GEOCHEMICAL CHARACTERIZATION OF VACA MUERTA PRODUCED WATER AND SHALLOW AQUIFERS IN THE NEUQUÉN BASIN

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ABSTRACT

El objetivo del trabajo es comprender mejor la geoquímica de los acuíferos de la Cuenca Neuquina para el correcto monitoreo de las aguas inyectadas en los pozos sumidero. Se utilizó una caracterización hidrogeológica de los acuíferos basada en registros petrofísicos, sísmicos y mediciones de presiones, agregando resultados de análisis geoquímicos de agua e interpretaciones centradas en el monitoreo del agua inyectada. Se midieron las composiciones iónicas e isotópicas del agua en 78 pozos y 3 instalaciones de procesamiento. Se reconoce cierta variabilidad geográfica en las composiciones químicas del agua de cada formación, interpretada como el resultado de la afluencia de agua meteórica impulsada por la topografía con posterior mezcla de aguas subterráneas, disolución mineral e interacciones agua-roca. Se utilizó un algoritmo (Pymix) para probar la sensibilidad del modelo generado para detectar potenciales mezclas de aguas utilizando miembros extremos. Las muestras de agua de producción de Vaca Muerta y de la formación Rayoso resultaron tener entre 0% y 6.9% de diferencia en las composiciones en agua de miembros extremos (diferencia porcentual Pymix vs real), en tanto las muestras de agua de producción de Vaca Muerta y las de la formación Centenario entre 0% y 10.2%, una mayor incertidumbre debido a la similitud en la geoquímica de estas aguas más salinas con origen más profundo. Este flujo de trabajo es un buen ejemplo de la utilización de información hidrogeoquímica para monitorear los pozos inyectores y sus respectivos pozos monitores, lo cual es clave para el desarrollo responsable de los yacimientos no convencionales, como Vaca Muerta.

INTRODUCTION

Groundwater geochemistry and hydrogeology of the Neuquén Basin in Argentina has gained more focus in the past several decades due to the development of hydrocarbon resources from the Vaca Muerta shale. For example, Magnano (2018) applied resistivity and other geophysical methods on exploratory and groundwater well logs and measured water to predict groundwater salinity ranging from 1,000 to 10,000 mg/l in shallow Late Cretaceous formations up to 700 m depth in the

Añelo hydrographic Basin. The study area shown in Figure 1 and 2 is just southeast of the Añelo hydrographic Basin. This work examines detailed water chemistry in aquifers up to 2200 m depth as it relates to water disposal injection monitoring in the Cruz de Lorena (CdL), Coiron Amargo Sur Oeste (CASO) and Sierras Blancas (SB) blocks.

The hydrogeologic framework currently being used for water resource related operations in the study area was performed for Shell by external consultants Tchilinguirian & Turic (2019) using in-house data and available Shell well logs, seismic, pressures and water samples compositions. The goals of this previous work were to understand the regional and local hydrogeology to determine adequate well casing points to protect shallow groundwater, and to characterize potential disposal and water source aquifers. For example, this baseline work was critical to determine the minimum surface casing points required to cover the aerated unsaturated or 'phreatic' zone nearest surface and depth to fully saturated shallow aquifer zones. For example, Figure 2 illustrates where measured pressures were taken in monitor wells at perforated zones to map the potential groundwater flow gradient direction within aquifers, that appear to flow to the northeast within Late Cretaceous Neuquén Group sandstone and siltstone strata.

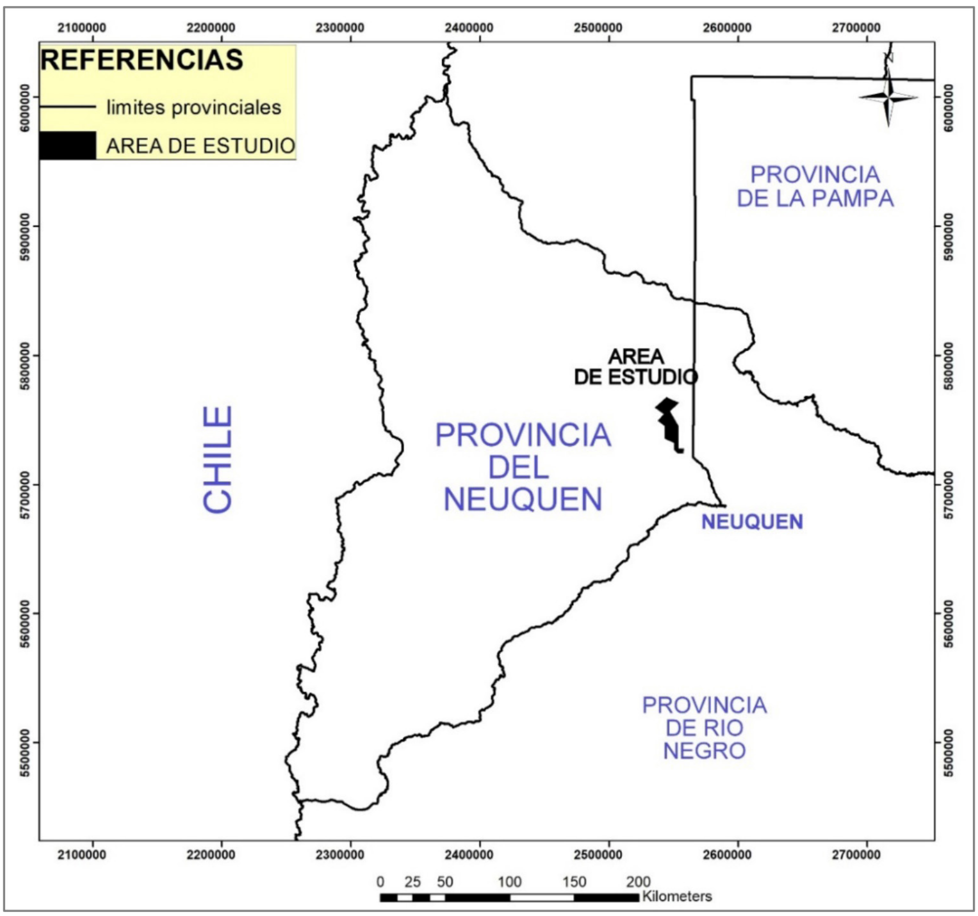

Figure 1. Location of the study area CdL, CASO and SB blocks in the Neuquén basin, Argentina (from Tchilinguirian & Turic, 2019).

