




Spatial variability of produced-water quality and alternative-source water analysis applied to the Permian Basin, USA

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Abstract

Interest in both environmental impact and potential beneficial uses of produced water (PW) has increased with growth in unconventional oil and gas production, especially in semi-arid regions, e.g. the Permian Basin, the most productive tight-oil region in the USA. Characterization of PW compositional variability is needed to evaluate environmental impact, treatment, and reuse potential. Geochemical variability of PW from Guadalupian (Middle Permian) to Ordovician formations was statistically and geostatistically evaluated in the western half of the Permian Basin (Delaware Basin, Central Basin Platform, and Northwest Shelf) using the US Geological Survey's Produced Waters Geochemical Database and the New Mexico Water and Infrastructure Data System. Mean total dissolved solids (TDS) of PW increased with depth in the Delaware Basin and Central Basin Platform to the Delaware and Wolfcamp formations (Guadalupian age). Mean TDS decreased with further increases in depth. In contrast, the mean salinity of PW was significantly higher within the shallow, younger formations (largest mean TDS in the Artesia Formation); TDS decreased with depth below Guadalupian age formations in the Northwest Shelf. Kriged contour maps of TDS and major ions illustrated spatial variability across the three geo-structural regions as a function of depth. The occurrence of meteoric waters in upper and deeper formations across the three regions was significant, and was attributed to Laramide Orogeny and Basin and Range extension uplifting and tilting effects and recent water flooding. These results quantify PW composition variability, and suggest that upon treatment, PW would support some uses such as onsite reuse and mining.

Keywords Brine water · Produced water · Water treatment · Hydraulic fracturing · Hydrochemistry

Introduction

Interest is growing in assessment of alternative or nontraditional water resources to meet increasing demand and to alleviate scarcity during periods of drought (GWPC 2019; USEPA 2017). Reclaimed municipal wastewater, contaminated surface water,

and brackish groundwater have been used to augment drinking water supplies upon treatment (McMahon et al. 2016; Stanton et al. 2017; Stanton and Dennehy 2017). More challenging, poor-quality waters with elevated total dissolved solids (TDS), including seawater, brine water, and industrial wastewater derived from oil and gas operations, are gaining increased interest as source water for water treatment operations (Butkovskiy et al. 2017; Jester 2013). Produced water (PW) is possibly the most challenging water type in terms of treatment and use/reuse (Butkovskiy et al. 2017; Graham et al. 2015; Horner et al. 2011). As the largest waste stream generated during oil and gas exploration and production, it is a mixture of formation water (generally brackish or brine) naturally present in reservoirs and water injected into reservoirs for pressure support, hydraulic fracturing, or reservoir treatment (Ahmadun et al. 2009; Veil et al. 2004). After flowback (for wells that are hydraulically fractured, this is injected water returned to land surface after end of injection), analyses of PW samples allow for characterization of formation water quality (Haluszczak et al. 2013). Although PW quality varies by formation, basin, and hydrocarbon type, it is typically highly saline,

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with TDS values that can be up to an order of magnitude larger than seawater. Variation in salinity can impact calculations of water and oil saturations from resistivity logs and hydrostatic pressure gradients in well pressure data. Understanding the variability of PW quality is critical in oil and gas field management and petroleum exploration for many reasons such as planning for saltwater disposal, secondary recovery projects, proper treatment of production fluids to prevent corrosion, and enhanced phase separation (Ostroff 1979).

