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Environmental Significance Statement

Produced water (PW) is the most massive waste stream generated by conventional and unconventional hydrocarbon exploration. Many of the current strategies for reuse and recycling of PW are inefficient because of varying water demand and the spatial and temporal variations in the chemical composition of PW. In this study, we selected PW data sets from three conventional and four unconventional oil and gas formations with varying lithology and depositional environment. This goal was to understand different parameters and processes that control the quality of PW generated from these hydrocarbon-bearing formations by analyzing relationships between their major ion concentrations, O, H, and Sr isotopic composition.

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Understanding controls on the geochemistry of hydrocarbon produced waters from different basins across the US

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ABSTRACT

The most massive waste stream generated by conventional and unconventional hydrocarbon exploration is the produced water (PW). The costs and environmental issues associated with the management and disposal of PW, which contains high concentrations of inorganic and organic pollutants, is one of the most challenging problems faced by the oil and gas industry. Many of the current strategies for the reuse and recycling of PW are inefficient because of varying water demand and the spatial and temporal variations in the chemical composition of PW. The chemical composition of PW is controlled by a multitude of factors and can vary significantly over time. This study aims to understand different parameters and processes that control the quality of PW generated from hydrocarbon-bearing Formations by analyzing relationships between their major ion concentrations, O, H, and Sr isotopic composition. We selected PW data sets from three conventional (Trenton, Edwards, and Wilcox Formations) and four unconventional (Lance, Marcellus, Bakken, and Mesaverde Formations) oil and gas Formations with varying lithology and depositional environment. Using comparative geochemical data analysis, we determined that the geochemical signature of PW is controlled by a complex interplay of several factors, including the original source of water (connate marine vs. non-marine), migration of the basinal fluids, the nature and degree of water-mineral-hydrocarbon interactions, water recharge, and processes such as evaporation and ultrafiltration processes, and production techniques (conventional vs. unconventional). The design of efficient PW recycle and reuse strategies requires a holistic understanding of the geological and hydrological history of each Formation and an account of temporal and spatial heterogeneities.

1. INTRODUCTION

One of the most challenging issues faced by both the unconventional and conventional oil and gas industry is the economic and environmentally-sustainable management of "produced water (PW)" a byproduct associated with their drilling, completions and production operations. Global production of PW is estimated to be > 70 billion barrels per annum, out of which 24.4 billion barrels are produced by the US alone (1,2). Most PW's are highly saline and can contain a variety of inorganic and organic contaminants, including calcium, magnesium, barium, sulfates, bromide; radioactive elements, oil and grease containing polyaromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylenes (BTEX), phenols, and organic acids, and; other chemical additives used in drilling and well stimulation (3–7). These chemicals can have severe environmental impacts if discharged improperly (5,8–14). Because of its high toxicity and high treatment cost, approximately 46% of the PW is injected into non-commercial and commercial disposal wells (11). This results both in wastage of a precious water resource and over pressurization and induced seismicity at the disposal sites in some cases (12,15,16). Considering the shortage of freshwater resources and environmental problems caused by PW disposal, there is a need for implementing better PW recycling and beneficial use strategies. Implementing improved strategies requires an understanding of the PW and how it changes both spatially and temporally in geological Formations of varying lithology, depositional environments, and hydrogeologic history (17).

The quantity and quality of PW can vary significantly in different oil and gas basins because of the variations in lithology and burial history of the geological Formation, hydrological history, extent of evaporation of paleo-seawater, diagenetic reactions, impact of meteoric recharge such as dissolution of evaporite minerals, hydrocarbons being produced, and the water or chemicals injected into the Formation (18). The conventional oil wells produce at an average of about 7 to 10 barrels, or 280 to 400 gallons, of water for every barrel of crude oil (11). The conventional oil wells produce more water than conventional gas wells, and the PW volumes generally increase over time in both types of wells as the oil and gas produced from the reservoirs start to decline (11,19). In nearly depleted fields, the volume of PW could reach 98%, with only 2% hydrocarbons in the produced volume (19,20).

Unlike conventional wells, where the PW is composed almost entirely of Formation water, the PW from unconventional wells is composed of both flowback water and Formation water (21). The "flowback water" is the water produced during the initial days of production and is primarily composed of the returning hydraulic fracturing fluids injected into the Formation during well development along with some of the Formation water. The water generated after this initial period is referred to as "PW" and is dominantly composed of Formation water (22). The cut off time between flowback and PW can range from days to years and is defined variably by different producers and researchers, and hence both waters are generally grouped as "flowback PW."

Median volumes of flowback PW from the six major unconventional oil and gas Formations in the US ranges from 0.5 to 3.8 million gallons or 1.7 to 14.3 million liters per well over the first 5-10 years of production (23). The quantity of flowback PW decreases rapidly after the first few months of production and is accompanied by a sharp increase in salinity (24–30). The mass balance calculations estimate that 92-96% of this flowback PW from unconventional wells is composed of natural Formation water or brine (23). Since the significant constituent of flowback PW in unconventional wells is also the Formation water, in this paper, we use the general term "PW" for both conventional and unconventional wells.

Numerous studies on PW chemistry suggest that the composition of PW depends mainly on the original source of water (connate marine vs connate fluvial, intra-basinal, freshwater recharge) and degree of evaporation (18,24,28,30). Other factors affecting PW composition are various diagenetic inorganic and organic interactions, hydrocarbons in the geological Formation, and ultrafiltration(18). PW from conventional reservoirs are also influenced by artificial fluids used in drilling and completions operations such as mud filtrates used for drilling, brines for well completion, and seawater for enhanced oil recovery (19,31–33). Further, PW and fresh 'make-up' water is commonly added from other Formations to reservoirs for EOR with unknown consequences for in-situ Formation water chemistry (21). In the case of unconventional systems, these interactions are also influenced by the chemical additives included with hydraulic fracturing fluids injected in the Formation (23,34–36). Alley et al. 2011 showed the potential for large differences in chemical and physical properties from different conventional and unconventional reservoirs, and therefore PW disposal and treatment strategies vary significantly.

The goal of this study was to understand the geochemical variations in PW derived from different petroleum systems (conventional vs. unconventional) of varying lithology (siliciclastic vs. carbonates) and depositional environments (fluvial vs. marine). We utilized the geochemical variations in the major ion concentrations and O, H, and Sr isotopic composition of PW to understand: the origin of Formation water (i.e., whether it is marine or non-marine connate water, evaporite dissolution-derived brines); nature and degree of water-mineral interactions; role and extent of freshwater recharge; role of processes such as evaporation and ultrafiltration, and; investigate the influence of oil/gas production technique (i.e. conventional vs. unconventional) in PW quality. The results could be utilized for better predictions of the PW quality at different sites and help to design better water management strategies.

2. SAMPLE SELECTION

Geochemical data of PW samples was compiled from USGS databases (38). All the data were organized and analyzed in an Excel database. The goal was to identify end-member Formations in conventional and unconventional petroleum reservoirs with contrasting lithology, depositional environment, and a complete dataset for the major ion concentrations and O, H Sr isotopic composition. The end-member Fomations chosen in the study are conventional vs. unconventional Formations, carbonates vs. siliciclastic Formations, and marine vs. non-marine Formations. Seven different Formations that were shortlisted based on the criterion mentioned above were Trenton, Edwards, Wilcox, Marcellus, Bakken, Lance, and Mesaverde. The conventional reservoirs chosen are carbonate-rich Trenton and Edwards Formation and clay-rich Wilcox Formation. On the other hand, the unconventional reservoirs are chert-arenite Lance Formation, organic-rich Marcellus Formation, low carbonate- sandstone Bakken Formation, Mesaverde Sandstone as shown in Table 1. The depositional environment, geological time period, and depth of these Formations are also variable. The PW's from Marcellus and Trenton Formations have been extensively studied by several researchers; however, there is a limited number of studies on PW's from Mesaverde, Lance, Wilcox, and Edwards Formations (39–42). Moreover, several of these studies were conducted during the 1980s and 1990s and significant new research on the local geology and hydrogeology of these Formations was published after that time period. In this study, we not only determine the role of local geology, hydrogeological history, and different chemical and physical processes on PW chemistry, but also evaluate if our interpretations are in agreement with the previous studies conducted on these Formations (including the original studies from which USGS compiled the dataset).

The geochemical parameters, including the major ions, stable isotopes (oxygen and hydrogen), and Sr isotope data of the 387 PW samples from these Formations, are listed in the supplementary table, ST1.

Table. 1 Reservoir type, age, lithology, and depositional environment of the Formations chosen for this study.

Formation	Reservoir type	Period	Lithology	Basin	Depositional Environment
Trenton	Conventional	Middle Ordovician	Limestone	Michigan	Shallow marine to relatively deep-water conditions
Edwards	Conventional	Early Cretaceous	Limestone	Gulf Coast	Extensive, shallow-water, marine platform bounded by deeper water basins
Wilcox	Conventional	Paleogene	Clay rich mudstones	Gulf Coast	Predominantly fluvial deltaic, with some turbidite deposition in deeper marine environments
Marcellus	Unconventional (Shale Gas)	Middle Devonian	Mudstones with low carbonates	Appalachian	Dysoxic to anoxic conditions marine environment
Bakken	Unconventional (Tight oil)	Late Devonian	Sandstones and siltstones with low to high carbonates	Williston	Epicontinental sea - shallow-water high energy conditions
Lance	Unconventional (Tight Gas)	Late Cretaceous	Chert-Arenite	Green River	Fluvial to Marginal marine conditions
Mesaverde	Unconventional (Tight Gas)	Late Cretaceous	Sandstones	Green River	Fluvial to Marginal marine conditions

3. RESULTS

3.1 Total Dissolved Solids (TDS)

The TDS values of the PW from all the Formations are shown in a box and whisker plot (Fig. 1). The TDS values of all the Formations range from 125 mg/L to 346100 mg/L. The highest mean values of TDS are observed in Bakken Formation (275069 mg/L), followed by Trenton (214,746 mg/L), Edwards (139,270 mg/L), Marcellus (133,185 mg/L), Wilcox (37433 mg/L), Lance (10847 mg/L), and Mesaverde (8861 mg/L) Formations (Fig. 1). The highest variation in TDS values are observed in Edwards Formation (values range from 139,500 mg/L to 346,100 mg/L) and least variations in Lance Formation (values range from 4,118 mg/L to 21,395 mg/L). The TDS values in Bakken Formation range from 128,124 mg/L to 338,868 mg/L, in Trenton Formation it ranges from 139,500 mg/L to 346,100 mg/L, in Wilcox Formation it ranges from 1658 mg/L to 135268 mg/L, in Marcellus Formation it ranges from 14800 mg/L to 316000 mg/L, in Mesaverde Formation it ranges from 125 mg/L to 13427 mg/L (Fig. 1) .

