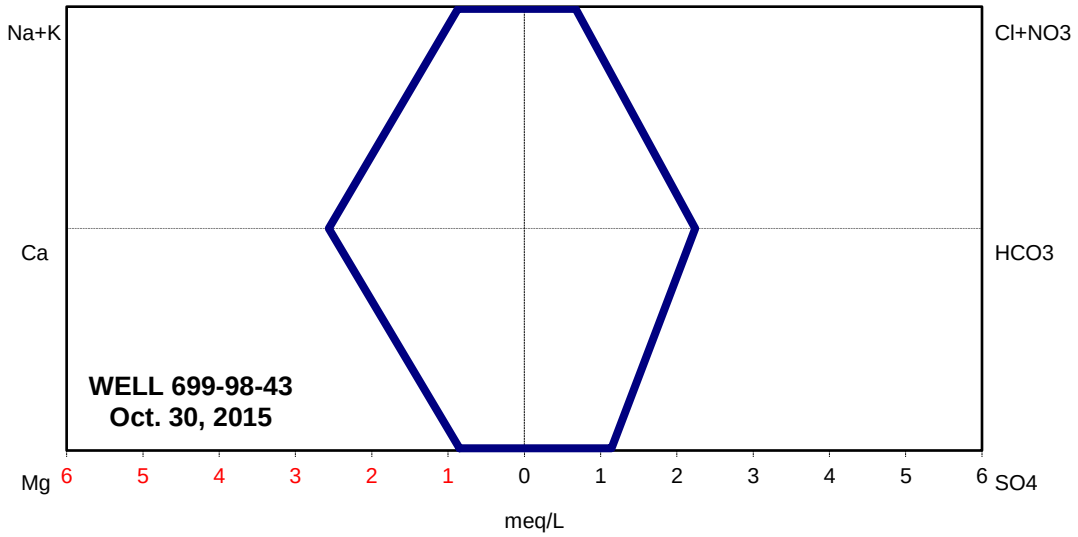
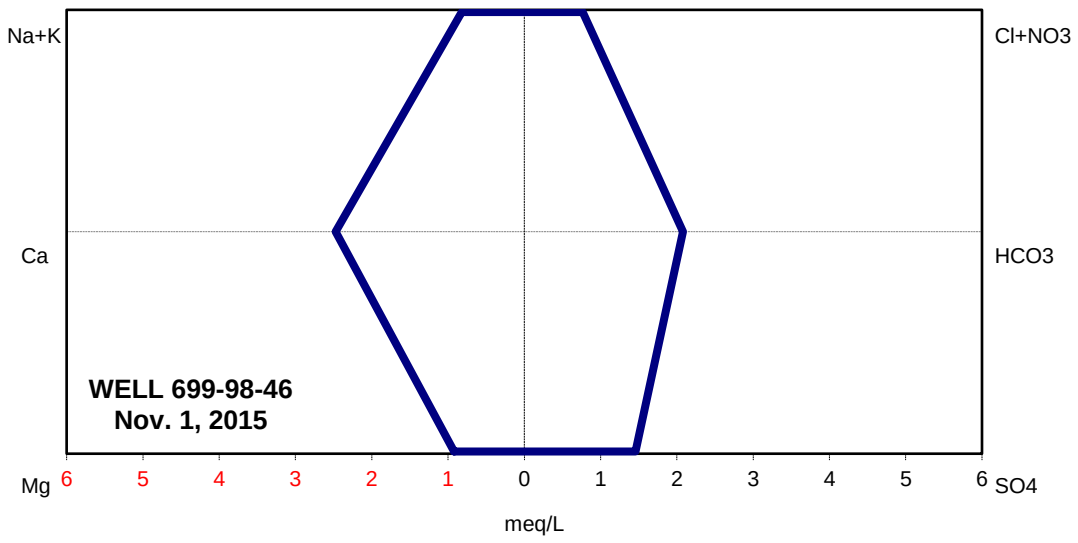
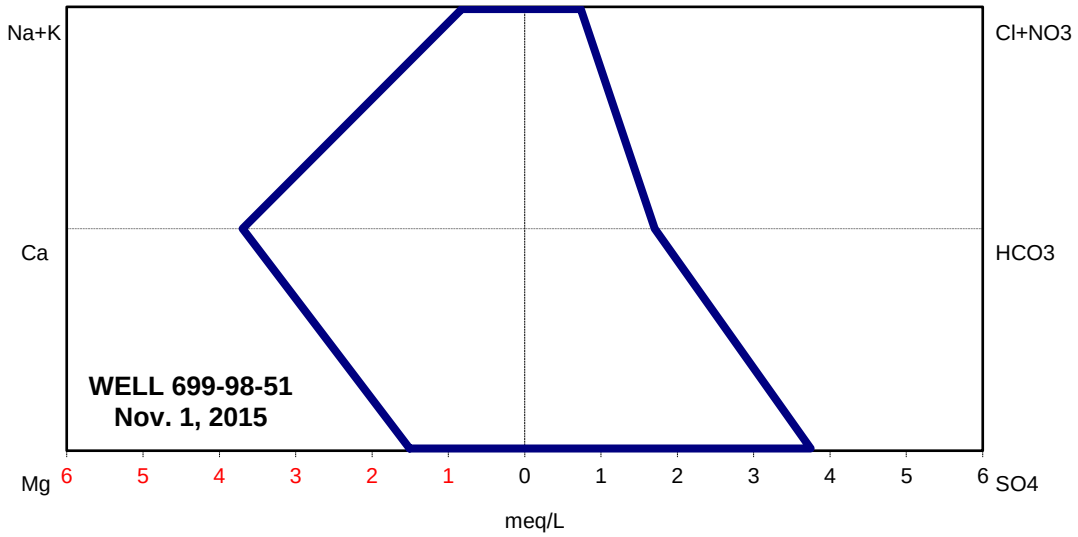
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-97-45
Oct. 28, 2015
Mg
6 5 4 3 2 1 0 1 2 3 4 5 6
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-97-51A
Nov. 4, 2015
Mg
6 5 4 3 2 1 0 1 2 3 4 5 6
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-98-43
Oct. 30, 2015
Mg
6 5 4 3 2 1 0 1 2 3 4 5 6
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-98-46
Nov. 1, 2015
Mg
6 5 4 3 2 1 0 1 2 3 4 5 6
SO4
meq/L


Na+K
Cl+NO3
Ca
HCO3
WELL 699-98-51
Nov. 1, 2015
Mg
6 5 4 3 2 1 0 1 2 3 4 5 6
SO4
meq/L