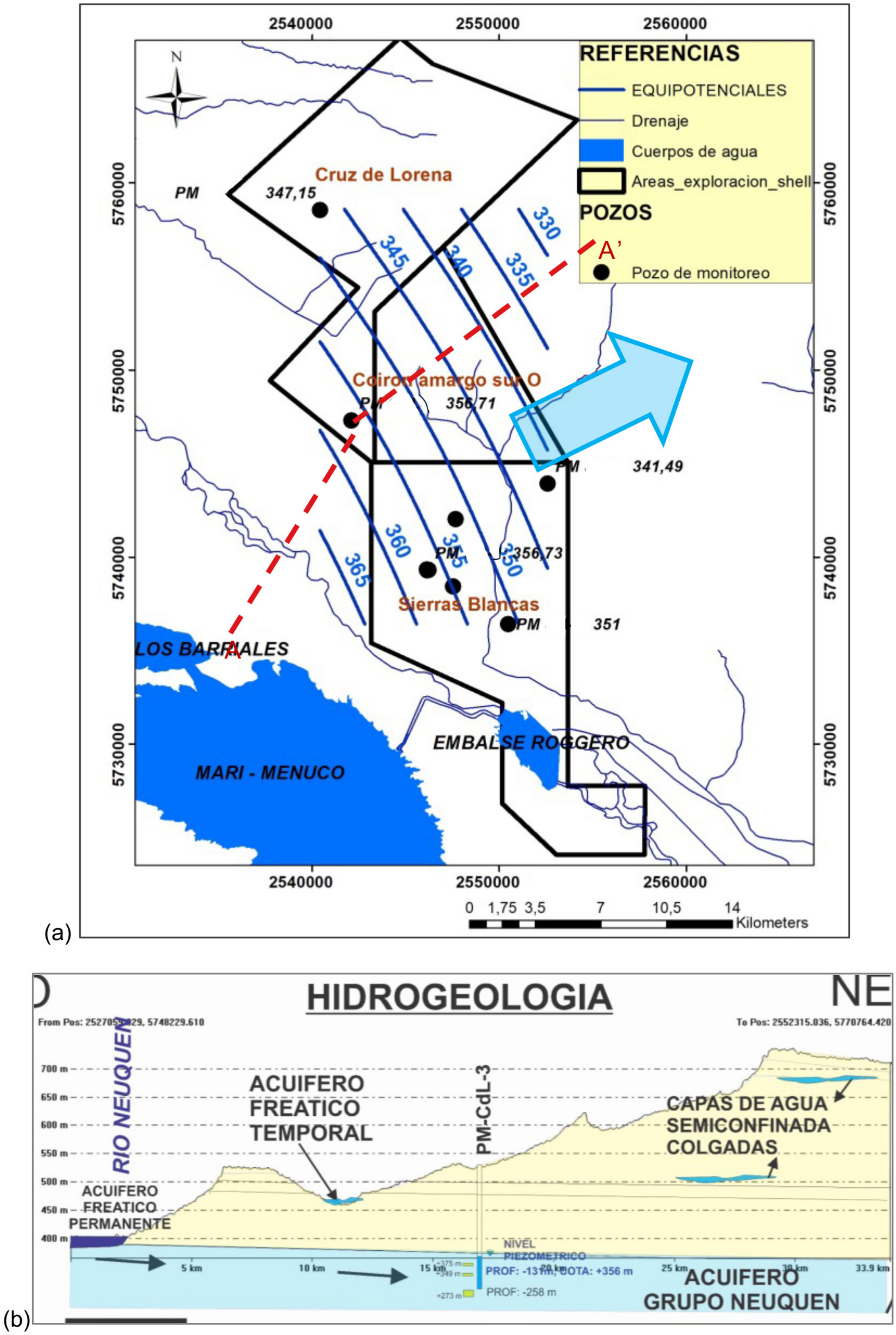

Figure 2. (a) The mapped groundwater potentiometric surface of the top 'phreatic' zone within the Neuquén Group aquifer in meters above sea level (ASL), plus (b) cross section A – A' illustration of the Neuquén Group and observed perched aquifers within the aerated unsaturated zone, including well PM-CdL-3 test location depths for top water depth and dry blocked shale seal integrity measurements at +273 m, +349 m and +375 m ASL (Figures modified from Tchilinguirian & Turic, 2019).

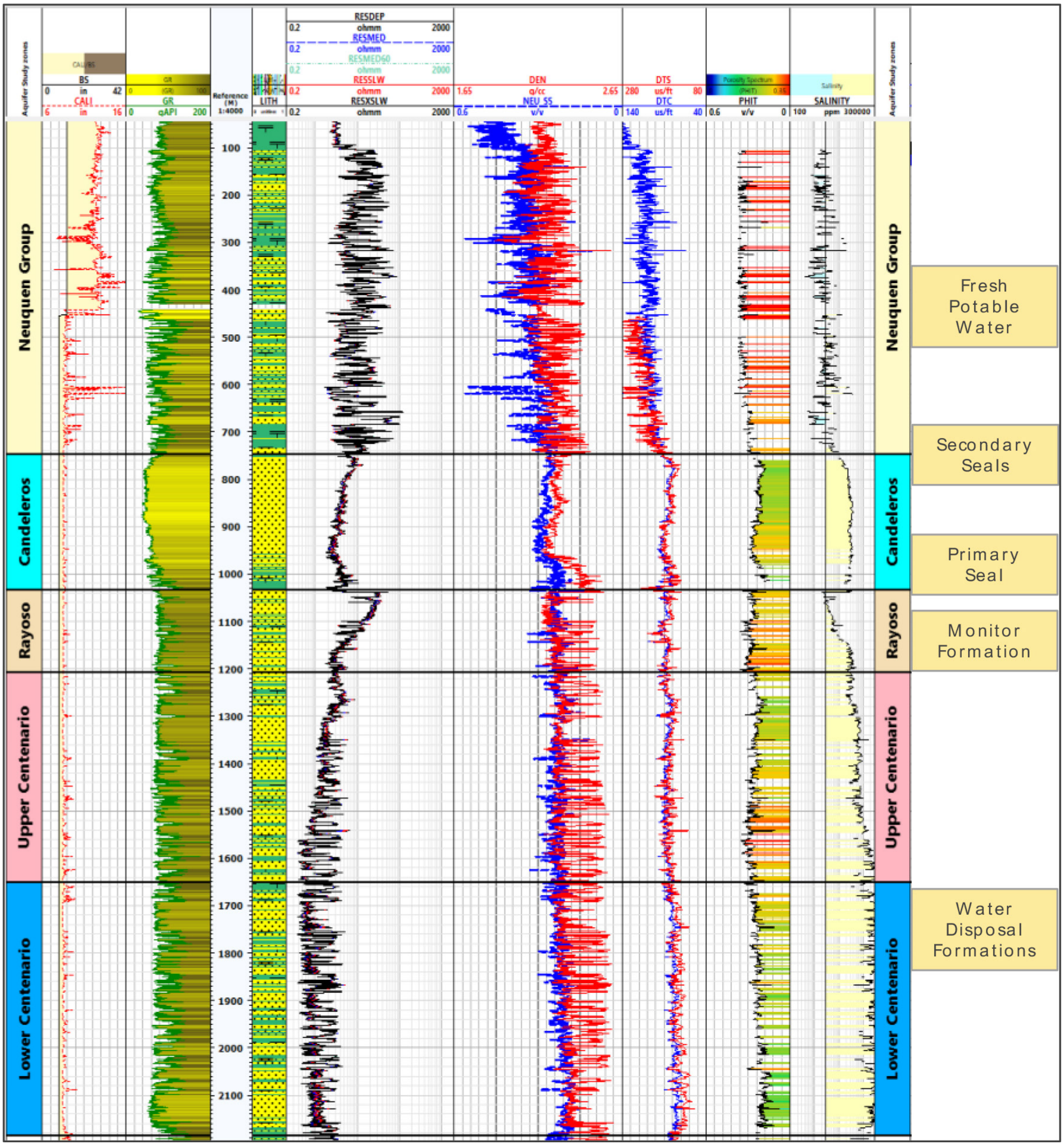

Figure 3. Downhole wireline petrophysical logs and calculated average porosity for each formation including the Upper and Lower Centenario water disposal zones and interpreted interbedded geologic seals including the Lower Candeleros shale and Lower Neuquén Group siltstones and shales.