Oil and gas operators and stakeholders in the Permian Basin are evaluating potential PW reuse options (Graham et al. 2015). The Permian Basin province, containing multiple geologic features in western Texas and eastern New Mexico, is one of the most productive hydrocarbon plays within North America, and contains conventional oil, tight oil, and natural-gas resources (Guerra et al. 2011; USEIA 2017). Approximately 100,000 acre-feet/year (1.2×10^8 m³/year) of PW is generated within New Mexico alone; the average ratio of PW to oil (v/v) in the Permian Basin is approximately 13:1 in conventional wells and 2.7:1 in unconventional wells (Scanlon et al. 2017). More than 70 million barrels (11 million m³) of PW have been generated in Lea and Eddy counties of New Mexico (Lee et al. 2002; OCD 2015); however, PW quality in the Permian Basin area typically is considered extremely poor and highly variable, which limits the feasibility for beneficial use of PW in this region (Galley 1958; Khan et al. 2016; Veil et al. 2004). The known range for TDS of PWs in the Permian Basin extends up to a max of ~400 g/L (Guerra et al. 2011). Various approaches also have been used in previous studies to classify formation water and PW chemical composition within the Permian Basin. Work by Engle and Blondes (2014) has evaluated the brine geochemistry of the Guadalupian-age Permian Basin formations in the study area. The geochemistry of PW has been explored using isotopic data and conservative elements (Barnaby et al. 2004; Pfister et al. 2017; Saller and Stueber 2018). Recently, Saller and Stueber (2018) examined the geochemistry of the study area and presented a new conceptual model for fluid flow over the life span of the Permian Basin. Despite the extensive production and geochemical evaluation, information on spatial salinity distribution in the Permian Basin has been limited. Regional salinity maps from half a century ago show low salinities emerging from the Sacramento Mountains of southeastern New Mexico and extending to the east-southeast into the Basin (McNeal 1965). Barnaby et al. (2004) suggest that regional water salinity trends for Pennsylvanian strata are poorly constrained in southeastern New Mexico, and previously published salinity maps contain no data from Eddy County (Bein and Dutton 1993; McNeal 1965). A recently developed compositional data analysis method, using isometric log ratios of ions, shows promise for Permian Basin PW characterization as it overcomes the limitations of conventional brine geochemical major-ion correlation analysis including

spurious relationships that occur with ion correlations especially for brines (Egozcue et al. 2003; Engle and Rowan 2013; Owen et al. 2016).

Diminishing water quality and supply in water-stressed areas like Lea and Eddy counties in New Mexico exacerbate the need for information on PW quality (Graham et al. 2015; Zemlick et al. 2018). Salinity information of PW can be used by various stakeholders such as water resources management authorities, farmers, industries, and water utilities to address water security. Therefore, the analysis and interpretation of PW TDS variability are necessary to understand the feasibility of reuse/recycle this water for possible beneficial uses (Graham et al. 2015; Homer et al. 2011). For instance, various stakeholders might be interested in using the PW either with or without treatment (Kondash et al. 2017). Identification of higher-quality water within the subsurface could support reuse feasibility assessment, and the interpreted water quality data will be useful for stakeholders who want to plan and design water-treatment technologies. PW compositional characterization also is critical for assessment of potential environmental impacts of improper waste disposal or spills (Herkeleth et al. 2007; Kharaka et al. 2007; Otton et al. 2007; Zielinski and Budahn 2007). The objective of this study is to characterize the spatial distribution and variability of PW quality in the Delaware Basin, Central Basin Platform, and Northwest Shelf (i.e., geo-structural regions) of the Permian Basin. This study also compares the geochemistry of the PW in these three geo-structural regions. The selection of treatment technologies and potential beneficial use options depend highly on feed water quality and thus have considerable impact on treatment costs. Assessment of water quality variability is critical to locating alternative water sources, and economically/feasibly managing alternative water use/reuse operations. Based on the characterization of PW quality, the potential of produced water treatment and reuse in the Permian Basin for different applications is discussed.

Materials and methods

Study area background

The Permian Basin is a combination of several geologic features, and those relevant to this study include the Central Basin Platform, an uplifted block which separates the Midland Basin in Texas and the Delaware Basin in Southeast New Mexico and Southwest Texas (Engle et al. 2016). The Northwest Shelf, also important to this study, lies to the north of the Delaware Basin and covers the majority of the New Mexico area. Figure 1 shows the locations of PW sample data points and pertinent features of the Permian Basin in the study area, and Fig. 2 presents a generalized geologic cross section. Due to the depositional history, there are significant variations in lithology, geochemistry, and hydrologic properties of the hydrocarbon reservoirs. In the study area,