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Appendix B

RUM Aquifer Stiff Diagrams

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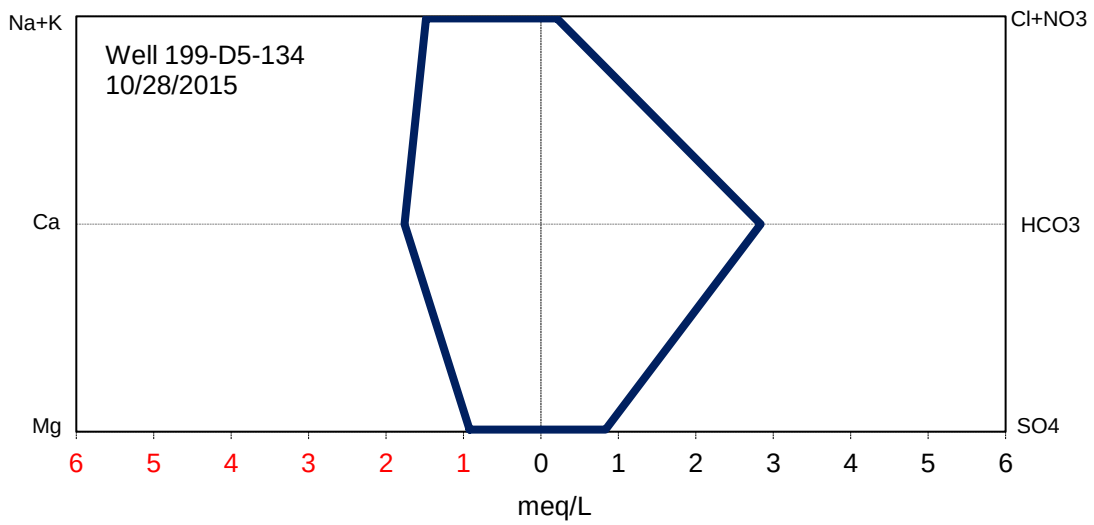
Well 199-D5-134
10/28/2015
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
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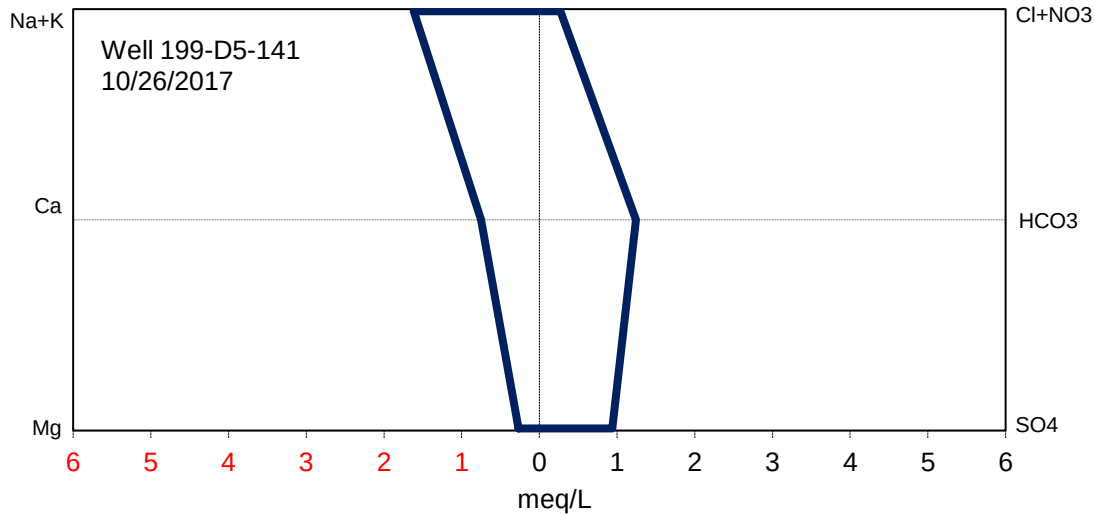