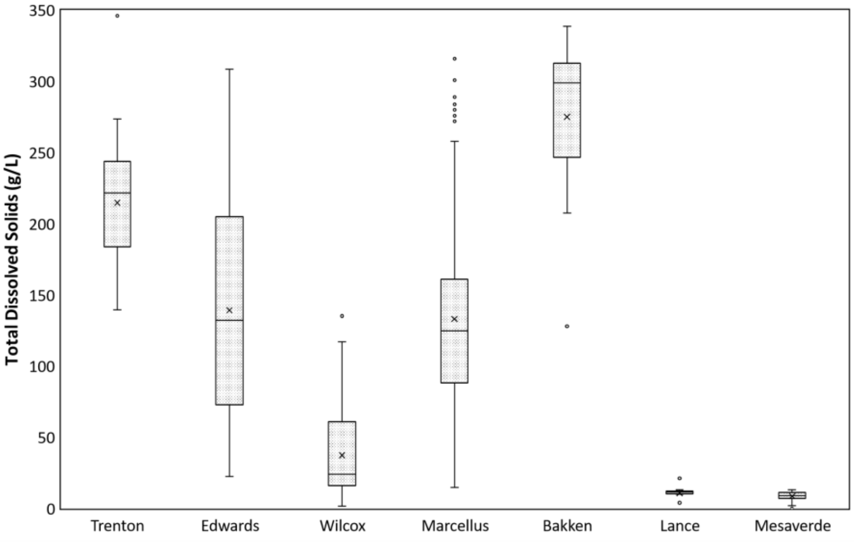

Figure 1. TDS values of PW from different Formations.

3.2 Major Ions

The major ions present in the PW from all the Formations are dominated by Cl followed by Na, then by Ca (Fig. 2). The mean Cl ions concentrations is highest in Bakken Formation (166416 mg/L), followed by Trenton (134,640 mg/L), Marcellus (80882 mg/L), Edwards (84613 mg/L), Wilcox (22688 mg/L), Lance (7366 mg/L), and Mesaverde Formations (3626 mg/L). The mean Na ions concentrations also show a similar trend in different Formations. However, the mean Ca ion concentrations are highest in Trenton, followed by Edwards, Bakken, Marcellus, Wilcox, Lance, and Mesaverde Formations. Other major ions include Mg and K (Fig. 3). However, they do not follow a particular trend in different Formations. Like the TDS results, the highest variation in major ion values is observed in Edwards Formation and the least variations in Lance Formation.

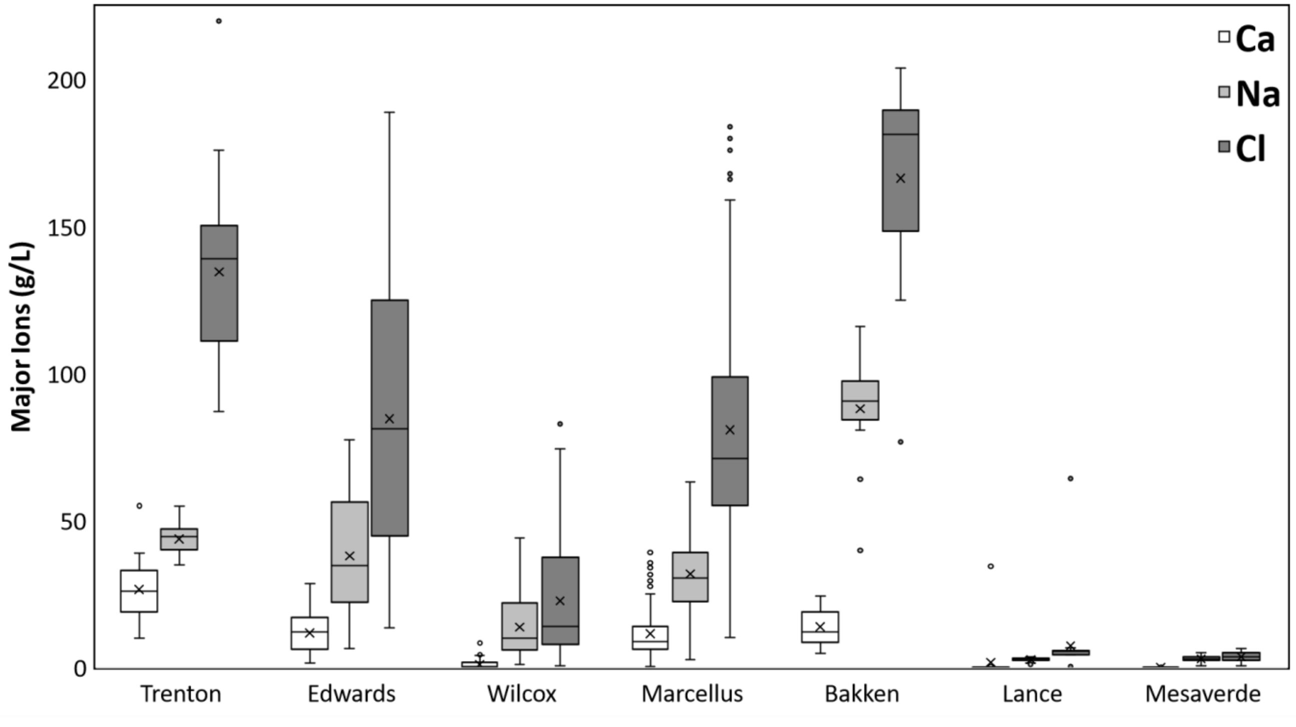

Figure 2. Concentrations of dominant major ions Ca, Na, and Cl in PW from different Formations.

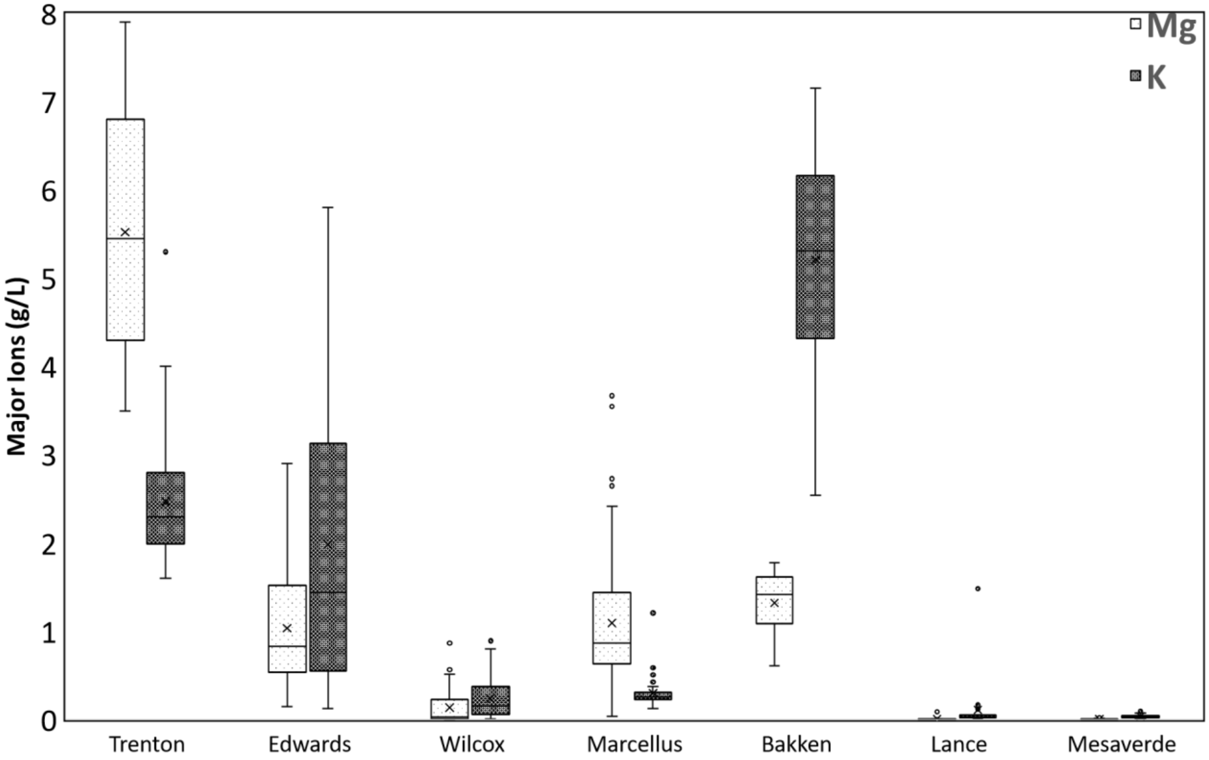

Figure 3. Concentrations of major ions Mg and K in PW from different Formations.

3.3 Sr concentrations and Sr Isotopes

Sr concentration in all the PW samples shows a large range from 0.097 mg/L to 10300 mg/L. The highest Sr ion concentration was present in Marcellus PWs (mean value 2362 mg/L), followed by Edwards (1568 mg/L), Bakken (945 mg/L), Trenton (568 mg/L), Wilcox (201 mg/L), Lance (24mg/L), and Mesaverde (3 mg/L) PW (Fig. 4). The $^{87}Sr/^{86}Sr$ isotope values in all the Formations range from 0.70660 to 0.72016. The highest mean $^{87}Sr/^{86}Sr$ ratio is observed in Mesaverde Formation (0.71641), followed by Lance (0.71218), Marcellus (0.71131), Wilcox (0.71044), Bakken (0.70999), Trenton (0.70989), and Edwards (0.70883) Formations (Fig. 5).