The current study focuses on the variability of water isotopic and ionic compositions in each formation and includes new Vaca Muerta produced water and downhole repeat formation test (RFT) water samples. Furthermore, geochemical mixing models based on end member water compositions from each zone were trialed to assess if natural tracers are useful to differentiate aquifer waters versus disposal of Vaca Muerta produced waters. Figure 3 of the downhole wireline logs and average porosity for each of the Middle to Late Cretaceous Candeleros, Rayoso, Centenario, Mulichinco and Quintuco formations. Since the Lower Centenario Formation is the water disposal zone, this baseline vertical profile should be measured to determine how effective the primary and secondary seals have been in geologic time, including the Lower Candeleros shale and Lower Neuquén Group cemented siltstones and shales.

Methods

Water samples were collected using surface production separator kits and downhole Repeat Formation Testers (RFT) from water disposal and monitor wells, as well as Vaca Muerta target wells during drilling of surface and intermediate boreholes. A total of 70 samples including 45 RFT water samples were collected from 11 monitor, disposal and Vaca Muerta horizontal wells since 2015 (Figure 4). Water samples are routinely collected from producing Vaca Muerta wells and central processing facilities of comingled produced water, as well as 'swabbed' water samples which have been taken from disposal zone perforations in several wells to verify downhole water sample measured compositions. Subsets of these samples were analyzed for elemental, isotopic and organic compound compositions at several laboratories in Argentina and the United States. These aqueous geochemical data provide the initial baseline conditions for water surveillance studies around water disposal injection wells and Shell-operated areas and end member composition for numerical water mixing models.

The numerical water mixing models in this study use a proprietary algorithm called Pymix that is a python-based tool designed to provide a more systematic fingerprinting from up to hundreds of potential components. The tool has been used for 1) probabilistic effective frac height estimation for Shell's unconventional plays to assess number of well layers to develop in the reservoir cube, 2) conventional reservoir allocation of comingled produced oils, and 3) surface casing vent flow gas allocation for well integrity and abandonment zone selections. Pymix was designed to allocate from many sample points or 'bins' with depth, for example using conventional and sidewall core oil extracts, or mud gas sample carbon isotopes. In this paper two end member mixing models of different water compositions are analyzed to understand the natural variance within this unique dataset. Pymix utilizes multivariate inputs to calculate deterministic 'Best Fit' and stochastic 'Monte Carlo' ranges of predicted outputs and displays results using probabilistic prediction distribution versus depth plots that are easy to compare. For example, bar plots show the % allocation from each bin or end member. Star plot outputs also show the mean sum error solution of the modeled versus produced fluid composition. Also, the error percentage range solution of each parameter in the model is reported, therefore it is easy to remove bad components in the model, or to test the outcome against the analytical measurement error and other associated input data uncertainty. The two end member mixing models used the mean sum of errors minimization method, and the mixing rule was enforced to mix on the ion mass (mg/l) but minimize errors on ionic and isotopic ratios.

Results

Chloride concentration and oxygen isotope depth profile data shown in Figure 5 are from 11 wells in the region of interest, and are from RFT tests, well swab tests and comingled produced Vaca Muerta water. Well-6 and Well-8 in Figure 4 are water disposal injectors wells. Well-7 and Well-9 are monitor wells located nearby the disposal wells to provide collection points from the Rayoso aquifers to collect time series swabbed water samples. The other wells identified in Figure 4 include shallow aquifer monitor wells, and Vaca Muerta horizontal well producer locations where RFT samples were collected during surface and intermediate drilling to characterize baseline aquifer compositions for these shallow aquifers across Shell operated acreage.

The measured chloride concentration and oxygen isotope compositions in Figure 5 indicate relatively low chloride and total dissolved solids (TDS) less than 5000 mg/l for most aquifers down to approximately 1050 m depth, and then a large increase in chlorides and isotopic enrichment is noted especially for the Upper and Lower Centenario formation up to 220,000 mg/l. The TDS, ionic and isotopic composition vary by geographic location. For example, the Upper Centenario Formation can have moderate to high TDS depending on location and depth, but the deeper Lower Centenario Formation always has high TDS. In contrast, the Vaca Muerta formation produced water is of lower TDS than the Centenario Formation, in the TDS range from 77,000 to 130,000 mg/l.

The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition of water samples in Figures 5 and 6 indicates at least two primary groups of waters exist. One water group is composed primarily of fresh meteoric water based on comparison with the nearby Rio Colorado River δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition, and the second group includes the Centenario and Vaca Muerta water samples. Interestingly, the Vaca Muerta δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition becomes more enriched over time and evolves into a distinct water endmember from the Centenario Formation in the most recent samples. It also appears that the Rayoso Formation waters are slightly further away from Rio Colorado meteoric water (Magnano, 2018) compared to the meteoric water line and Neuquén and Candeleros formation waters.

Chloride ion mixing plots in Figure 7 can be helpful to understand the evolution of groundwaters because chloride is considered a conservative aqueous species during groundwater evolution. The possible sources of high TDS brines over 100,000 mg/l are typically related to water mixing with paleo-evaporitic brine or salt dissolution, plus perhaps clay reactions as in unconventional reservoirs (e.g. Fay, 2010). Modern sea water with ~35,000 mg/l TDS and unique composition is also a good reference point to compare water ionic fingerprints. For example, the present-day average sea water, Vaca Muerta and Centenario formation water points in Figure 7 each have distinct Na^+, Ca^{2+}, SO_4^{2-} and Mg^{2+} ion concentrations compared to conservative Cl^- ion. Just based on TDS alone, these deeper formation waters are distinct from the low-TDS Neuquén Group and Candeleros formation meteoric waters. Rayoso RFT water samples in some locations do have higher slightly higher TDS compared to the Neuquén Group and Candeleros formation, which may be related with low levels of natural water mixing between the Rayoso and Upper Centenario formations over geologic time.