meq/L


Well 199-D5-141
10/26/2017
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
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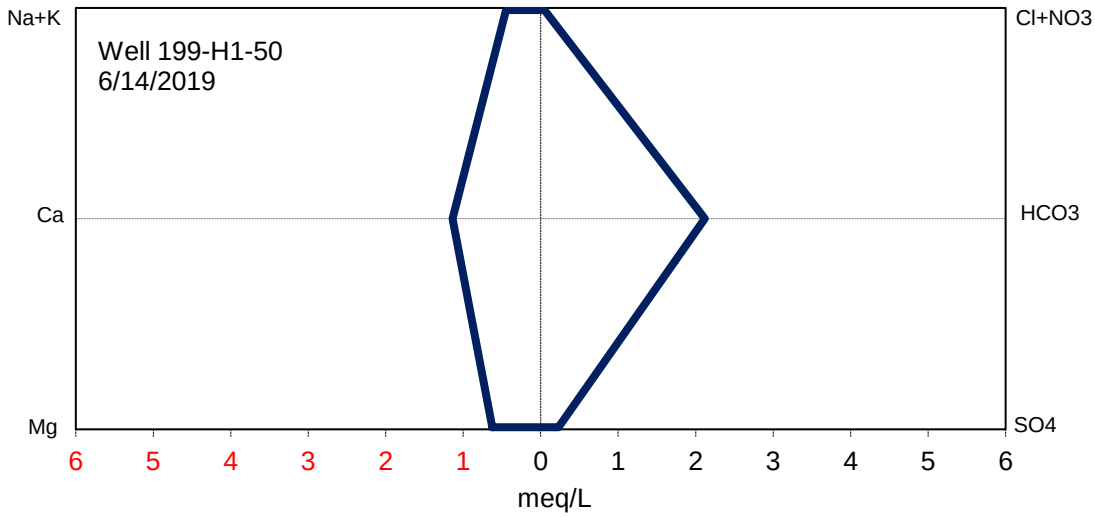
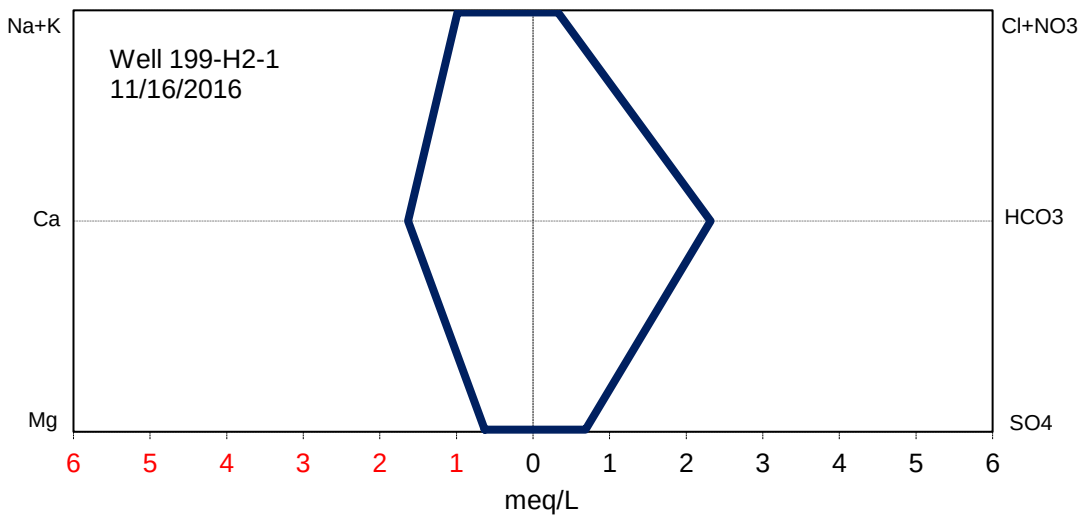
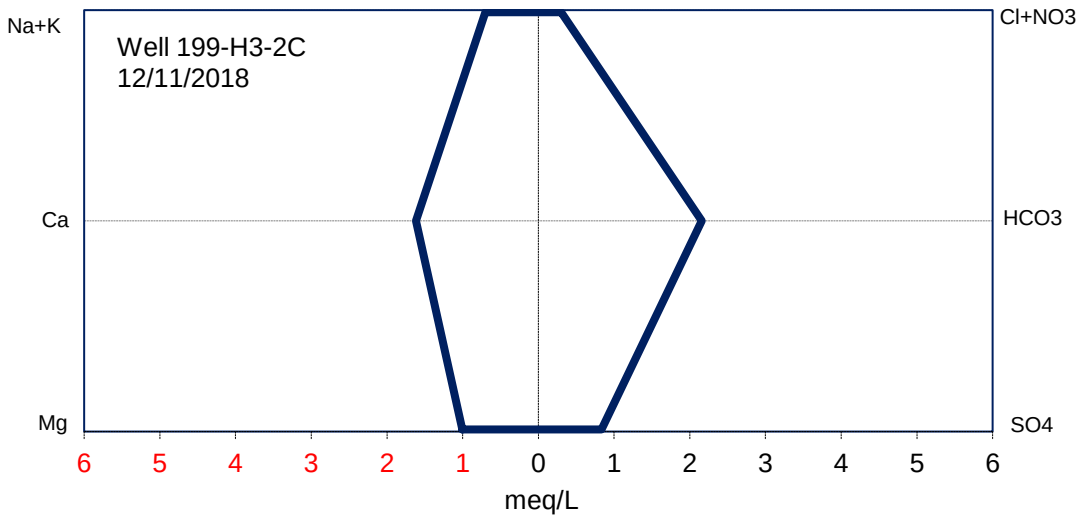
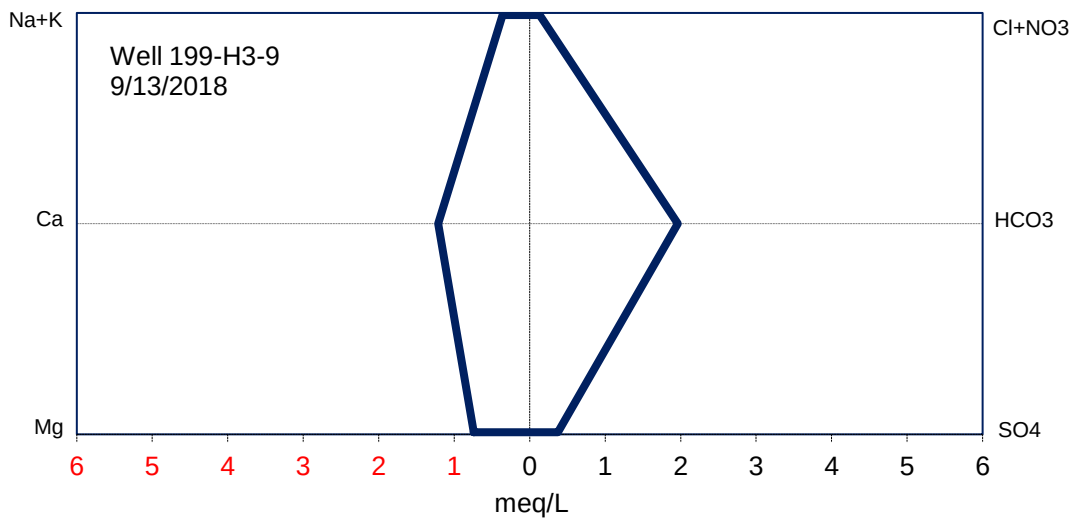
meq/L