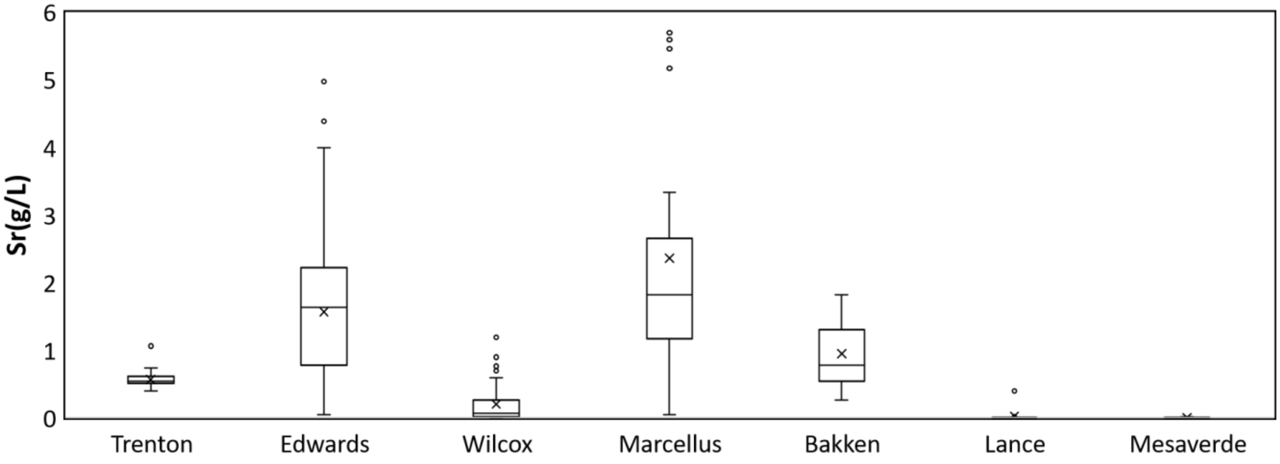

Figure 4. Sr Concentrations in PW from different Formations

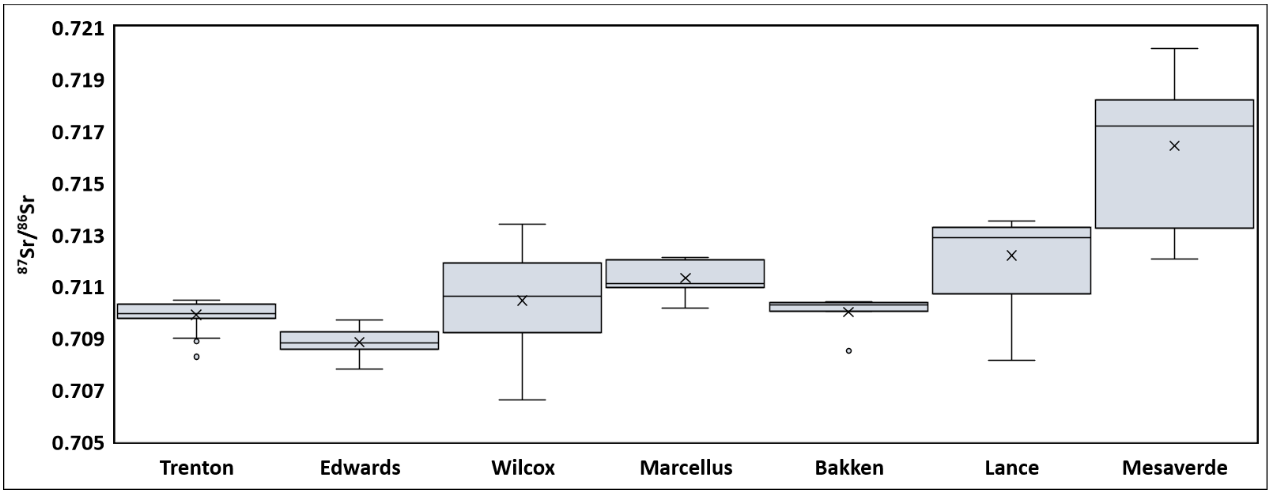

Figure 5. ^{87}Sr/^{86}Sr values in PW from different Formations.

3.4 Oxygen and hydrogen Isotopes:

The δ^{18}O values from all the Formations range from -10 to 18 ‰ VPDB. The highest (mean) δ^{18}O values were observed in Edwards (8.8 ‰ VPDB), followed by Bakken (4.7 ‰ VPDB), Wilcox (1.0 ‰ VPDB), Trenton (-2.0 ‰ VPDB), Marcellus (-2.1 ‰ VPDB), Lance (-2.9 ‰ VPDB), and Mesaverde (-4.9 ‰ VPDB) (Fig. 6). The δ^{18}O values in Edwards Formation range from -3.6 to 18.0 ‰ VPDB, in Bakken from -10.0 to 11.6 ‰ VPDB, in Wilcox from -5.4 to

9.7 ‰ VPDB, in Trenton from -3.1 to 0.4 ‰ VPDB, in Lance from -6.0 to -0.1 ‰ VPDB, in Marcellus -5.6 to -0.4 ‰ VPDB, in Mesaverde -9.2 to -1.9 ‰ VPDB (Fig. 6).

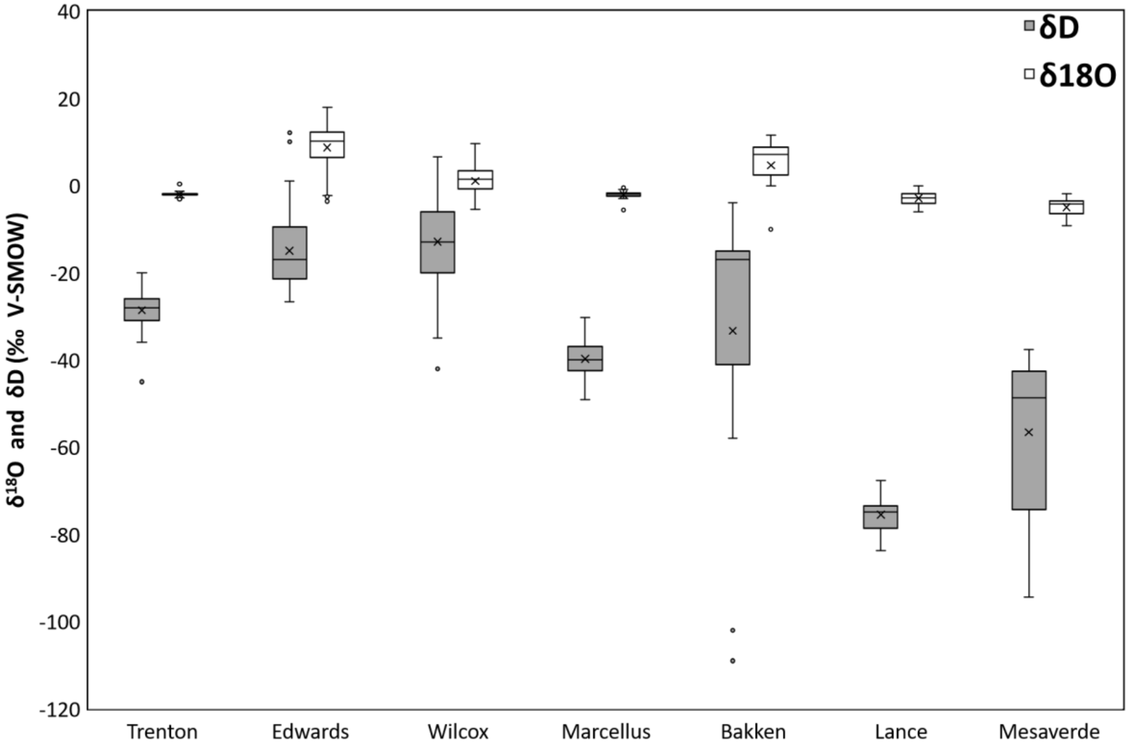

Figure 6. Range of δ^{18}O and δD values of PW from different Formations.

The δD values range from -109 to 12.1 ‰ VSMOW. The highest (mean) δ^{18}O values were observed in Edwards Formation (-15.0 ‰ VSMOW), followed by Trenton (-28.6 ‰VSMOW), Bakken (-33.3‰VSMOW), Marcellus (-39.7 ‰ VSMOW), Mesaverde (-56.6 ‰VSMOW), Wilcox (-12.9‰VSMOW), and Lance (-75.5 ‰VSMOW) Formations (Fig. 6). The δD values in Edwards Formation ranges from -26.6 to 12.1 ‰ VSMOW, in Trenton from -45.0 to -20.0 ‰ VSMOW, in Bakken from -109.0 to -4.0 ‰ VSMOW, in Marcellus from -49.1 to -30.2 ‰VSMOW, in Mesaverde from -94.4 to -37.6‰ VSMOW, in Wilcox from -42.0 to 6.6 ‰VSMOW, and in Lance from -83.7 to -67.6 ‰ VSMOW (Fig. 6).

3.5 Statistical Analysis

One-way ANOVA and Tukey's post hoc comparisons were used to determine similarity/differences in concentrations of TDS, and major ions Na, Ca, and Cl between different PW samples (Supplementary Table 1 to 4). Significant similarities ($\alpha = 0.05$) in TDS concentrations were observed between Marcellus vs. Edwards PW, Wilcox vs. Mesaverde PW, Wilcox vs. Lance PW, Lance vs. Mesaverde PW. For Na, similarities ($\alpha = 0.05$) were observed between Trenton vs. Edwards PW, Lance vs. Mesaverde PW. For Cl, similarities ($\alpha = 0.05$) were observed between Marcellus vs. Edwards PW, Lance vs. Wilcox PW, Lance vs. Mesaverde PW. For Ca, similarities ($\alpha = 0.05$) were observed between Bakken vs. Edwards PW, Bakken vs. Marcellus PW, Edwards vs. Marcellus PW, Lance vs. Mesaverde PW, Lance vs. Wilcox PW, Wilcox vs. Mesaverde PW.

4. DISCUSSION

4.1 Geochemical and isotopic composition of PW’s

In this section, we compare the geochemical and isotopic parameters such as TDS and major ion concentrations, Na-Cl-Br systematics, Sr systematics, Ca/Na vs. Cl cross plots, O and H isotopes of the PW samples from all Formations. The primary aim is to determine the major geochemical differences and trends in PW's within the same Formation and between different end-member Formations. These geochemical signatures were used to understand how the local geology and hydrogeological history impacted PW chemistry in different Formations.