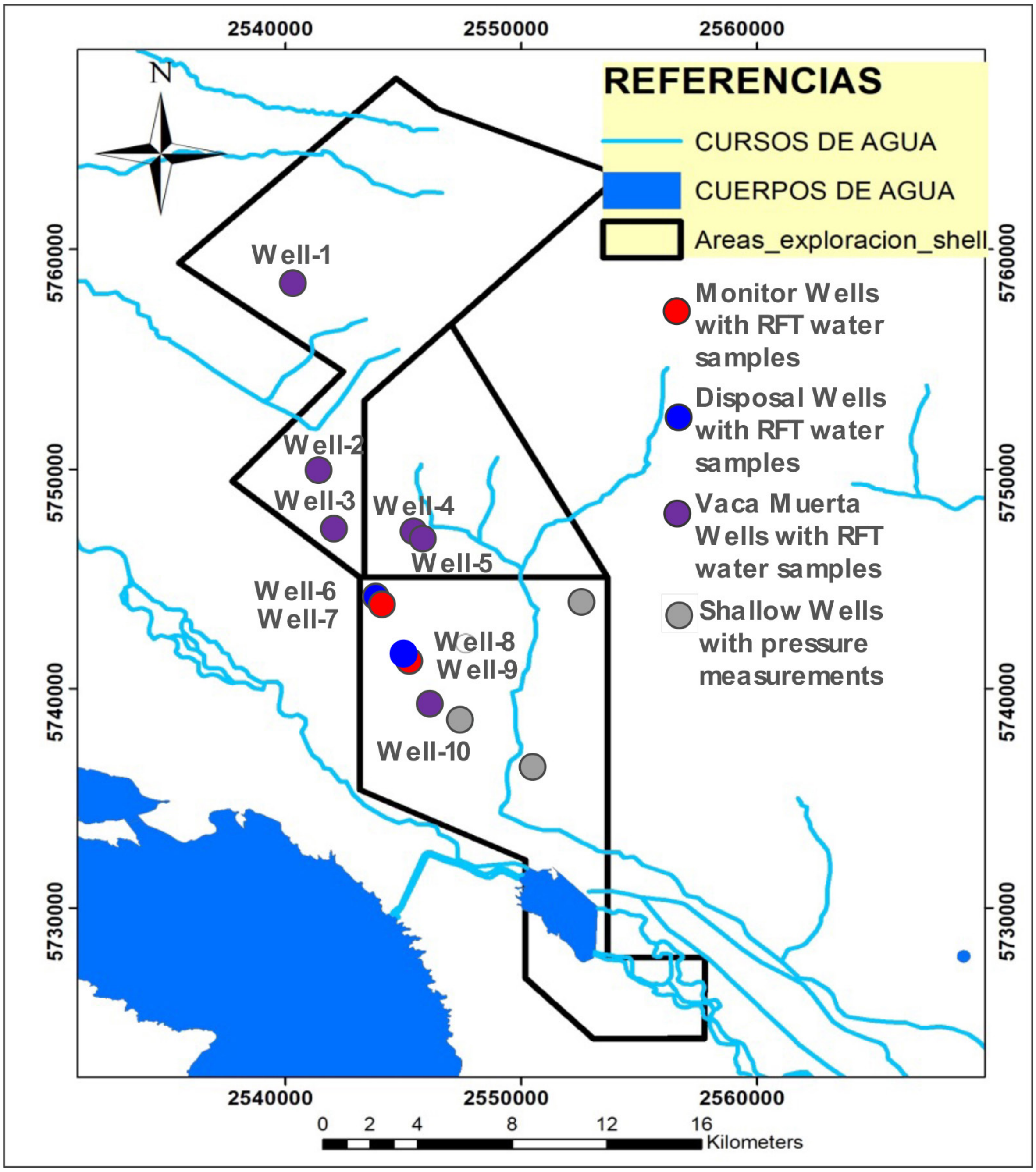

Figure 4. Well locations for water samples collected from surface production separator kits and downhole Repeat Formation Testers (RFT) at disposal and monitor wells, plus Vaca Muerta horizontal target wells in surface and intermediate sections (Modified from Tchilinguirian & Turic, 2019).

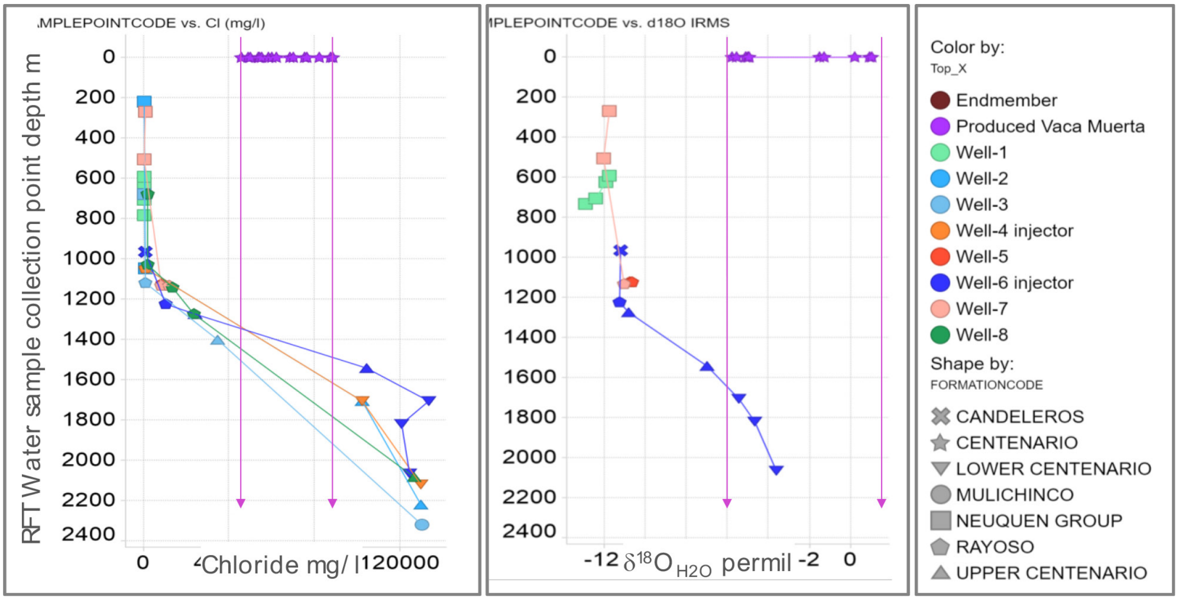

Figure 5. Chloride ion concentration and oxygen stable isotopes $\delta^{18}O_{H2O}$ permil for RFT and well swab test water samples.

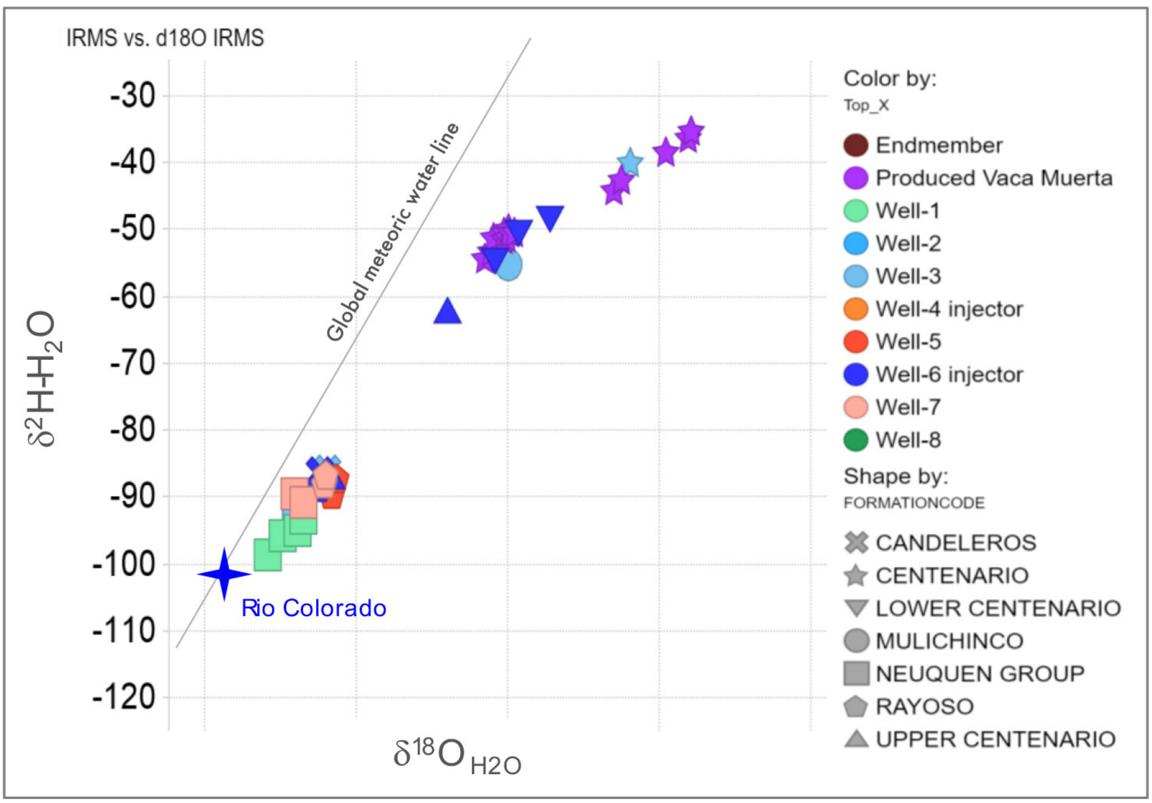

Figure 6. Oxygen $\delta^{18}O_{H2O}$ and δ^2H_{H2O} hydrogen stable isotopes in permil units for RFT, well swab test and Vaca Muerta produced water samples. Local meteoric water Rio Colorado River isotopic composition from Magnano, 2018.