Well 199-H1-50
6/14/2019
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H2-1
11/16/2016
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-2C
12/11/2018
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-9
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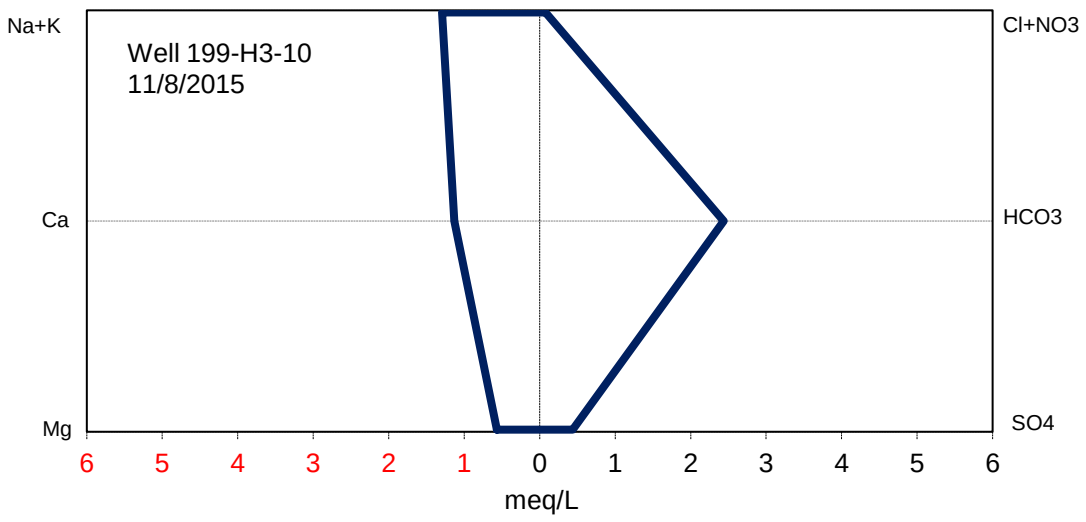
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-10
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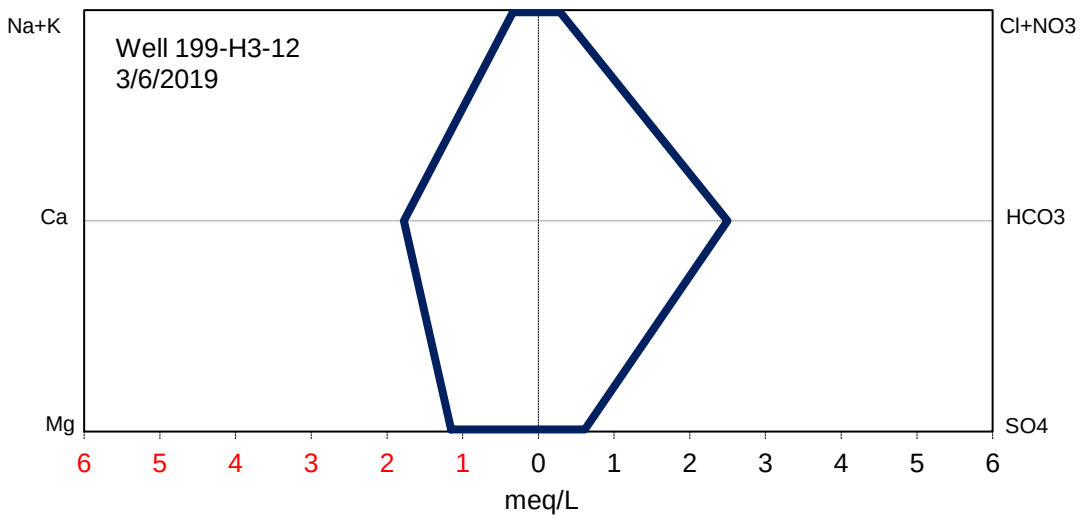
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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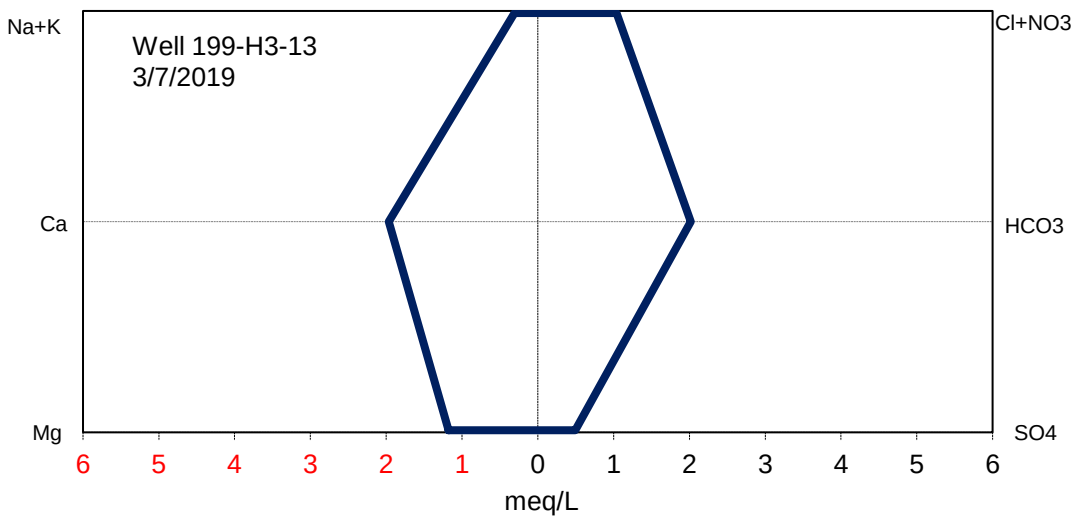
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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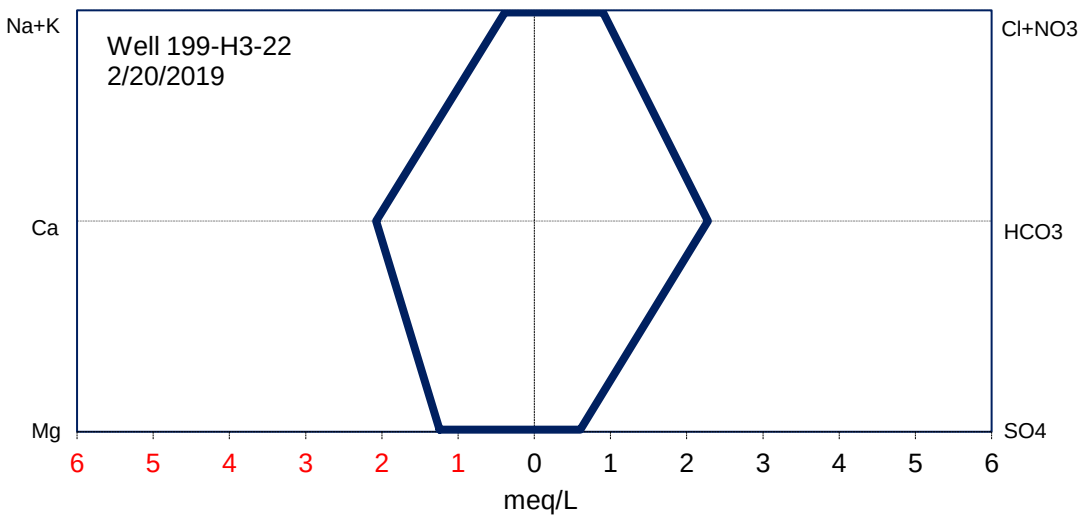
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-22