4.1.1 TDS and major ion concentrations

We created a correlation plot of major ions with TDS primarily to determine the sources of TDS in PW. We observed that regardless of the lithology of the Formation or the petroleum system (unconventional vs. conventional), the total dissolved solids are remarkably well correlated (R^2= 0.98) with the distribution of major cations and anions (Fig. 7). This indicates that regardless of lithology or depositional environments, the inorganic salts are major contributors of TDS in the PW. The TDS and major ion concentrations can also be utilized to evaluate: 1) the origin of PW salinity (i.e., whether it is non-marine connate water, evaporated paleo-seawater (marine) connate water, or freshwater dissolution of evaporite minerals); 2) understand the extent of freshwater recharge and dilution of Formation waters; 3) understand diagenetic reactions (or 'water-mineral

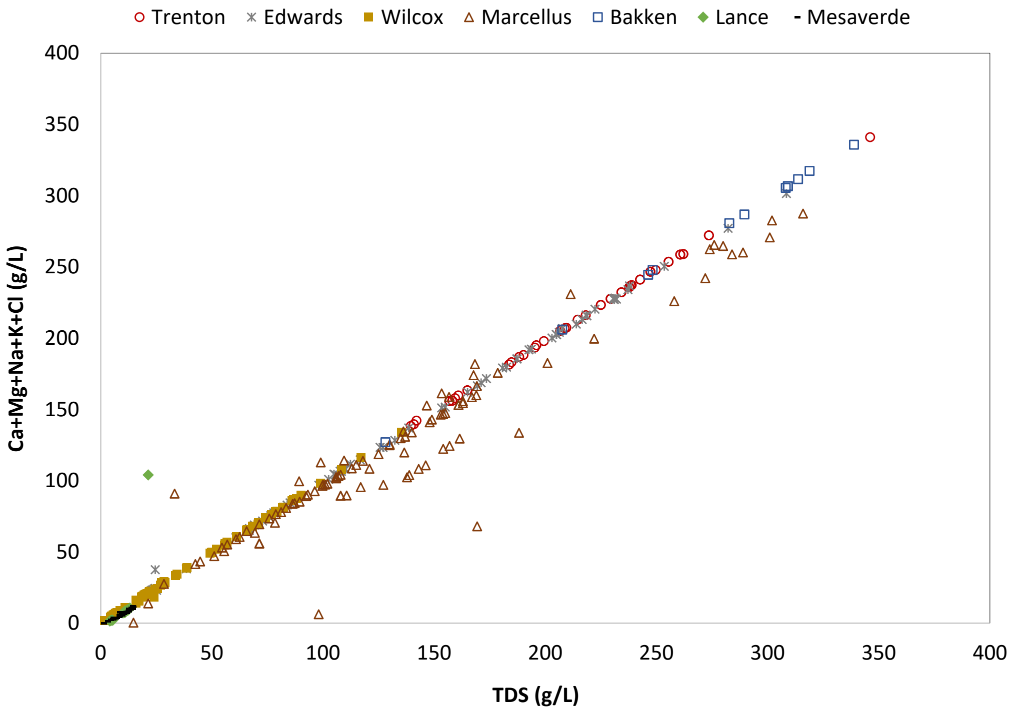

Figure 7. Plot of major ions vs. solutes (TDS) in the PWs from different Formations.

interactions') modifying fluid chemistry; and 4) investigate the influence of oil/gas production technique i.e conventional vs. unconventional (Bartos and Hallberg, 2018; Blauch et al., 2009; Capo et al., 2014; Funayama and Hanor, 1995; Mcintosh et al., 2011; Pacheco, 2005; Phan et al., 2020, 2019, 2018; Rowan et al., 2015; Sharma et al., 2014). The PW from Lance and Mesaverde Formations have the lowest TDS and major ion concentration (Fig. 7). The salt concentrations in the PW are lower in both Lance and Mesaverde Formations primarily because both Formations have fluvial origin of water and are active aquifers that are recharged through precipitation and snowmelt by outcrop infiltration and downward leakage from overlying strata (43,51–53). Further, although Lance and Mesavede Formations are separated by the Meeteetse-Lewis confining unit (54) they might be hydrologically connected where the confining unit is absent (43). Therefore, it is plausible that PW from both these Formations has similar origin. The statistical similarities (p value for similarity <0.05) in TDS and major ions between Lance and Mesaverde also supports this hypothesis (Supplementary Table. 1 to 4).

The TDS and major ion concentration of PW’s from the Wilcox Formation in the Texas region of the Gulf Coast Basin lie in lower to lower-middle value range as compared to other PWs. Wilcox Formation is known to be deposited in a dominantly normal marine environment with some minor fluvio-deltaic input (55). Therefore, PW from Wilcox Formation most likely represents connate marine saline water with relatively higher TDS levels. These relatively higher TDS and major ion concentrations could also be attributed to the pervasive introduction of brines derived from the subsurface dissolution of up-dip salt domes as suggested by (42,45). On the other hand, the Wilcox PWs with lower TDS range might be results of the expulsion of low salinity waters, termed as "shale water," derived in part from dehydration reactions, including the transformation of smectite to illite or by addition of organic acids by kerogen (42,47,56). Another possibility for low TDS could be fresh meteoric water recharge, especially if the samples are derived from shallower Formations (42). These lower TDS (and major ion) PW samples could have led to statistical similarities (p value <0.05) of Wilcox PWs with Mesaverde and Lance PWs (Supplementary Table. 1 to 4). Similar low-salinity values have also been noted at Wilcox PWs at the Righthand Creek field in Allen Parish, LA (47).

Trenton PWs in the Michigan Basin had the second-highest TDS and major ion concentrations (after Bakken). Trenton limestone is known to be deposited in a shallow platform, ramp, and peritidal settings and have undergone dolomitization due to interaction with hot saline hydrothermal brines (57–62). These hydrothermal, basinal saline brines are likely to be the major source of high TDS and major ions in the Trenton PWs. The lower TDS Trenton PWs are plausibly sourced from the part of the basin that received freshwater recharge during the Pleistocene by melting of the Laurentide Ice Sheet resulting in dilution (46,63,64).

PWs from the Edwards Formation had intermediate TDS and major ion concentrations but showed the largest range and variations in values when compared to other Formations (Fig. 1 ,2, 3 and 7). The broader range of values can be attributed to the varying origins of the Formation waters. Although it is established that limestones of Edwards Formation were deposited in a shallow-marine platform, studies have indicated that there are at least two distinct hydrological and geochemical regimes (65). Based on hydrogen and oxygen isotopes and radiocarbon data, it has been interpreted that there is a shallower up dip regime recharged by fresh meteoric water in recent geologic time (less than tens of thousands of years) and a deeper (down dip) regime that is hydrologically isolated and has been thermally altered by reactions with the carbonate rocks (65,66). The deeper saline zone is thought to be hydrologically isolated because of faults that function as barriers to downdip flow of recharge water (65). This compartmentalization of the hydrologic regime possibly results in the wide range of TDS and major ion values observed in the PWs from Edwards Formation.

The PW from unconventional Marcellus shale wells also shows a broad range of TDS and major ion concentrations, as shown in Fig. 1 and 7. The Marcellus Formation is known to be deposited in a deeper marine environment (67–70). Previous studies on Marcellus PW suggested that salinity originated predominantly from the evaporative concentration of paleo-seawater past the onset of halite precipitation (25,28,30,34,48,49,71,72). The higher TDS Marcellus PW represents waters from later production stages (24,28,30,48,49,71). On the other hand, PW samples showing lower TDS and major ion concentrations are from early stages of production and represent a mixture of returning injected fresh water-based hydraulic fracturing fluids and small amounts of saline Formation water. The scattered TDS plots of Marcellus PW (as compared to other PW samples) could also indicate that the shale Formation is more heterogeneous. This heterogeneity is primarily because the low permeability of the Formation results in limited communication between isolated pools of fluids. These broader TDS and major ion ranges for both Marcellus PWs and Edwards PWs samples could have led to statistical similarities between them (p value <0.05, Supplementary Table. 1 to 4).

Unconventional Bakken Formation PW's have very high TDS and inorganic ion concentrations. Previous studies have indicated that the middle Bakken Formation was deposited in an epicontinental sea under shallow marine high-energy conditions (73–75). Several hypotheses have been proposed for the high TDS and major ion concentrations, including seawater evaporation, halite dissolution, migration of high salinity brines from evaporitic environments stratigraphically above or below the Bakken Formation (allochthonous source), or by salinity enrichment of native pore water by membrane filtration (autochthonous source) (73,76).

4.1.2 Na, Cl, and Br systematics

The Na/Br and Cl/Br rations have been extensively used to determine whether salinity in Formation water resulted from evaporative concentration of seawater or from the dissolution of halite (30,73,77–81). During seawater evaporation, halite precipitates, removing Na and Cl ions from solution in a 1∶1 mole ratio. Bromide is almost entirely excluded from the lattice of halite and is rarely incorporated into other mineral phases allowing it to become increasingly concentrated in the residual brine during evaporation (41,82). On the other hand, brines formed from halite dissolution releases Na and Cl ions, and almost no Br ions, making the brines very low in Br or high Na/Br and Cl/Br ratios. Na/Br and Cl/Br in the residual fluid plot as a trend with a constant slope (1∶1 in molar units) extending from seawater toward lower ratios (Walter et al., 1990). Halite dissolution yields Na/Br and Cl/Br ratios that increase along with the same trend away from seawater composition. If the brines are from any other sources such as meteoric recharge or mineral dissolution (other than halite), they plot away from the seawater evaporation -halite precipitation trendline. Therefore, the position of PW samples related to this trend when plotted on the Na/Br vs. Cl/Br plot helps delineate whether salinity is derived from seawater evaporation, halite dissolution, or an independent source (41,81,82).

We plotted the ratio of Na/Br against Cl/Br on an equivalent basis to understand the geochemical evolution of the PWs (Fig. 8). There was a good correlation between Na/Br and Cl/Br in all of the PW samples. All PW samples from Marcellus, Trenton, and Edwards Formations and several of the Bakken and Wilcox samples lie to the left of modern seawater composition (83) indicating that these highly saline Na-Cl type fluids are predominantly derived from seawater evaporation. Previous studies on PWs from Bakken and Marcellus Shale made similar observations (30,73). Although most of the sample from these Formations lie along the seawater evaporation trend line, a wide variation can be observed in the Na/Br and Cl/Br values indicating a varying degree of evaporation, and/or dilution with fresh waters via recharge or introduction of hydraulic fracturing fluids (30,73,79,81). It is interesting to note that although Edwards Formation is generally divided into two distinct hydrological and geochemical regimes (a shallower recharged