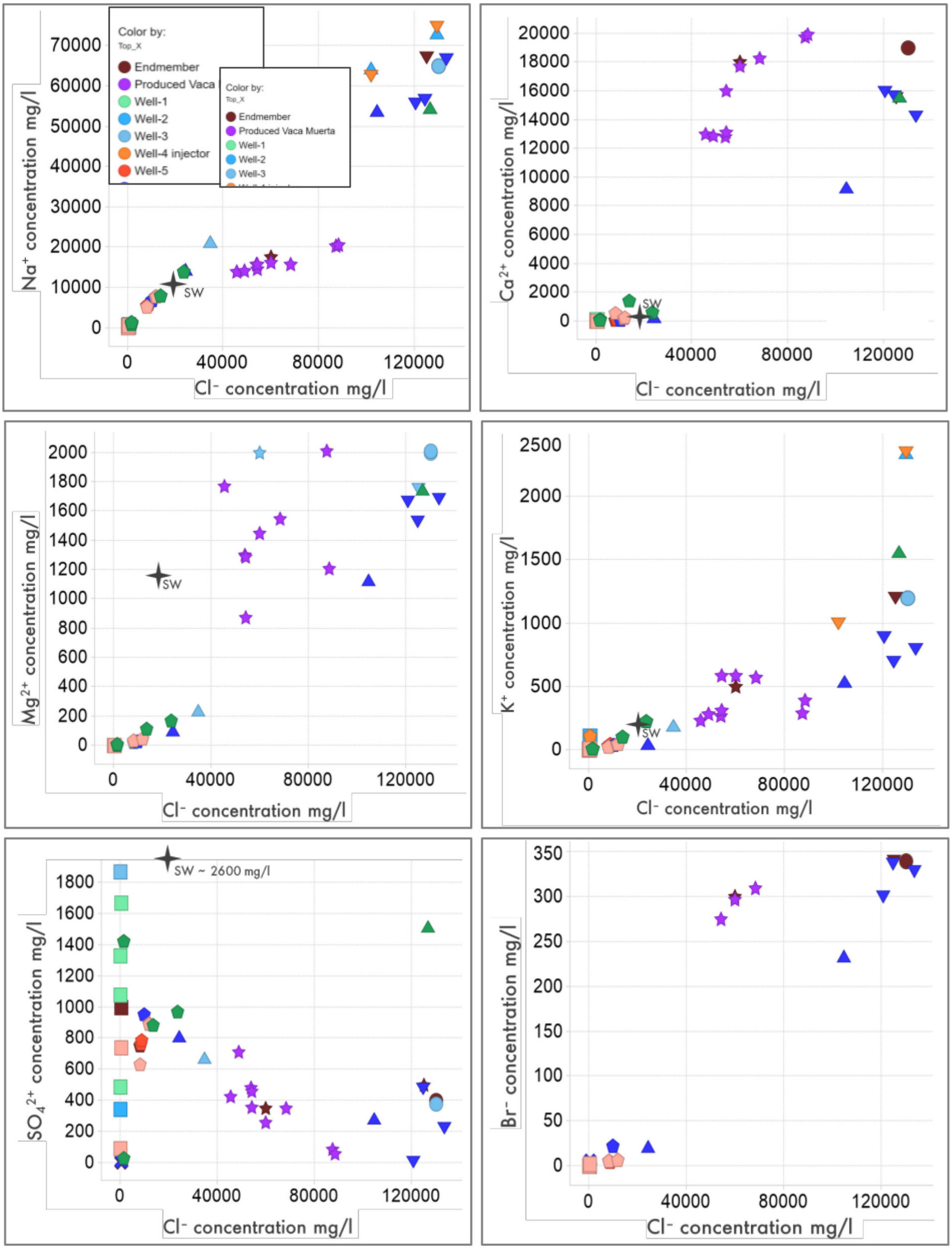

Figure 7. Conservative mixing plots of key dissolved ions in mg/l versus chloride in mg/l including Na^+, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-} and Br^-, as well as the approximate composition of seawater (SW grey stars). Sample points with 0 mg/l indicates that no data is available for that ion.

DISCUSSION

Groundwater provenance

The relative differences in δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition, salinity and ionic species measured in RFT and produced water samples from the Neuquén Basin appear to show, in part, large and unique fingerprints for some formation aquifers and depths (Figures 5 to 7). The origin of these isotopic and ionic differences have other analogs in nature that indicate that more enriched δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition and increased total dissolved solids (TDS mg/l) are the result of rock-water interactions that can occur during groundwater flow at time spans on the order of 10 to 10,000,000 of years (e.g. Fay, 2010). Sources of water and potential mixtures of groundwater include topographically driven meteoric water, paleo seawater trapped during deposition, very high TDS paleo-evaporitic brines, and/or salt and evaporite mineral dissolution.

The Vaca Muerta waters have relatively high Ca^{2+} and Mg^{2+} concentrations that may be attributed to diagenesis of carbonate minerals, aluminosilicate mineral dissolution, or ion exchange (e.g. Milliken, 1989). Also, both the Vaca Muerta and Duvernay shale produced waters appear to have similar relatively high Ca^{2+} and Mg^{2+} ions and this fingerprint can be interpreted to result from ion exchange from the clays with external brine mixing via faults (Fay and Bryndzia, 2016). By comparison, the Centenario waters have relatively high Na^+, Cl^- and Br^- concentrations with TDS up to 220,000 mg/l, and may be interpreted to result from pure halite and evaporite mineral dissolution water end member (e.g. McCaffrey *et al.*, 1987). Furthermore, the relatively high Na^+, Cl^- and Br^- concentrations in Centenario waters are also analogous to the compositions of produced waters from the Marcellus shale unconventional wells in Pennsylvania where very high TDS is due to severe desiccation from dry gas thermally mature shales, plus significant impact from dissolution of the underlying Salina halite salt and evaporites with hydraulic frac water (Bryndzia and Fay, 2016).

The exact source of salinity in the Centenario Formation is not known. Mechanisms proposed for the high salinity in the Centenario Formation suggest that high pressure conditions a shale (aquiclude) can act as a semipermeable membrane allowing the passage of water and selectively preventing the passage of ions in a process similar to reverse osmosis (e.g. Kwaterka *et al.*, 2021). Bryndzia *et al.* (2019) also suggested that clay membranes, osmosis and diffusion process could cause salinity differences up to 100,000 mg/l across shale sand interfaces to explain high salinity water from Wolfcamp shale horizontal wells in the Delaware Basin, Texas. However, in this Wolfcamp case ions diffuse into shales from sandstone brine filled aquifers and water and oil diffuse out of the shale. This proposed movement of water through Wolfcamp is opposite to what is proposed for the Centenario brines in Argentina, where water moves though diffusion and advection through the shales, likely upward into the Rayoso Formation with lower pressure. In both the Centenario and Wolfcamp examples it is difficult to reconcile the mass balance that would be needed for this mechanism of salinity increase to occur. For example, to get Centenario water via semipermeable membrane osmosis and diffusion up to 210,000 mg/l from original sea water at 35,000 mg/l, the water volume required to move through the membrane is at least 1.5 times the water volume in the Centenario Formation present day. This would require a lot of overpressure within the Centenario Formation. The Wolfcamp example is also counter to the natural compaction and thermal maturity drive to desiccate shales since thermal maturation and expulsion of hydrocarbons in organic-rich shales lead to lower water saturations and high cation exchange capacities. A simpler explanation to high salinities in the Centenario is that it resulted from the mixing of paleo-evaporitic brines that are common in foreland basins (e.g. Fay, 2010). Salt and evaporite mineral dissolution may occur along basin edges, but no salt deposits have been found nearby. Bentonite clays may be present in some areas in some Late Cretaceous strata of the Neuquén that could provide some Na-rich cation exchange (Musso *et al.*, 2022). Further work including strontium, sulfur and other elemental isotopes could help to unravel the sources of salinity in the Centenario Formation.