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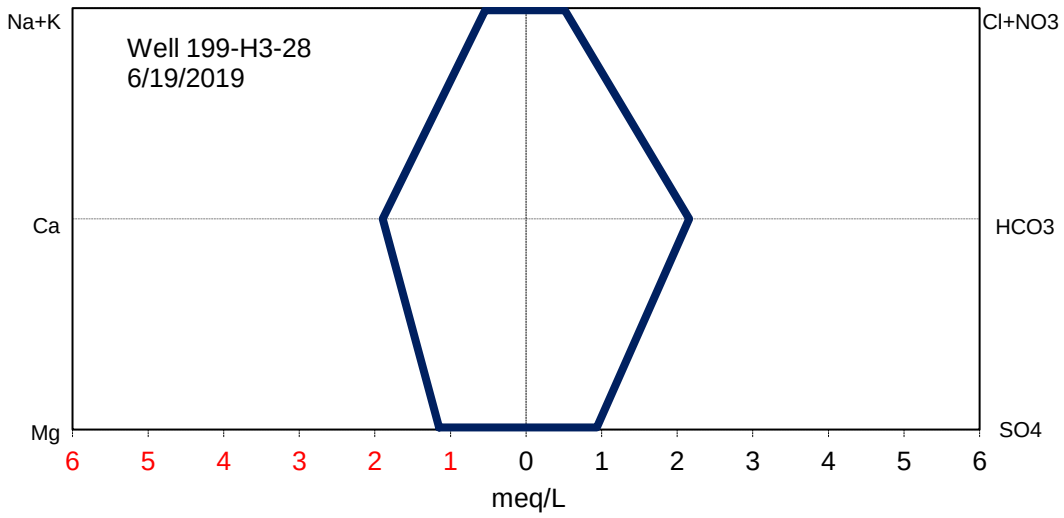
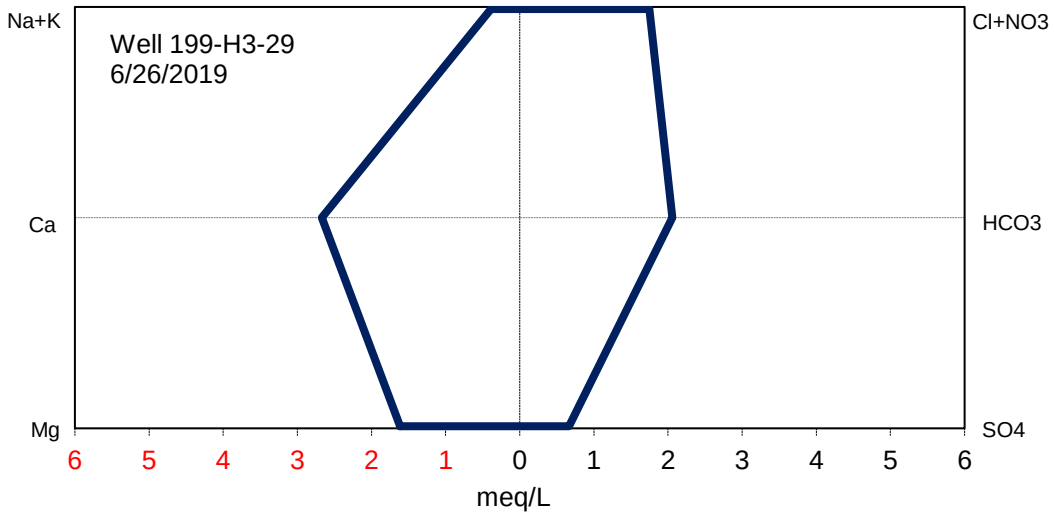
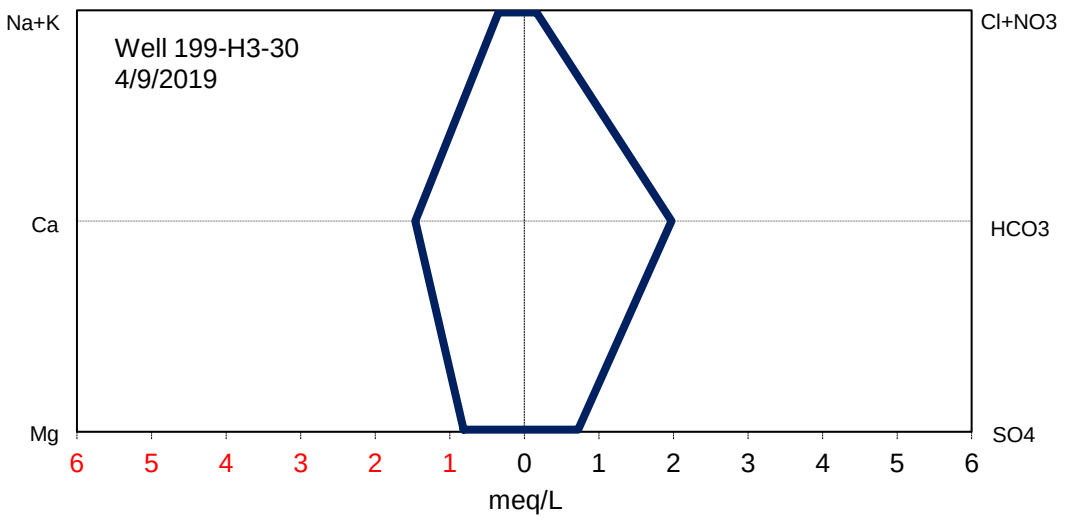
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-28
6/19/2019
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-29
6/26/2019
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H3-30
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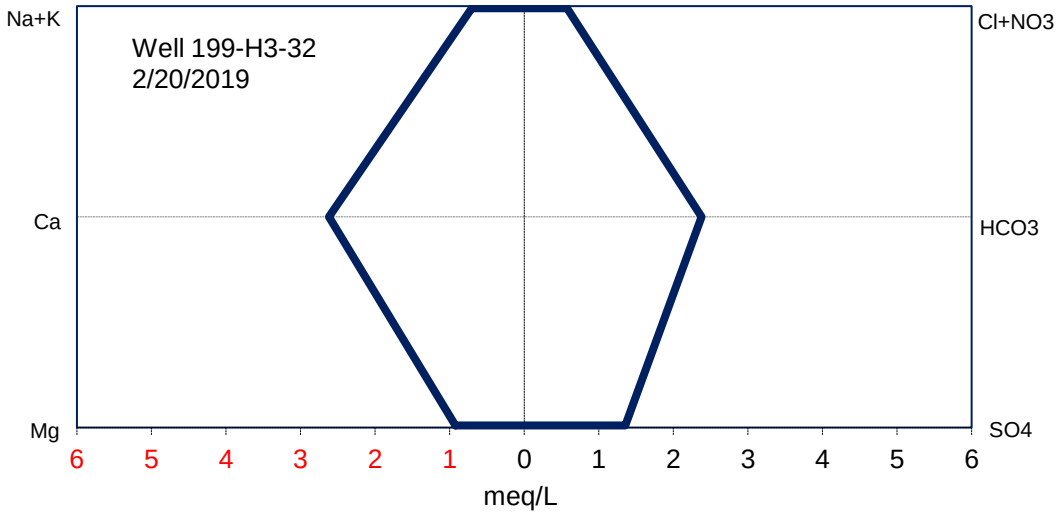
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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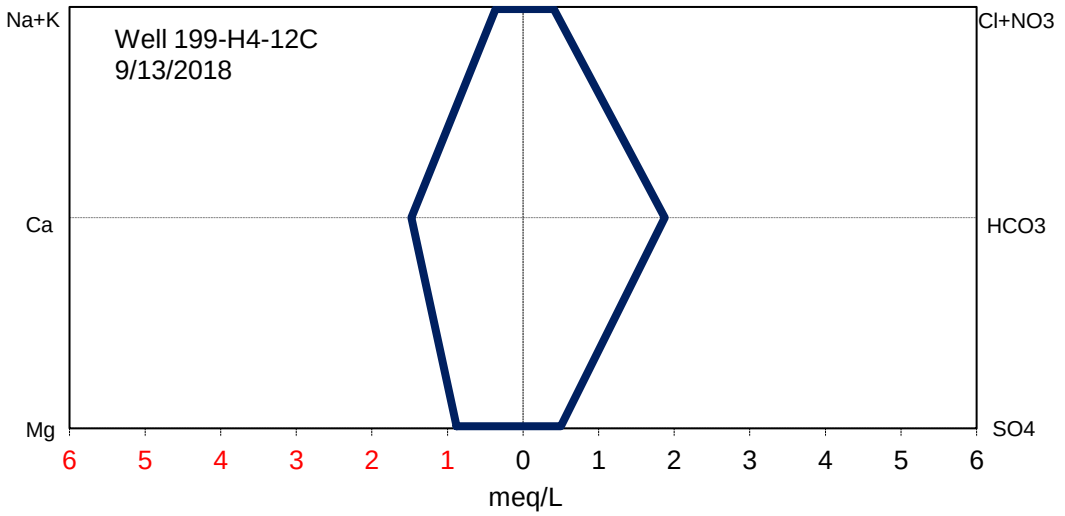
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 199-H4-12C
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Mg
Cl+NO3
HCO3
SO4
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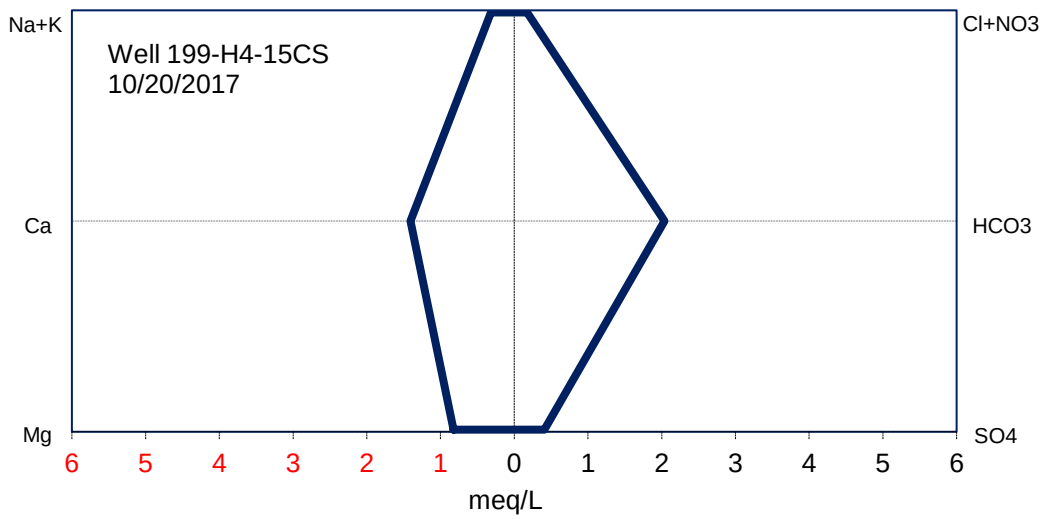
meq/L