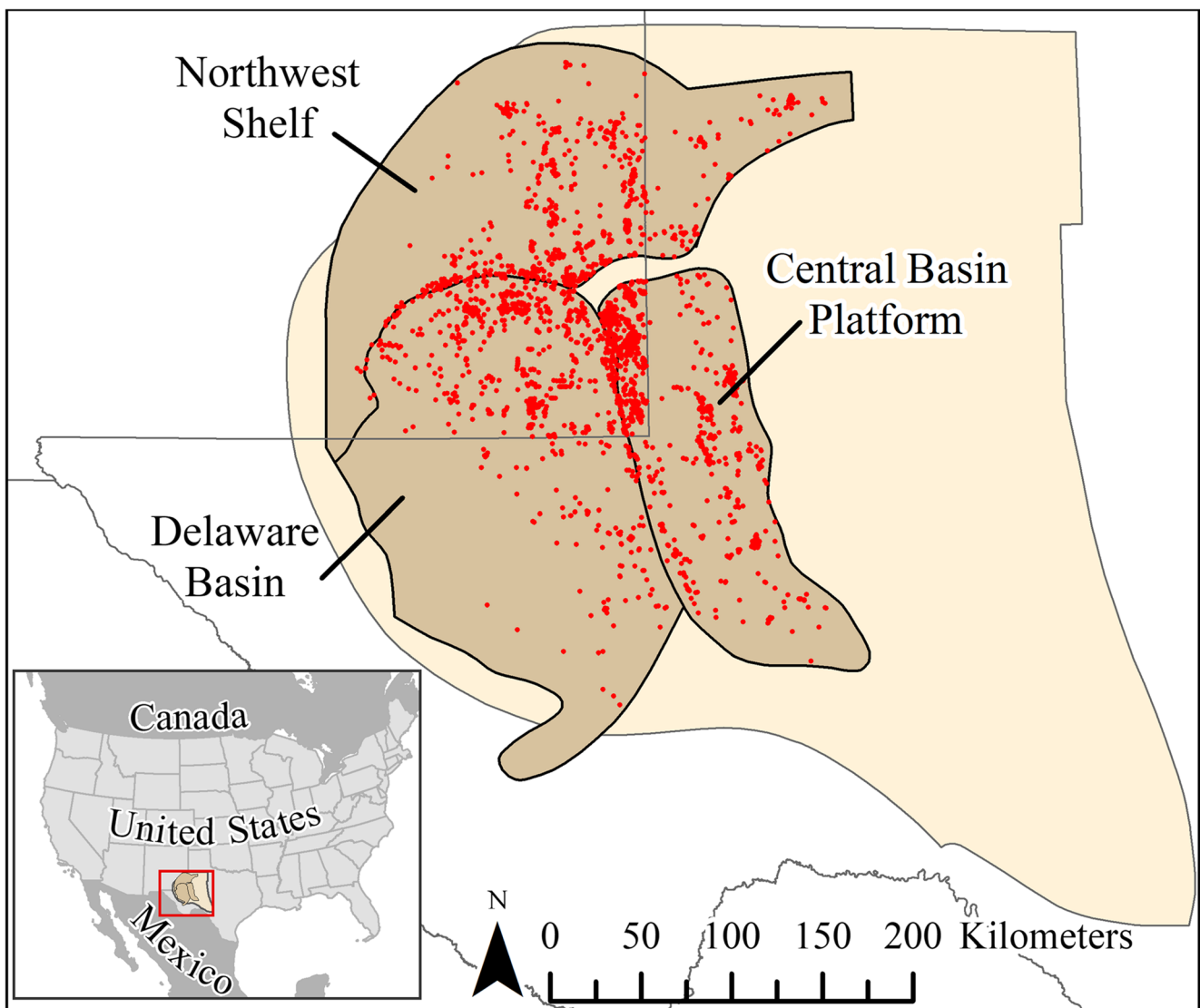


Fig. 1 Map showing location of sample points (red dots) in the three geo-structural regions of the Permian Basin and illustrating the extent of the Permian Basin

the rock units from Guadalupian (273–259 million years ago) and Ordovician (485–444 million years ago) age deposits are the youngest and oldest formations, respectively, from which oil and gas are produced, as shown in Table 1 (Dutton et al. 2005). Pre-Pennsylvanian strata that consist primarily of those contained in the precursor to the Permian Basin, the Tobosa Basin, are composed of marine carbonates and shales. Permian-age sediments constitute a sequence of geologic strata including evaporites, carbonates, discontinuous fluvial-deltaic arkosic sandstones, very fine siltstone, and marine shales. Historically, much of the hydrocarbon production was derived from conventional structural and stratigraphic traps in Guadalupian- and Leonardian-age reservoirs (Dutton et al. 2005). More recently, with the advent of combined horizontal drilling and hydraulic fracturing, low permeability, organic-rich source rocks in the Leonardian (e.g., Spraberry,

Bone Spring, Avalon, Wolfcamp A, etc.), Wolfcampian (i.e., Wolfcamp B and C shales), and Pennsylvanian (e.g., Wolfcamp D/“Cline” shale) reservoirs have been targets for production. Above the hydrocarbon-bearing reservoir rocks of the Permian Basin, there is an evaporite layer (primarily anhydrite and halite) overlain by fluvial, deltaic, and lacustrine deposits of the Triassic Dockum Group and the Neogene Ogallala and/or Cretaceous Edwards-Trinity, depending upon location (Senger and Fogg 1987).