Another noteworthy observation in Figure 7 is that the shallow, low-TDS waters in the Neuquén Group, Candeleros and Rayoso formations have relatively high SO_4^{2-} and HCO_3^- concentrations up to 1,000 mg/l and higher pH compared to Centenario and Vaca Muerta formation waters (7.5-8.5 versus 5.5 to 6.5). This high alkalinity and pH in shallowest formations may be due to meteoric water and carbonic acid influx, coupled with relatively high rates of groundwater flow and low temperature rock-water reactions. Mineral scale formation due to water mixing of disposed Vaca Muerta water injected in Centenario injection wells should be modeled to understand potential impacts to permeability.

The evolution the comingled Vaca Muerta produced water δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition over time is interesting because early produced water (e.g. $\delta^{18}O_{H2O}$ ranging from –6 to –5 permil) suggested they were very similar to Centenario waters (e.g. $\delta^{18}O_{H2O}$ ranging from –7 to –4 permil). More recent comingled Vaca Muerta produced waters likely from wells that have produced longer durations show more enriched δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition with $\delta^{18}O_{H2O}$ ranging from –2 to +1 permil. Since the early time δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition are more depleted, or more negative, then it could be due to new wells coming online resulting in water dilution of this relatively low salinity frac make up water (i.e. Rio Colorado surface water). Once all the Vaca Muerta wells clean-up of early time frac make up water (e.g. 1 to 2 months) then the primary source of produced water will progress to an enriched, or more positive, isotopic composition. This physiochemical process is related primarily to connate and bound water exchange from mineral surfaces at reservoir pressure and temperatures that occur present day as a result of rapid equilibrium of frac make up water with reservoir waters (Bryndzia and Fay, 2014). For example, at high present day reservoir temperature such as the Duvernay shale that is at 110 degrees Celsius near Kaybob, Alberta, the produced water isotopes can have even more enriched δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition with $\delta^{18}O_{H2O}$ ranging from +3 to +5 permil (Bryndzia and Fay, 2016), compared to the Vaca Muerta formation currently ~80 degrees Celsius and $\delta^{18}O_{H2O}$ up to +2 permil.

End member mixing models

In addition to groundwater water provenance and rock-water interaction interpretations, these end member water fingerprints for each formation can potentially be used to assess potential real time water disposal mixing scenarios. If Rayoso formation water can be differentiated from the injected Vaca Muerta water mixture based on isotopic and ionic composition is one key question to answer. Similarly, it is also important to know if the Centenario Formation water can be reliably differentiated from the Vaca Muerta waters that are being injected. In both cases the ultimate goal is to determine the reliable percent of water mixing that can be measured in future monitor well samples from the Rayoso formation. This information would be useful to test for any potential cross formational ground water flow and mixing through possible faults and fractures or poor well cement bond above the perforated disposal zone. Alternatively, if natural isotopic and ionic compositions cannot be used, then radioactive or chemical tracers injected into the disposal water could be used for verification that the disposed water is contained within the Centenario Formation. Similar numerical mixing models could still apply with potentially complex dilution occurring with injected tracers.

Two scenarios using Shell's proprietary Pymix algorithm end member mixing tool were run to test the utility of natural tracers including δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic and ionic compositions in Table 1 for water injection disposal well applications. These endmembers are the average interpreted values because some variability in water compositions occurs, especially for Vaca Muerta comingled produced water. The colored circles in Figure 8 illustrate general groupings of the data used to define the water end member compositions.

Formation	Na^+ mg/l	K^+ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Ba^{2+} mg/l	Sr^{2+} mg/l	Cl^- mg/l	Br^- mg/l	HCO_3^- mg/l	SO_4^- mg/l	TDS mg/l
Neuquen	600	30	50	2	2	2	500	2	600	1,000	2,788
Candelerios	400	30	50	2	2	2	450	2	600	5	1,543
Rayoso	8,000	100	800	120	5	9	13,500	15	300	900	23,749
Centenario	65,000	1,200	15,500	1,750	400	900	125,000	340	50	500	210,640
Mulichinco	65,000	1,200	19,000	2,000	10	900	130,000	340	50	400	218,900
Vaca Muerta	17,500	500	18,000	2,000	100	1,800	60,000	300	100	350	100,650

Formation	Mg_K	Ca_Na	Ca_Mg	Sr_Na	Ba_Ca	SO4_Cl	HCO3_Cl	Br_Cl	δ^{18}O-H2O	δ^2H-H2O
Neuquen	0.07	0.08	25	0.003	0.040	2.000	1.200	0.0040	-12	-91
Candelerios	0.07	0.13	25	0.005	0.040	0.011	1.333	0.0044	-11	-86
Rayoso	1.20	0.10	7	0.001	0.006	0.067	0.022	0.0011	-11	-87
Centenario	1.46	0.24	9	0.014	0.026	0.004	0.000	0.0027	-5	-55
Mulichinco	1.67	0.29	10	0.014	0.001	0.003	0.000	0.0026	-5	-55
Vaca Muerta	4.00	1.03	9	0.103	0.006	0.006	0.002	0.0050	-1	-40

Table 1. End member water ionic concentrations, ion ratios, hydrogen and oxygen stable isotopes, and TDS for each formation sampled from RFT and production test water samples used to calculate the sensitivity of potential water mixtures related to potential cross formation aquifer mixing.

The water composition end members defined in Table 1 were first used to examine mathematical mixtures between two end member cases. Then, actual water samples were tested to see if that formation water sample could be identified. The results in Figure 9 and 10 are displayed as percent difference between the end member Pymix modeled water composition (blue star) to the actual the produced water sample composition (grey star). The vertical axis is depth but is arbitrary in these two end member model cases. Table 2 shows Pymix model results for interpolated mixtures and actual RFT water samples. For example, the Vaca Muerta versus Centenario prediction for 6 RFT water samples percent difference Pymix versus actual predictions results are 0% to 10.2%. The Table 2 contains percent difference of Pymix prediction versus actual for all samples as well as the number of Monte Carlo matches with less than 10% mean parameter error. The mathematically derived mixtures have only a single Monte Carlo Matches solution because the mixing rule was enforced to mix on the ion mass (mg/l) but to minimize errors on ionic and isotopic ratios. Simply mixing only with ionic or other ratios may not provide such an exact result depending on input parameter variance and potential nonlinearity.

The Pymix output plots in Figure 9 shows two large bars versus depth representing 1) the Lower Centenario end member average water composition and 2) comingled produced Vaca Muerta end member water composition. The depth track is arbitrary in these cases but Pymix can perform mixing models using many endmembers along depth to utilize many RFT or other types of fluid samples, but this is beyond the scope of this paper. Since it is known that these are pure Centenario and Vaca Muerta formation waters, then any difference in the prediction can help us understand the predictive potential of this dataset to monitor water disposal zones and surrounding groundwater aquifers.