Well 199-H4-15CS
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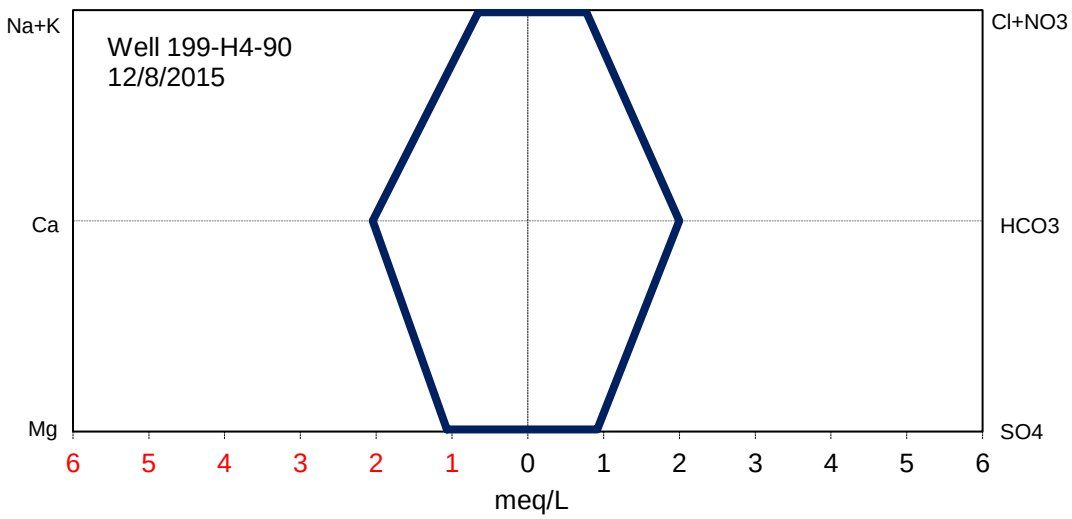
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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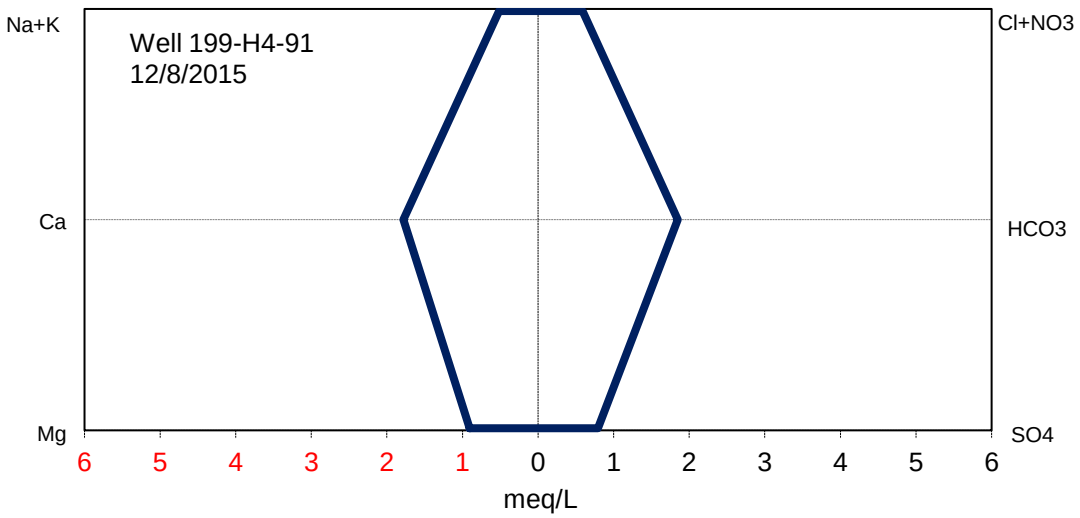
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
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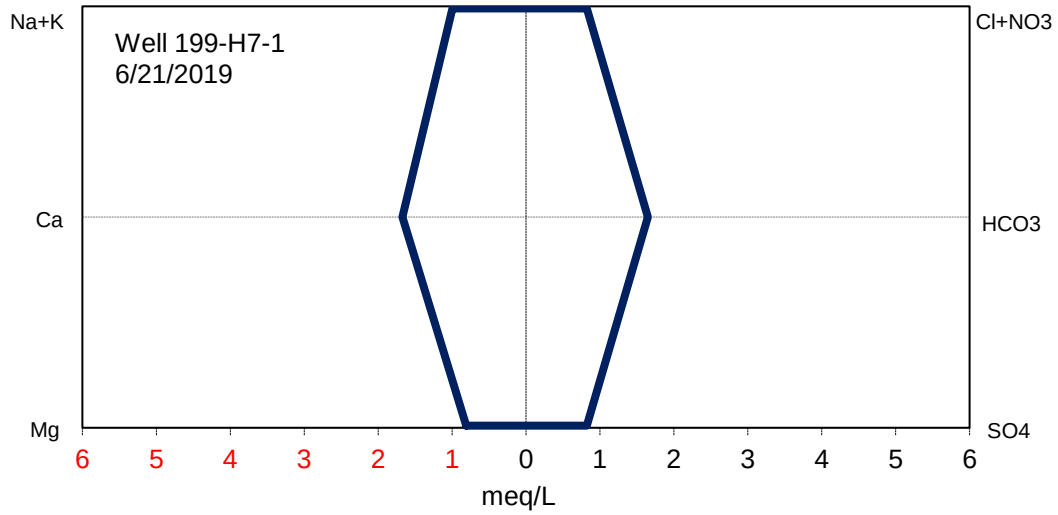
meq/L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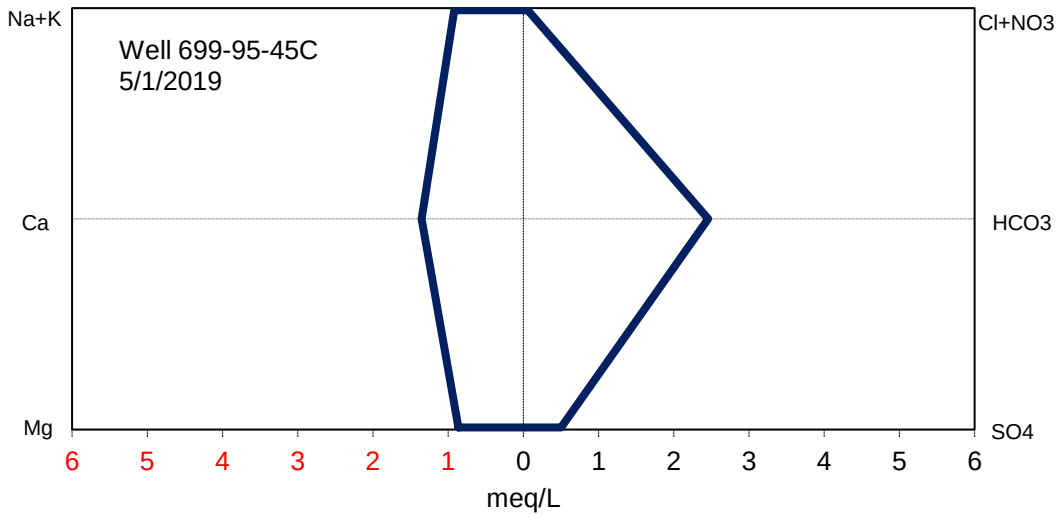
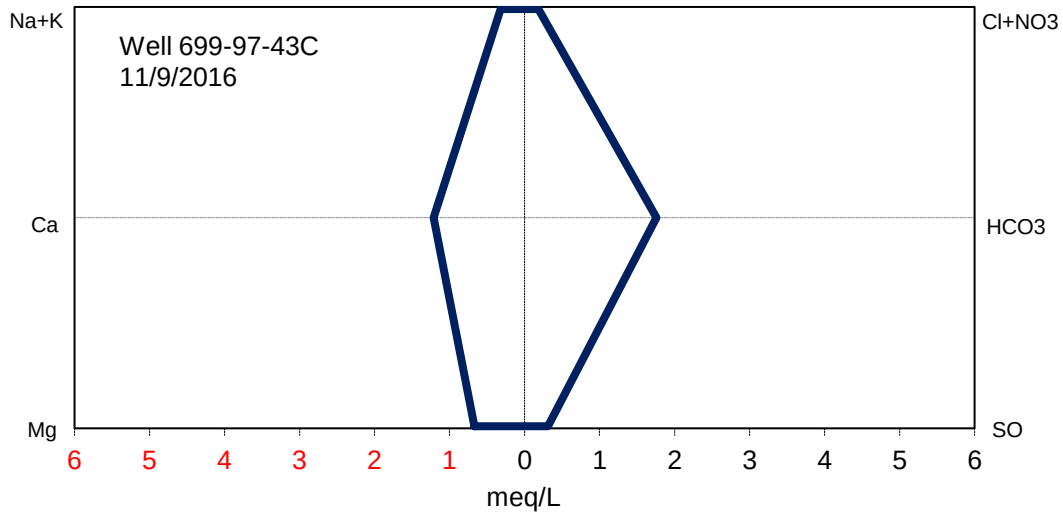
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 699-95-45C
5/1/2019
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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Ca
Mg
Cl+NO3
HCO3
SO
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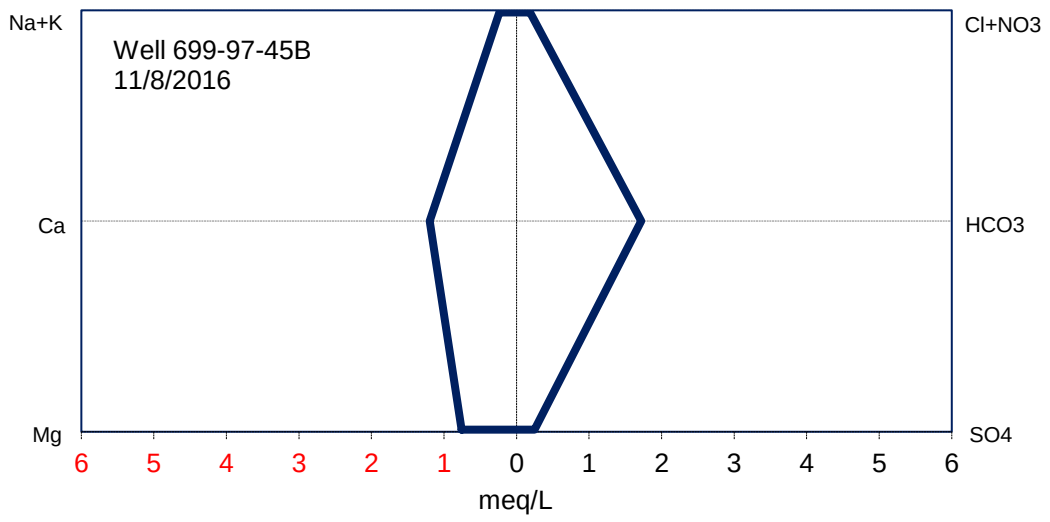
meq/L