Analysis and interpretation of produced water quality

The US Geological Survey (USGS) has compiled a database of PW chemistry in oil and gas producing zones throughout the US to monitor and archive PW quality data, and all available PW quality databases—i.e., USGS Produced Waters Geochemical

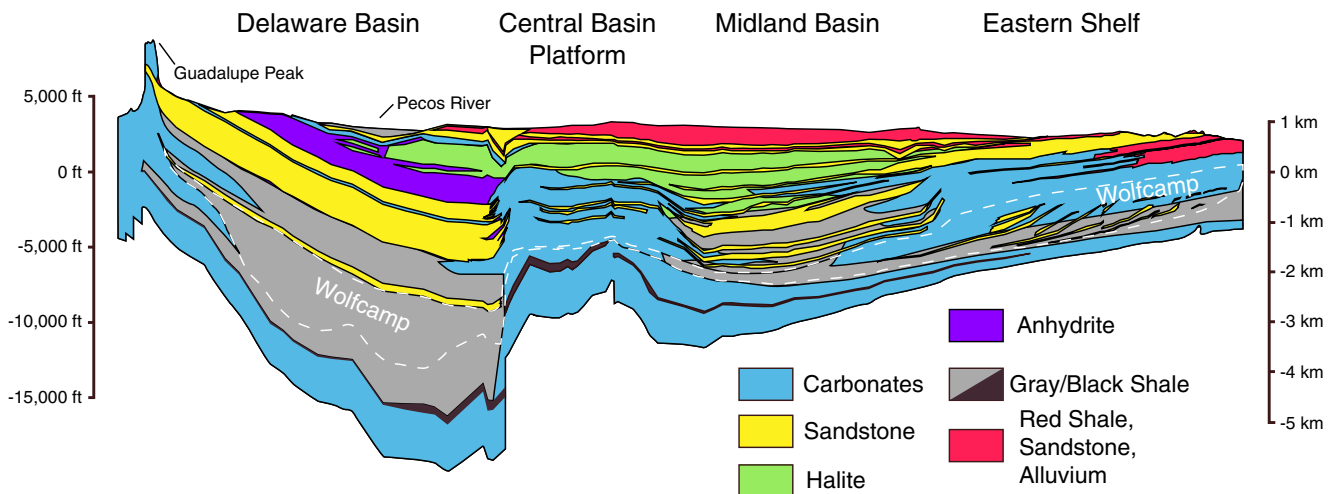


Fig. 2 A generalized geologic west–east trending cross-section of the Permian Basin modified from Matchus and Jones (1984)

Database and New Mexico Water and Infrastructure Data System (NM WAIDS)—have been used herein to describe the variability of salinity and water constituents in the study area. Within the study area, the database—Version 2.2 (Blondes et al. 2015)—contains data from 4,115 samples (generally from production wells) that have unique formation names (Table 1) and TDS values; these data were supplemented by 772 data from samples obtained from the New Mexico PW database with data collected from 2007 to 2015 (Fig. 1). Relevant information used from the database included sampled well location, identification number, sampling date, and concentration data (Na, Cl, Ca, Mg, SO_4 , HCO_3 , K, Br). The samples that did not have TDS and formation names were not included in this evaluation. Additionally, duplicate samples found in both databases were identified based on locations, TDS, and formation names, and removed. To describe and interpret the salinity and chemical constituents of the PW, four techniques were used: univariate statistics, geostatistics, compositional data analysis, and generic classifications. In this study, a classical univariate statistical approach was used to evaluate mean, quartile, geometric mean, and range for TDS and water constituents. Formations were divided into eight groups according to their geologic age and depth (Table 1), and analyzed separately for each group within each of the three geo-structural regions. Spatial distribution and variability of PW TDS were characterized by contour maps produced through ordinary kriging using ArcGIS. In instances where wells were sampled multiple times, sometimes with differences in measured TDS between samples greater than 100 g/L, the maximum values of the TDS measured at those locations were used to conservatively estimate TDS between measurement locations. The hole-effect semivariogram model was used (Ma and Jones 2001), because it consistently produced lower average standard error when compared to other semivariogram models (e.g., Stable, Gaussian, Spherical, etc.). Prediction standard error maps were produced for all kriged contour maps (ESRI 2017).