For the Vaca Muerta versus Rayoso prediction, the percent difference Pymix prediction versus actual ranges from 0% to 6.9% for 5 samples including RFT and well tests. This result indicates that natural H_2O isotopic and ionic compositions can be used to monitor groundwater aquifers and water injection disposal wells, but within 5% to 10% volumetric mixture resolution. Although the results are encouraging to monitor disposal wells in this region, the high variability of the Vaca Muerta comingled water composition increases the uncertainty of the modeled predictions. It is therefore important to take multiple time series samples from monitor and injection wells, and from any other zones to understand how water composition may change through time and across zones. Additional isotopic analysis of sulfate, strontium, bromide and other elements could help to reduce the overall uncertainty by providing additional independent geochemical tracers since the current dataset of ions, ionic ratios and isotopes is highly covariant therefore any additional independent parameters would improve confidence.

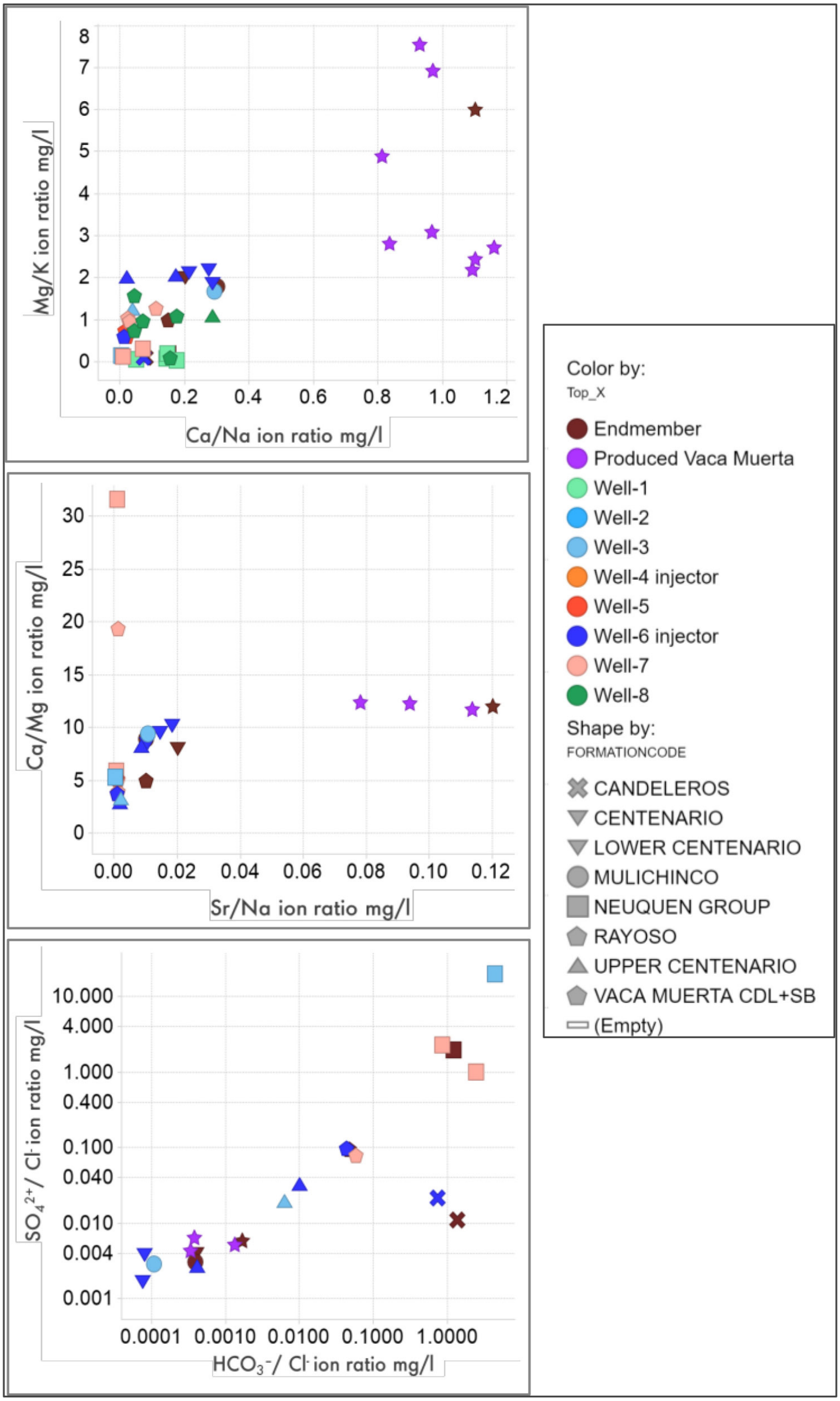

Figure 8. Major ion concentration ratios in mg/l plotted with colored circles to define interpreted average end member water families (blue = Neuquén, green = Rayoso, yellow = Centenario, purple = Vaca Muerta). Different numbers of samples are plotted for each ratio due to missing ions from lab analysis.

Water Mixture or RFT Water Sample End Members	Type	Pymix %	Actual %	% Difference Pymix vs Actual
100:0%_Vaca Muerta:Centenario	Model	100	100	0
80:20%_Vaca Muerta:Centenario	Model	80	80	0
60:40%_Vaca Muerta:Centenario	Model	60	60	0
40:60%_Vaca Muerta:Centenario	Model	40	40	0
20:80%_Vaca Muerta:Centenario	Model	20	20	0
0:100%_Vaca Muerta:Centenario	Model	0	0	0
Well-8 injector Downhole RTF Sample Lower Centenario	Water	0	0	0
Well-8 injector Downhole RTF Sample Lower Centenario	Water	6	0	6
Well-8 injector Well Test Lower Centenario	Water	10	0	10
SOV South Comingled Vaca Muerta Water	Water	90	100	10
SOV South Comingled Vaca Muerta Water	Water	100	100	0
SOV South Comingled Vaca Muerta Water	Water	100	100	0
100:0%_Vaca Muerta:Rayoso	Model	100	100	0
80:20%_Vaca Muerta:Rayoso	Model	80	80	0
60:40%_Vaca Muerta:Rayoso	Model	60	60	0
40:60%_Vaca Muerta:Rayoso	Model	40	40	0
20:80%_Vaca Muerta:Rayoso	Model	20	20	0
0:100%_Vaca Muerta:Rayoso	Model	0	0	0
Well-9 Well Test Rayoso	Water	93	100	7
Well-9 Well Test Rayoso	Water	93	100	7
Well-7 Well Test Rayoso	Water	100	100	0
Well-7 Well Test Rayoso	Water	100	100	0
Well-8 injector Downhole MDT Sample RAYOSO	Water	96	100	4

Table 2. Pymix predictions versus actuals for mathematical water mixtures (Model type) or RFT or produced water samples (Water type) based on δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic and ionic composition end members.