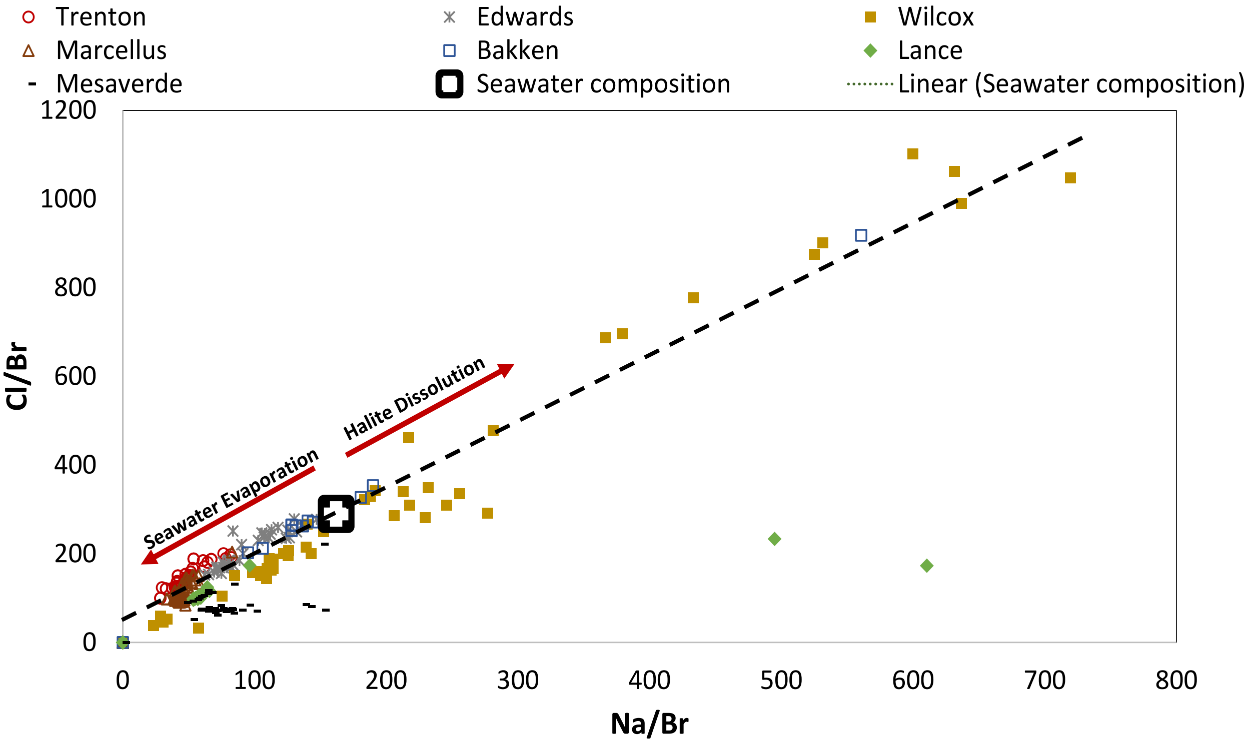

Figure 8: Plot of Cl/Br vs. Na/Br in PWs from different Formations.

meteoric water and a deeper saline water regime) the Cl/Br and Na/Br ratios of all samples fall along the seawater evaporation trend. This could be because of two possibilities 1) the PW samples are mostly from deeper hydrologically isolated part of the Edwards Formation 2) the PW samples are from both hydrologically active and isolated regimes but the Cl/Br and Na/Br ratio of recharged water is similar to seawater evaporation trend (84,85). Some of the Bakken PW samples and a significant number of Wilcox PW lie to the right of seawater composition, indicating halite dissolution. In Wilcox Formation, the high Na/Br and Cl/Br ratios could be a result of the pervasive introduction of brines from the dissolution of up-dip salt domes as suggested by Funayama and Hanor, 1995. The original study (from which the PW data was taken by USGS) did not show such evidence of brines from the dissolution salt domes (42).

PW samples that have low Cl/Br and Na/Br ratios and lie along the seawater evaporation trend indicate that samples have undergone extensive seawater evaporation. However, this does not hold true for Lance and Mesaverde PWs as they are mainly derived from freshwater recharge, as discussed in the previous section. This points to the limitation of using Cl/Br and Na/Br plots plot if there are multiple sources of Formation water. The low Cl/Br and Na/Br in Lance and Mesaverde Formations probably just indicate that the meteoric water recharging these aquifers were depleted in Cl/Br and Na/Br as compared to modern seawater. Further, interestingly a majority of Mesaverde PWs were enriched in Na as compared to Cl indicating ion exchange reactions (Ca replacing Na) and rock–water interactions (such as albite dissolution) that have been occurring for longer periods within the aquifer (51,84,86).

4.1.3 Strontium Isotopes

The isotopic ratio of radiogenic ^{87}Sr (produced by the decay of ^{87}Rb) to stable ^{86}Sr isotope have been used extensively to understand the origin of water, trace water–rock interactions and to identify and quantify sources of water constituents in areas impacted by human activity (25,73,87–94). Unlike stable isotopes of oxygen, hydrogen, and carbon, the isotope composition of Sr is not affected by evaporation and/or biological activity. However, Sr isotopes ($^{87}Sr/^{86}Sr$) can only be used as a natural tracer if the isotope ratios of the potential end members are distinct. If potential end-members have distinct Sr isotopic ratios, Sr isotopes can be used as sensitive indicators of even minute amounts of contamination from brines, and potentially to identify waters interacting with rocks from specific stratigraphic units (25,87,94). We used strontium isotopes to investigate the origin of PW and their possible interaction with sedimentary Formations. The highest $^{87}Sr/^{86}Sr$ ratios are observed in PW from the Late Cretaceous Mesaverde Formations (Fig. 9). The marine $^{87}Sr/^{86}Sr$ ratios ranged from 0.70730 in the Late Turonian to 0.70772 at the Campanian/Maastrichtian boundary (95). The $^{87}Sr/^{86}Sr$ in the Mesaverde PW's are much higher relative to seawater isotopic composition, indicating an enriched ^{87}Sr source. The Mesaverde Formation are dominantly composed of quartz and feldspar that is depleted in Rb/Sr (43). Therefore, the high $^{87}Sr/^{86}Sr$ ratios could be attributed to recharge by waters with high $^{87}Sr/^{86}Sr$ and low Sr concentrations instead of the in-situ mineral-water interactions. The Mesaverde Formation has been known to be recharged by precipitation and snowmelt by outcrop infiltration (43,51–53). These low ionic strength waters react quickly with minerals in the soil and soil substrate, enriching $^{87}Sr/^{86}Sr$ isotopic ratio (94,96) and infiltrating into the Mesaverde Formation.

McLaughlin et al., 2011 also reported high $^{87}Sr/^{86}Sr$ values in spring waters originating from Mesaverde Formation.

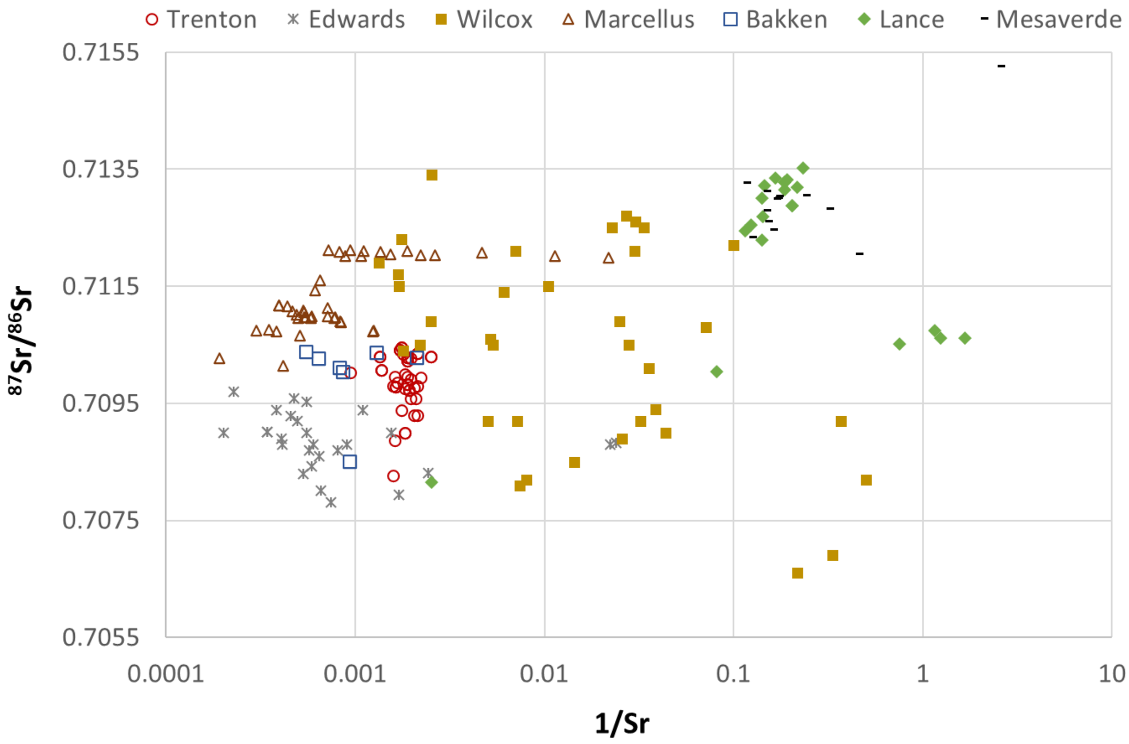

Figure 9. Plot of $^{87}Sr/^{86}Sr$ vs. 1/Sr in produced from different Formations.

Further, Mesaverde PWs indicate two groups of samples, both groups have higher $^{87}Sr/^{86}Sr$ than Late Cretaceous seawater $^{87}Sr/^{86}Sr$ isotopes, but one group is relatively much more enriched in ^{87}Sr as compared to the other (Fig. 9). This may be indicative of an alternate source of aquifer recharge or from dilution of water-mineral (mineral with low $^{87}Sr/^{86}Sr$) interactions such as dolomite dissolution (as postulated by Henderson, 1985 for Mesaverde Formation). The Lance PW's fall in the range similar to the Mesaverde PW's (Fig. 9) with relatively lower $^{87}Sr/^{86}Sr$ values indicating that both these Formations are hydrologically connected and have a similar source of aquifer recharge.

The Marcellus PW's show a narrow range of $^{87}Sr/^{86}Sr$ values (0.710 to 0.712) and higher Sr concentrations (Fig. 9). Similar values have been reported for Marcellus PWs previously (25). These $^{87}Sr/^{86}Sr$ values are higher than the range of Middle Devonian seawater values, in fact more than any Phanerozoic seawater (25,98,99). The enriched $^{87}Sr/^{86}Sr$ could be due to interaction with ^{87}Sr enriched clays in Marcellus Formation or due to interaction of basinal fluids with adjacent units enriched in ^{87}Sr before being incorporated (as brine or salt) in the Marcellus Formation (25). However, if the basinal fluids interacted with adjacent units, the Marcellus PW would inherit the isotope signatures of brines or salts from those units, and it is highly unlikely that they would have such narrow range of $^{87}Sr/^{86}Sr$ values reported here and elsewhere (25,28,48,49). Therefore, $^{87}Sr/^{86}Sr$ ratios are Sr concentrations in the Marcellus PW's are best explained by interactions with salts or brines with the clay minerals having high $^{87}Sr/^{86}Sr$ ratios and Sr concentrations.

The PW's from Bakken Formation also show a very narrow range of $^{87}Sr/^{86}Sr$ values (with the exception of 1 sample) ranging from 0.7100 to 0.7104 and high Sr concentrations (Fig. 9). Similar values are reported previously by Peterman et al., 2017. The Bakken Formation was deposited in seawater with a $^{87}Sr/^{86}Sr$ values ranging from 0.7078 to 0.7082 (100). Bakken Formation is composed of a mixture of minerals with different Rb/Sr ratios ranging from low (plagioclase and carbonates) to high (illite and microcline) values (73) with average Rb/Sr ratio of Middle Bakken Formation, being reported between 0.716 and 0.722 (73,101). Therefore, the high $^{87}Sr/^{86}Sr$ values of Bakken PW's most likely indicate long-term interactions with silicate minerals in the Formation. The low $^{87}Sr/^{86}Sr$ value in one of the Bakken PW samples might be due to a relatively low concentration of silicate/clay minerals or due to basinal fluid migration with low $^{87}Sr/^{86}Sr$ ratios in that part of the basin.