Well 699-97-45B
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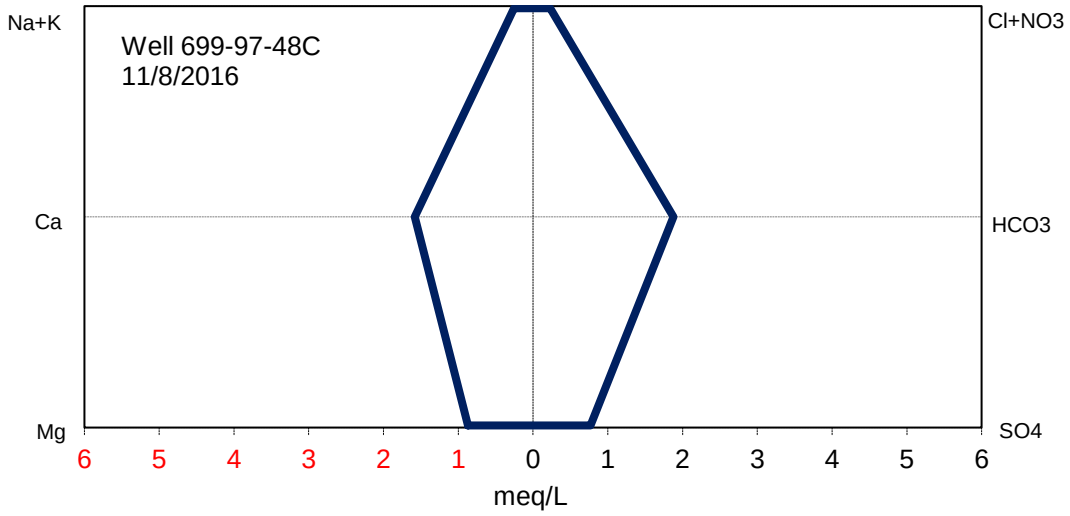
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L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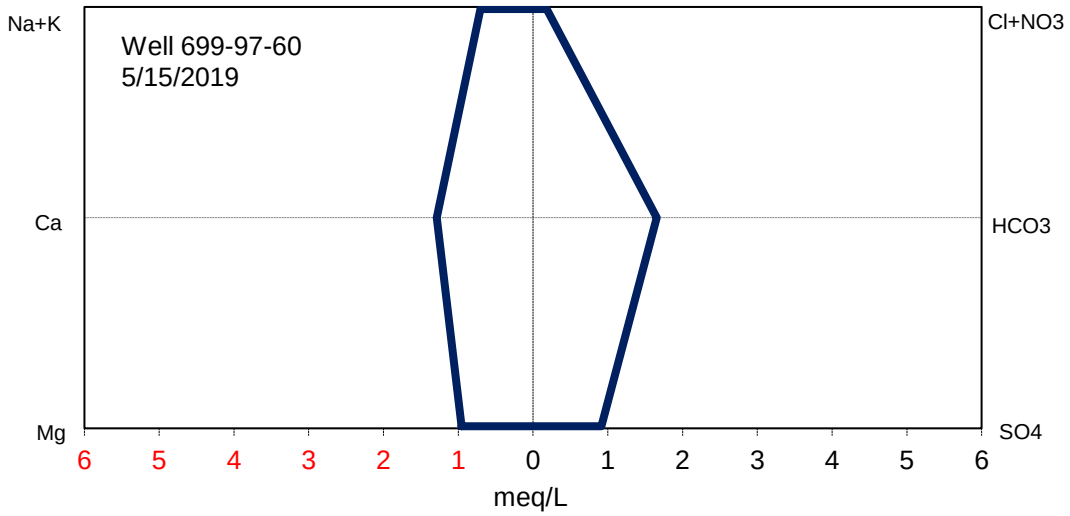
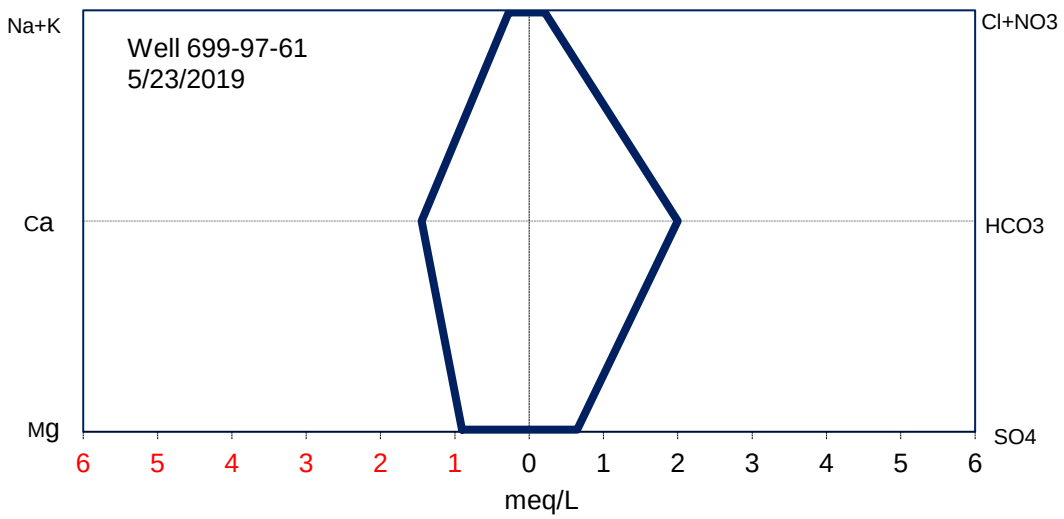
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 699-97-60
5/15/2019
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Well 699-97-61
5/23/2019
Na+K
Ca
Mg
Cl+NO3
HCO3
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L