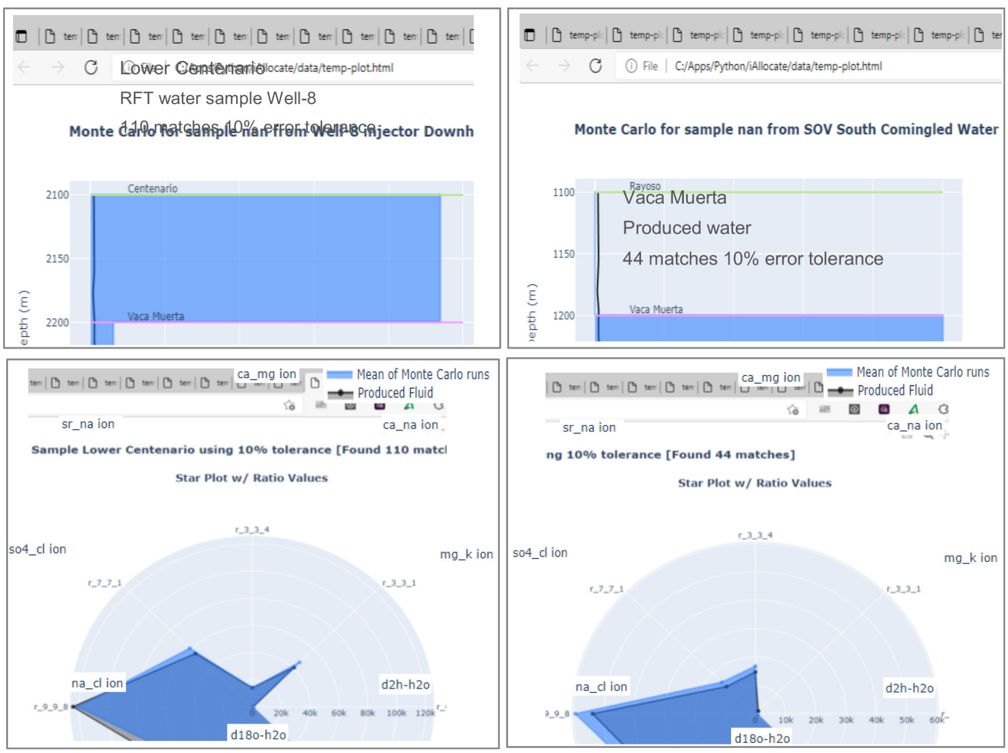

Figure 9. Pymix standard outputs plots for 1) Lower Centenario RFT water and 2) produced Vaca Muerta water average composition two end member mixing model. Top panel included an approximate depth profile for the defined two end member water zone compositions, plus a star plot that compares the end member Pymix 'Mean of Monte Carlo Runs' modeled composition (blue) to actual the produced water sample composition (grey). A perfect 0% error model would have the exact same blue and the grey stars in the plots.

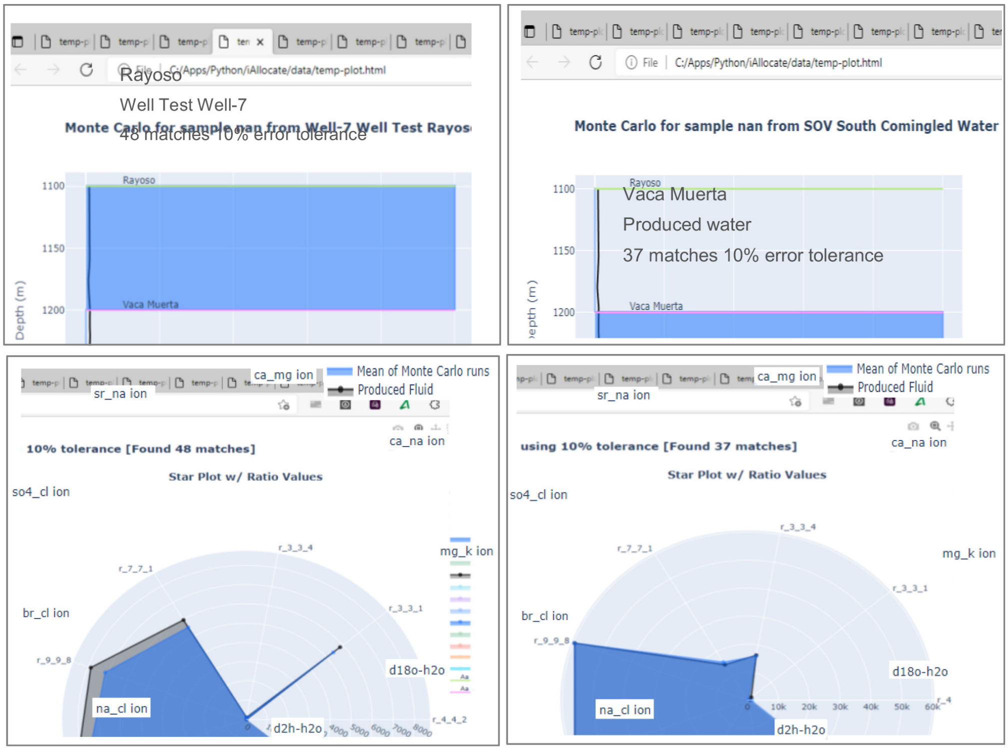

Figure 10. Pymix standard outputs plots for 1) Lower Centenario RFT water and 2) produced Vaca Muerta water average composition two end member mixing model. Top panel included an approximate depth profile for the defined two end member water zone compositions, plus a star plot that compares the end member Pymix 'Mean of Monte Carlo Runs' modeled composition (blue) to actual the produced water sample composition (grey).

CONCLUSIONS

This study helped to understand the evolution of groundwater by using geochemical compositions of numerous Quaternary to Cretaceous aged aquifers and formations in the Neuquén Basin. It appears that multiple different sources of water mix in the region including meteoric water influx into shallow aquifers. Topographic drive up to 1000 m is common in the Neuquén Basin. Mixing with paleo-evaporitic brines is maybe the simplest explanation for the source of high TDS brines. Salt and evaporite mineral dissolution may occur somewhere in the basin but it is not known of any source of halite nearby. Perhaps the Auquilco Formation known for evaporite minerals such as anhydrite and gypsum deposits in the region is a candidate if halite is actually present in other contemporaneous strata nearby, however this formation is stratigraphically deeper than the Vaca Muerta in the area. Centenario high TDS waters could be millions of years old Cretaceous aged modified sea water, and/or have migrated over 100 km in foreland basins. Either way, it is clear that the Centenario Formation is a suitable water disposal zone since the Vaca Muerta produced water is somewhat lower salinity.

The baseline geochemical data from 70 water samples suggests that injected Vaca Muerta and Centenario and Rayoso connate waters can be distinguished with a good level of confidence. The Pymix water end member models appear to be good tools to assess future water samples and potential changes over time. Examples of Pymix end member water mixing model results and sensitivity analyses indicate adequate variance in the natural dataset and confidence limits greater than 90% in most cases.

The Vaca Muerta produced comingled water appears to have a unique fingerprint that has evolved slightly over time. Vaca Muerta flowback water has similar ionic and isotopic fingerprints to other shales like the Duvernay Formation in Canada. The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ isotopic composition data match the predicted temperature controlled isotopic equilibrium with clay bound water at reservoir temperature.

The goal of a water surveillance strategy in water disposal and monitor wells is to ensure that water being injected to a target aquifer or zone is not in communication with water in shallower aquifers that should be preserved. This work presents the technical baseline that enables the implementation of surveillance analysis and modelling using water geochemical fingerprints. Alternative surveillance methods include the injection of a pulse of tracer in water disposal wells. The uncertainty associated with the path of that pulse in the subsurface is a major disadvantage of this method. Based on the results obtained with the proposed water wells surveillance strategy it is recommended to implement a strategy based on geochemistry, and only if cross-communication is flagged by the model, deploy a tracer pulse to confirm what is indicated by geochemistry.

The continued monitoring and sampling of shallower aquifers via RFT tests, as well as sample collection from monitor well swab tests and produced comingled Vaca Muerta water will help to reduce the overall uncertainty and build confidence in the data and predictions. In the future, it will be important to take multiple time series samples of monitor producing wells to verify interpretations. Also, additional isotopic analysis of sulfate, strontium, bromide and other elements could help to reduce the overall uncertainty.

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