Edwards PW samples are characterized by relatively low $^{87}Sr/^{86}Sr$ ratios but the highest Sr concentrations (Fig. 9). The average $^{87}Sr/^{86}Sr$ ratio in Jurassic seawater was 0.7070, and the average ratio in Cretaceous seawater ranged from 0.7071 to 0.7080; marine limestones should generally reflect the seawater ratio at the time of deposition (65). The high Sr concentration PW is indicative of carbonate dissolution in Edwards Formation (65). However, the majority of the Edward PW's have a higher $^{87}Sr/^{86}Sr$ ratio (as compared to paleo seawater composition), that cannot be attributed to the dissolution of carbonates depleted in $^{87}Sr/^{86}Sr$. Therefore, the source of enriched $^{87}Sr/^{86}Sr$ is probably an allochthonous brine derived from silicate diagenesis as proposed by Land and Prezbindowski, 1985. Although the silicate sediments (Tertiary clastic sediments) in the Texas Gulf Coast subsurface lie stratigraphically above the Edwards aquifer in kilometer-scale, the vertical water convection could move silicate-influenced brines into the Edwards aquifer (102). Further, Groschen and Buszka, 1997 observed that the $^{87}Sr/^{86}Sr$ of the stagnant-group (hydrologically isolated) samples was higher than the $^{87}Sr/^{86}Sr$ of the hydrologically active-group samples. Since most of the $^{87}Sr/^{86}Sr$ ratios observed here are similar to the $^{87}Sr/^{86}Sr$ ratio of the stagnant-group samples, it can be inferred that PW samples in this study are mostly from deeper saline water regime. These results are interesting as the original study (39) did not made such interpretations as the local geology was not well understood. This interpretation is also supported by Na, Cl, Br systematics of Edwards PW.

Trenton Formation had a similar $^{87}Sr/^{86}Sr$ ratio compared to Edwards Formation but a lower Sr concentration. Middle Ordovician seawater has been reported to have $^{87}Sr/^{86}Sr$ of ~0.7080 to ~0.7090 (98,103). Since the majority of the Trenton PWs have higher $^{87}Sr/^{86}Sr$ ratios, a basinal fluid enriched in $^{87}Sr/^{86}Sr$ could be the source of this enrichment. Although the original study (60) did not indicate such intra-basinal migration, other studies in Trenton Formation have provided evidence of the interaction of hot saline hydrothermal brines with the carbonate country rock (57,59,62) and it is plausible that these brines had higher $^{87}Sr/^{86}Sr$ values but a lower Sr concentration. Sr concentrations could have also been lowered by glacial recharge (46,63,64). However, further investigation is needed to confirm this hypothesis.

The Wilcox PW's have a wide range of $^{87}Sr/^{86}Sr$ values and Sr concentration indicative of different types of mineral-water reactions and/or multiple brines sources. The seawater composition of Paleocene to Early Eocene age has values of 0.7076 to 0.7078 (98). The majority of Wilcox PW's have much higher $^{87}Sr/^{86}Sr$ values indicating Rb or ^{87}Sr enriched sources. One of the plausible causes of enrichment could be the pervasive introduction of brines derived from the subsurface dissolution of Sr enriched up-dip salt domes, as suggested by Funayama and Hanor, 1995. Other possibilities include clay mineral water interaction, conversion of smectite to illite, albitization of plagioclase, dilution of potassium feldspar (Wilcoxon, 1989, Pacheco, 2005), or ^{87}Sr released from detrital silicate phases during diagenetic alteration such as ankerite dissolution (104). The wide range in $^{87}Sr/^{86}Sr$ and Sr concentration values indicate that a combination of these processes controlled the Sr geochemistry in Wilcox PW's and a further detailed investigation of PW's and rocks derived from different parts of the basin is required to develop a better understanding.

4.1.4 Calcite Dissolution and Dolomite Precipitation

High Ca/Na vs. Cl in the PW's are indicative of carbonate dissolution in the Formation (48). The majority of the produced waters from Trenton show high Ca/Na vs. Cl, indicating significant carbonate dissolution in the Formation (Fig. 10). The PW's from Edwards Formation can be divided into two groups one with high Ca/Na indicating significant carbonate dissolution and the other with lower Ca/Na indicating little or no carbonate dissolution (Fig. 10). Variable dissolution in similar lithologies (carbonate) and Formation water source (connate marine) suggest that the dissolution is mainly controlled by pH (probably by organic acids). A relatively high Ca/Na vs. Cl in Marcellus Shales also indicates significant carbonate dissolution, as observed by Phan et al., 2020. These observations correlate well with Formation mineralogy, as Trenton and Edwards Formations are dominantly composed of limestones, and Marcellus Shale has a significant amount of carbonate minerals (48,105). No such relationship is observed in other Formations (Fig.10). The PW's from all these three Formations also have high Sr concentrations (as noted in the previous section). These observations suggest that a significant amount of Ca and Sr is released by carbonate-rich Formation minerals in the PW and can be used to track the sources of PW. These observations indicate that even if the Formations have similar lithology (such as Trenton and Edwards) and a similar source of water (connate marine), they can generate different PW signatures. Interestingly, a relatively high Ca/Na ratio in Marcellus PW's compared to Edwards PW's (from group A) indicates that even a dominantly siliciclastic Formation can release more Ca by carbonate dissolution than a dominant limestone lithology. Therefore, a holistic understanding of Formation lithology, sources of Formation water, pH, Eh, and possible mineral-water interactions is necessary to determine the type and quality of PWs.

The Ca/Mg ratio, on the other hand, is a good indicator of dolomitization. It has been observed that Ca/Mg molar ratio reaches to a value of approximately 3 when the system is at equilibrium with dolomite at the reservoir Formation temperature and is unable to further dolomitize limestones (106–109). The average Ca/Mg molar ratio of 2.9 in Trenton limestone indicates that it has undergone dolomitization to a maximum extent, probably by saline hydrothermal fluids (57–59,61,62). A high Ca/Mg molar ratio in Edwards limestone (8.3) and

Marcellus (6.3) indicate that there might be dolomitization in these Formations but it has still not reached equilibrium.

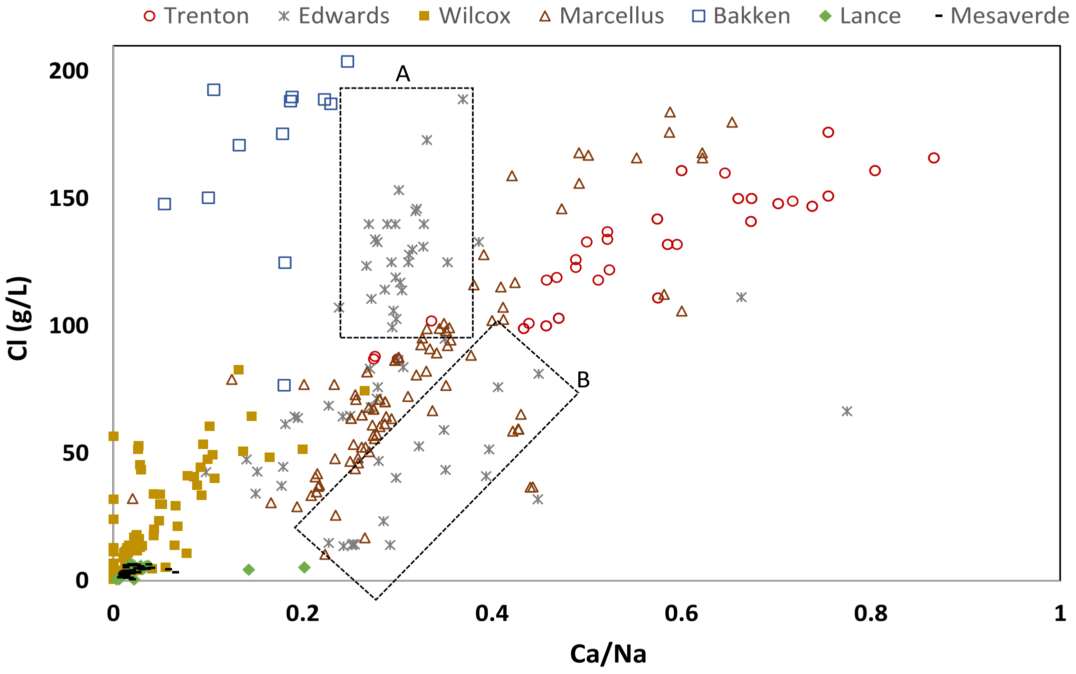

Figure 10 Plot of Cl vs. Ca/Na in PWs of different Formations. A and B represents different groups of PW within Edwards Formation. Group B samples have undergone more carbonate dissolution than Group B

4.1.5 O and H isotopes

Oxygen ($\delta^{18}O$) and hydrogen (δD) isotopes are commonly used as a geochemical fingerprint to distinguish potential sources of water, and their interaction/mixing with other water sources or rocks. The processes that control the isotopic composition of Formation waters in sedimentary basins are: (1) the isotopic composition of the source water (meteoric vs. seawater); (2) isotopic exchange between water and other fluids, especially petroleum; (3) isotopic exchange between water, minerals, and CO_2; (4) evaporation and condensation, and; (5) fractionation caused by ultrafiltration by membrane properties of rocks because of the presence of nano-sized pores, especially in shales or compacted clays (79,110–117). Several studies have used oxygen and hydrogen isotopes to evaluate the origin of PW and their interactions (Groschen and Buszka, 1997; Maekawa et al., 2006; Moldovanyi et al., 1993; Phan et al., 2020, 2018; Rowan et al., 2015; Stewart et al., 2015; Stueber et al., 1998; Sharma et al., 2014, Warner et al., 2012). However, most of these studies concluded that seawater evaporation and meteoric recharge are the most critical processes that control O and H isotopes.

We used the relationship of stable isotopic values of oxygen ($\delta^{18}O$) and hydrogen (δD) for the PWs together with the global meteoric water line (GMWL) and local meteoric waters of the respective regions to further characterize the source of geochemical changes. The local meteoric water lines (LMWL) were constructed for each region using the hydrogen (δD) and oxygen isotope ratios ($\delta^{18}O$) from selected sites of the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) and BENCHMARK surface water networks, to provide the best proxy record for precipitation (122).