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Appendix C

Columbia River Sample Stiff Diagrams

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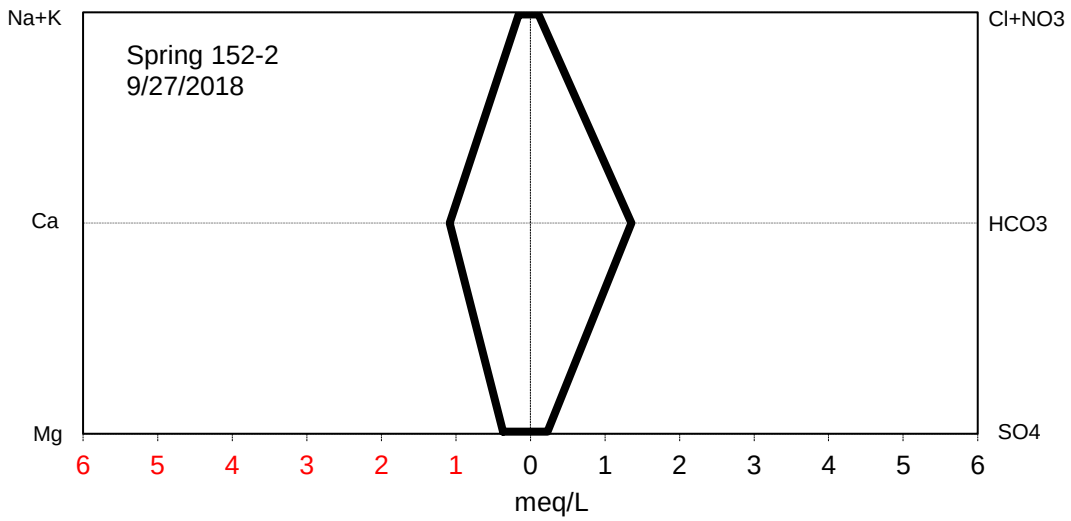
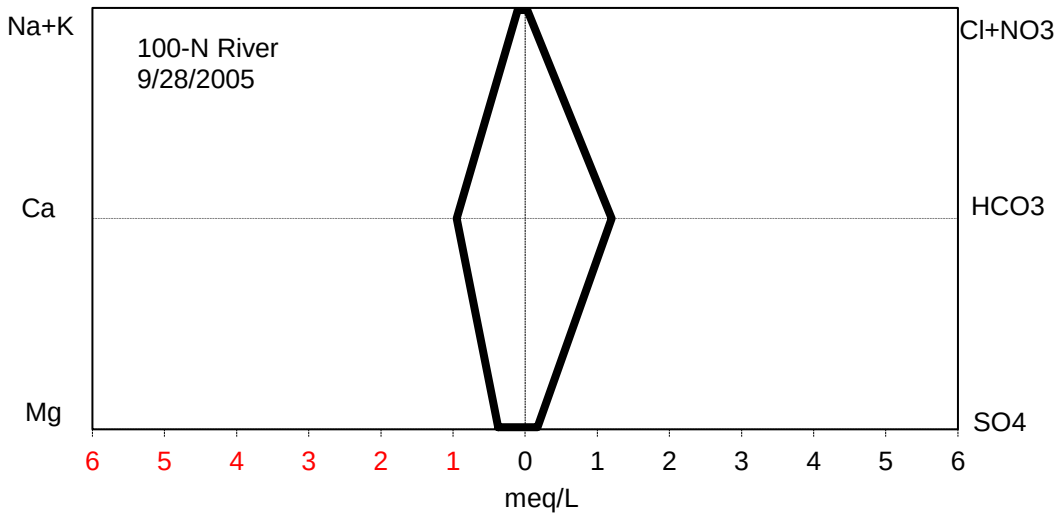

Na+K
Cl+NO3
Spring 152-2
9/27/2018
Ca
HCO3
Mg
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L


Na+K
Cl+NO3
100-N River
9/28/2005
Ca
HCO3
Mg
SO4
6 5 4 3 2 1 0 1 2 3 4 5 6
meq/L

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Appendix D

Stiff Diagrams, Alternative Radial Plots, and Supporting Data and Calculations

Microsoft Excel® Spreadsheets
100-N Area_River_balance_calculations.xlsx
PiperPlot_HR-3.xls
RUM_aquifer_balance_calculations.xlsx
Unconfined_aquifer_balance_calculations.xlsx

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