Except for the PW samples from Wilcox and Mesaverde Formations and a few samples from Marcellus, the PW samples from other Formations show a general shift in the $\delta^{18}O$ and δD, with a large $\delta^{18}O$ enrichment relative to meteoric water, but a relatively small enrichment in δD (Fig. 11). This indicates that PW's are primarily composed of Formation waters that have undergone extensive evaporation, especially in Trenton, Bakken, Marcellus, Lance Formations. These isotopes may have been further modified by meteoric recharge, clay dewatering or ultrafiltration. Other processes that enrich the O isotopes are carbonate interaction (79,113,114,116).

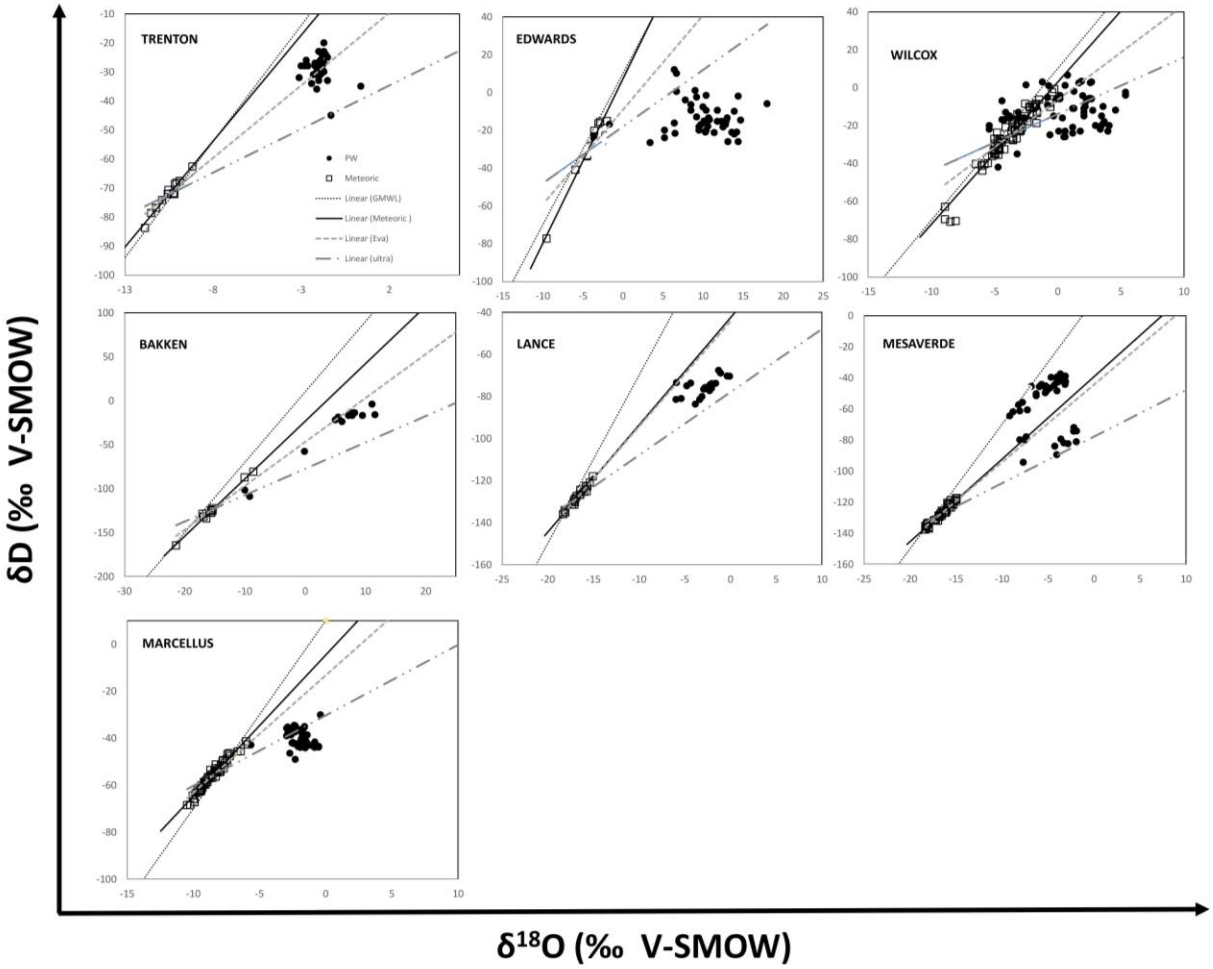

Figure 11 Plot of δD vs. δ18O for the PWs of different Formations plotted together with the local meteoric water constructed by using local O and H isotope data of local waters of individual regions. For the legend: GWML = Global Meteoric Water Line; Meteoric = local meteoric water line; Eva = evaporation; ultra = ultrafiltration.

To further delineate the processes controlling the δ^{18}O and δD, signatures of PW samples were plotted with respect to an "evaporation" and "ultrafiltration" line of meteoric water with slope 5 and 3, respectively for each Formation (as proposed by Mazurek et al., 2009). The enrichment slopes of most of the PW's in Trenton and Bakken Formations coincided with calculated slopes of evaporation (slope of 5), indicating that these extensive evaporated seawaters might have received meteoric water recharge. Most of the PW's from the Marcellus Formation lie along the calculated slopes for ultrafiltration. This suggests that Formation waters primarily derived from seawater evaporation are later affected by ultrafiltration by clay minerals, which fractionate both isotopes and lowers the δ^{18}O and δD concentrations in the hyper-filtrated PW (114). This observation corroborates well with the enriched Sr isotopic composition in Marcellus PWs. Another possible cause for enrichment of δ^{18}O in Marcellus produced water is related to carbonate mineral interactions as discussed previously. A lot of Marcellus PW samples plot closely to meteoric water, indicating they are from the early production stage and are composed mostly of returning hydraulic fracturing fluids (28,30). Edwards PWs show considerable δ^{18}O enrichment indicating the occurrence of water-carbonate interactions accompanied with seawater evaporation (50). Similar isotopic enrichment in δ^{18}O has been reported in brines from several sedimentary basins worldwide and is attributed to isotopic exchange reactions between waters and associated carbonate minerals (e.g., Clayton et al. 1966; Hitchon and Friedman 1969; Kharaka and Thordsen 1992).

The PWs from the Lance Formation and some from the Mesaverde Formation have isotopic values that fall between the evaporation and ultrafiltration curves, which indicates two end member mixing of evaporation and ultrafiltration derived PWs. This suggests the recharged water in these Formations underwent membrane filtration on percolation through soils or soil substrates (probably by soil clay minerals) and then underwent evaporation in the Formation. Mesaverde and Lance also have a few data points along the meteoric water line, indicating dominant meteoric charge. Another interesting observation was that the meteoric water line of samples from Mesaverde and Lance PW regions coincide with the evaporation trend line indicating the meteoric waters sampled from these regions have undergone evaporation. Several PW samples from

Mesaverde Formation fall to the left of the evaporation trend line possibly indicating silicate dehydration (116). However, this hypothesis needs further investigation.

The PW's from the Wilcox Formation showed a wide spread of isotopic values indicating a hydrologically-complex system with possible different sources of connate water (marine vs. fluvial deltaic as suggested by Slatt et al., 1992), pervasive introduction of brines derived from the subsurface dissolution of up dip salt domes (45), or up dip migration or expulsion of low salinity waters derived in part from clay dehydration reactions or meteoric recharge (47,56).

4.2 Major controls on Produced Water quality

In this section we utilize the geochemical signatures and key processes we discussed in section 4.1 to delineate the role of the key variables in controlling the PW quality in different Formations.

4.2.1 Origin of fluids

The origin of fluids is a primary factor that controls the quality of produced waters (in terms of TDS, major ions, and Sr concentration). The source of fluids in different Formations can be fluvial or marine connate water, intra-basinal fluids, and hydrothermal fluid (Bartos and Hallberg, 2018; Blauch et al., 2009; Capo et al., 2014; Funayama and Hanor, 1995; Mcintosh et al., 2011; Pacheco, 2005; Phan et al., 2020, 2019, 2018; Rowan et al., 2015; Sharma et al., 2014).

Both Lance and Mesaverde Formations have low TDS, major ion and Sr concentration reflective of their fluvial depositional environment, and therefore have the best overall PW quality expected to result in less extensive treatment prior to beneficial PW use. Wilcox Formation is deposited in a mixed marine-fluvio-deltaic environment (55). This is one of the primary reasons that TDS, major ion, and Sr concentration of PWs from the Wilcox Formation lie in the intermediate range as compared to other PWs, making their PW quality intermediate (e.g., slightly more challenging to treat to various target water quality standards). The considerable variation in Wilcox PWs indicates that several other processes control its quality (discussed later). The Marcellus Formation was deposited in a deeper marine environment (67–70). The higher TDS, and major ions in the majority of the Marcellus Formation PW samples is primarily due to marine connate water, and therefore have low PW quality (e.g., more extensive water treatment techniques required for beneficial use). The PW quality from Marcellus is worsened by other processes such as evaporation and carbonate dissolution (discussed later). Trenton PWs had the second-highest TDS and major ion concentrations (after Bakken). This is primarily because the Trenton Formation sourced waters from paleo-seawater and intra-basinal saline hydrothermal brines. Trenton PW quality might have been improved due to meteoric water recharge (discussed later). Bakken PWs have the highest major ions and TDS and high Sr concentration, therefore have the lowest PW quality. This low PW quality is mainly attributed to paleo-seawater origin of fluids, and probable migration of high salinity Intra basinal brines, which further degraded the PW quality. Edwards Formation PW showed a signature of original marine connate seawater mixed with migrated of deeper saline brines. However, the mean TDS and major ion concentration from Edwards Formation is intermediate and has high Sr concentration, indicating that other factors (discussed later) were the primary controls on quality of PW.

This discussion shows that the PW quality derived from majority of the Formations is primarily controlled by origin of fluids. A generalized trend of PW quality from different sources is marine connate water mixed with intrabasinal brines ≤ marine connate water < fluvial connate water.

4.2.2 Conventional vs. Unconventional reservoirs

The PW generated from conventional reservoirs is composed entirely of Formation water whereas in unconventional Formations PW is a mixture of flowback water and Formation water. It has been well documented that the PW generated in the initial days or weeks of unconventional reservoir production is primarily composed of fracturing fluids injected into the Formation and has better quality with lower major ion, TDS and Sr concentrations. PW from the later stages is primarily composed of Formation water, has much higher salinity and poor water quality (e.g., more dissolved solutes that require treatment for different beneficial use options). The unconventional reservoirs considered in this study are Marcellus, Bakken, Lance and Mesaverde Formations. A broad range of major ion, TDS, and Sr concentrations are observed in Marcellus PWs. The samples with lower and higher TDS and major ion concentrations can be attributed to early and later stages of production. On the other hand, all of the Bakken PW samples included in our analysis have poor PW quality with high TDS and salt concentration, indicating all these samples are from later stages of production.

All the PW samples from Lance and Mesaverde Formations have low TDS, major ions and Sr concentrations and have good water quality. This is primaririly because the PW's are derived from Formation water which primarily had fluvial origin and has received significant meteoric water recharge (discussed in the next section). These observations indicate that to properly evaluate PW quality, it is important to keep in perspective not only the stages of production but also the hydrogeology of the Formations.

4.2.3 Role of water recharge

Meteoric water recharge improves the PW quality by diluting the major ions, Sr and TDS. Both Lance and Mesaverde Formations are active aquifers that are recharged through precipitation and snowmelt by outcrop infiltration and downward leakage from overlying strata as indicated by the O and H isotope data. Due to this reason, they have the lowest TDS or salt content, and have the best overall PW quality. Evidence of meteoric water recharge is also observed in some of the PWs derived from Trenron Formation, probably by melting of the Laurentide Ice Sheet resulting in dilution of TDS, trace metals and Sr (Mcintosh et al., 2011). In the Wilcox Formation, some of the PW samples from may have also been affected by meteoric recharge as suggested by O and H isotope data (samples plotted close the meteoric water data in Fig. 11), especially in samples derived from shallower Formations (Land and Macpherson, 1992). Shallower Edwards Formation PW have been previously reported to receive meteroric water recharge (65), however, the samples considered in this study do not seem to show such signature implying the PW samples were derived from a deeper hydrologically isolated regime. PWs from other Formations did not show any clear indication of meteoric water recharge.

4.2.4 Role of mineral reactions

Different types of mineral-water interactions can either improve or worsen the PW quality. Dissolution reactions such as carbonate dissolution can increase the major ions, TDS concentration, and Sr concentrations. Signatures of carbonate dissolution are observed in Trenton, Marcellus, and Edwards PWs (Fig. 10, section 4.4), indicating that, although these Formations had similar original sources of water (connate seawater), their PW quality was further hampered by carbonate dissolution. Other common mineral reactions like dolomitization can increase Ca ionic concentration in PW's and could have played a key role in decreasing PW quality in Trenton Formation (section 4.4). Halite dissolution increases the Na and Cl ionic concentration, increasing the TDS and worsening the PW quality. Some of the Bakken PW samples and a significant number of Wilcox PW lie to the right of seawater composition on Na/Br and Cl/Br plots, indicating halite dissolution could be the primary cause of the poorer water quality. Clay dehydration reactions can improve PW quality by releasing water. The smectite to illite transformation in Wilcox Formation (as evidenced by O and H isotopes) could have released water and helped improve the quality of some the Wilcox PW's. The two opposing effects of halite dissolution and clay dehydration could be the plausible reason for the intermediate TDS and PW quality from Wilcox Formation. Lance and Mesaverde PW's did not show clear evidence of mineral dissolution or precipitation reactions. However, their high $^{87}Sr/^{86}Sr$ ratio shows a possible indication of clay-water interaction.

4.2.5 Role of Physical processes

Physical processes like evaporation and ultrafiltration play a crucial role in the evolution of the chemistry of Formation water. Evaporation of saline water increases the major ion concentration and TDS of PWs, decreasing their quality. Ultrafiltration on the other hand, has been postulated to reduce the major ion and TDS concentration, improving the PW quality (Coplen and Hanshaw, 1973). PW's from Marcellus, Trenton, Edwards and majority of the samples from Bakken Formation which are originally derived from marine connate water, show evidence of seawater evaporation (Fig. 8 and Fig. 11), indicating that evaporation plays a key role in controlling the PW quality from these Formations. Some of the Wilcox PW's also show evidence of evaporation, however the majority of the samples do not. Lance PWs show evidence of evaporation (Fig. 11), however, since these samples have low (original) major ion and TDS concentrations, evaporation does not significantly effect their PW quality. Some of the Mesaverde and Marcellus PW samples show some evidence of ultrafiltration. However, further analysis and evaluation need to be performed to assess the true impact of ultrafiltration on PW quality from these fromations.

CONCLUSIONS & FUTURE DIRECTIONS

Recycling and reuse of produced waters is an issue of immediate importance considering the shortage of freshwater resources, costs associated with its transport, and the environmental problems caused by its improper management. In this study, we utilized the major ion concentrations, O, H and Sr isotopic of PWs from conventional and unconventional Formations with varying lithology and depositional environments to understand the role of local geology and hydrology on PW chemistry. Using these geochemical tools, we delineated the dominant variables, namely origin of PW, impact of artificial (hydraulic fracturing fluid) and natural water recharge, degree of mineral-water interactions and physical processes on PW quality, as summarized in Fig. 12.

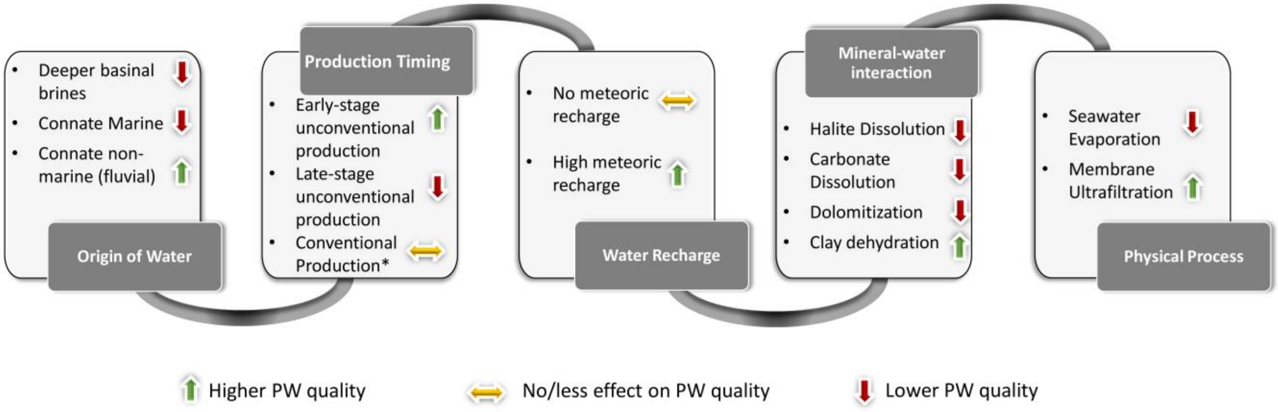

Figure 12 Role of origin of water, production type and timing, Water recharge, mineral-water interactions, and physical processes on PW quality (where quality is inversely related to the extent of treatment required for beneficial use or surface discharge). * indicates that PW quality from conventional reservoirs does not change significantly at different production timing.

Of the Formations we analyzed, the Mesaverde and Lance Formations had better PW quality due to the fluvial origin of Formation water and meteoric freshwater recharge. Lance PW show signatures of evaporation, whereas Mesaverde PW showed evidence of ultrafiltration. Wilcox PW had intermediate PW quality and are derived from a hydrologically complex origin. The Wilcox PW showed evidence of evaporated seawater, the pervasive introduction of brines from the dissolution of salt domes, meteoric recharge, and clay dehydration. The Bakken and Trenton PW's had the poorest PW quality and are primarily composed of connate seawater that underwent evaporation. Some of Bakken PWs showed evidence of halite dissolution. Trenton PWs showed evidence of carbonate dissolution and dolomitization by introduction of intra-basinal hydrothermal brine. Marcellus PWs had variable PW quality, showing signatures of seawater evaporation, carbonate dissolution and possibly ultrafiltration. Some of the better quality Marcellus PW's correspond to early stages of production and represent a mixture of fresh water based hydraulic fracturing fluids and Formation water. Edwards PWs had intermediate quality originating from evaporated seawater derived form a deeper hydrologically isolated regime. Although the Edwards Formation is carbonate rich, some of the PW samples did not show evidence of carbonate dissolution.

Our study indicates that significant geochemical variations can exist in PW's from the same Formation in different parts of the basin. Therefore to accurately predict PW quality, we need to develop a more holistic understanding of the geological and hydrological history of the Formation, the mineralogical interactions and physical processes. This study also demonstrated that the role of geologic ultrafiltration on PW quality is underestimated, and further research is needed to evaluate its impact on trace metal and major ion partitioning. There is also a need to develop more robust geochemical tracers that can distinguish contribution from meteoric water recharge vs fresh water based hydraulic fracturing fluids, carbonate interaction vs. ultrafiltration, and in-situ halite dissolution vs. salt dome derived intra-basinal fluids.

Further, due to the limited availability of geochemical data we utilized only major ions and stable isotopes to understand variations in PW quality. However, trace metals, pH and Eh of solution, dissolved organic constituents such as polyaromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylenes (BTEX), phenols, and organic acids, and; other chemical additives used in drilling and well stimulation significantly impact the water quality and should also be more frequently analyzed and reported, wherever budget permits. These chemicals are toxic, which can induce severe health hazards, and otherwise may be challenging to remove from PW. Other important parameters that need to be documented are PW quantity and timing of production, especially in unconventional reservoirs. Accurate measurements of these parameters can then be used to optimize design of water handling and treatment facilities, reduce water handling costs, and make long-term strategies for overcoming water-shortage issues.

5. AUTHOR CONTRIBUTIONS

S.S: Initial conception of idea S.S; V.A; & RA: Data collection, Data analysis, Wrote original draft of manuscript. YW & AH: Final edits and review of manuscript.

6. CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. ACKNOWLEDGEMENTS

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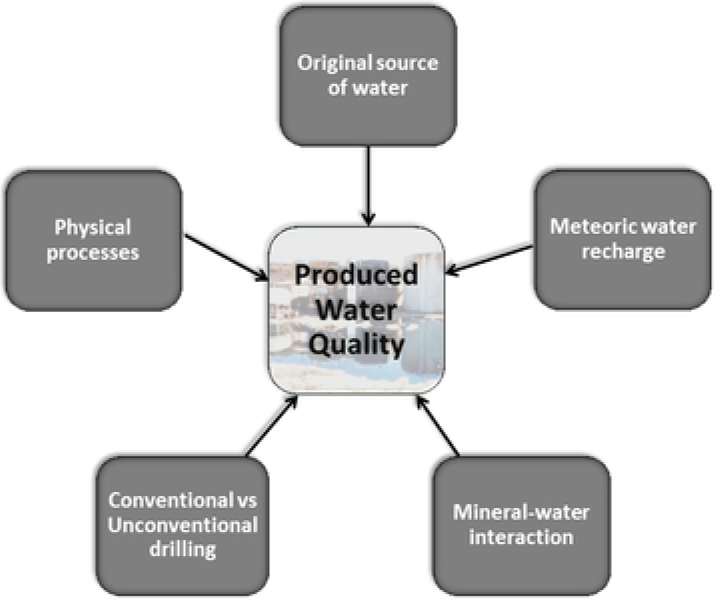

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