Due to the large variability in salt-to-water ratios in brines, sub-compositions of multivariate mole concentration data were converted into isometric log-ratio (ilr) coordinates before plotting the data (Egozcue et al. 2003; Engle and Rowan 2013). The number of constituents of interest first was converted into non-overlapping groups known as a sequential binary partition to maximize geochemical interpretation (Egozcue and Pawłowsky-Glahn 2005). The corresponding ilr coordinates (z_i) were calculated using the sequential binary partition as follows (Engle et al. 2016):

$$z_i = \sqrt{\frac{r_i s_i}{r_i + s_i}} \ln \frac{(x_j)^{\frac{1}{r_i}}}{(x_l)^{\frac{1}{s_i}}} \quad (1)$$

where r_i and s_i are the number of constituents, and x_j and x_l are the constituents coded with +1 and -1, respectively. The benefit of using the ilr compositional data analysis technique is because the data follow the standard Euclidean geometry once they are transformed into ilr coordinates (Blondes et al. 2015).

For classification of PW, TDS and major ions were used to evaluate the types of water present in the study area, and their impacts on potential of treatment and reuse. In addition to major cations and anions, available Br data also were used to identify possible sources of water constituents. Using an empirical scheme specific to the Permian Basin (Davidson 2003), the PW was classified into fresh meteoric, paleoseawater brines, and saline mixed water types (i.e., mixture of meteoric and brine types). Under the classification scheme, fresh meteoric water was defined for samples with a TDS values less than 75 g/L and Cl/ SO_4 mass ratio below 50. The paleoseawater brine classification constituted TDS values above 125 g/L and Cl/ SO_4 mass ratio greater than 50, while the saline mixed water type had TDS values in the ranges 75–125 g/L with Cl/ SO_4 mass ratio below 50 (Davidson 2003).

Table 1 Stratigraphic column of geological formations and group designations in the three geo-structural regions (modified from Dutton et al. 2005)

Group identification No.	Geologic age (formation)	Delaware Basin	Central Basin Platform	Northwest Shelf
Group 1	Guadalupian (Artesia)	Tansill		
		Yates	Yates	Yates
		Seven Rivers	Seven Rivers	Seven Rivers
		Queen	Queen	Penrose
		Penrose	Penrose	Queen
		Grayburg	Grayburg	Grayburg
Group 2	Guadalupian (San Andres)	San Andres	San Andres	San Andres
	Guadalupian (Delaware)	Bell Canyon	Cherry Canyon	
		Brushy Canyon		Delaware
		Cherry Canyon		
	Leonardian	Delaware		
		Glorieta	Glorieta	Glorieta
		Avalon Shale	Blinebry	Paddock
		Bone Spring	Clear Fork	Blinebry
		Yeso	Yeso	Clear Fork
		Drinkard	Tubb	
Group 3	Wolfcampian	Wolfcamp	Wolfcamp	Wolfcamp
		Cisco	Cisco	Cisco
		Canyon	Canyon	Canyon
		Strawn	Strawn	Strawn
		Atoka		Atoka
	Pennsylvanian	Morrow		Morrow
		Woodford	Woodford	Woodford
		Thirty-one	Thirty-one	Thirty-one
		Fusselman	Fusselman	Fusselman
		Montoya	Montoya	Montoya
Devonian		Simpson		
		Ellenburger	Ellenburger	

Results and discussion

Variation of salinity by region and formation

Variability of TDS and dissolved constituents of the PW was evaluated both areally and with depth. Of the 4887 samples within the study area, 32% of the samples were from the Delaware Basin. The Central Basin Platform comprised 39% of the total samples, and the remaining samples (29%) were from the Northwest Shelf. The trend of largest to smallest mean TDS was from 136 g/L for the Delaware Basin, 116 g/L for the Northwest Shelf, and 95 g/L for the Central Basin Platform, although the relative standard deviations were large, indicating significant overlap. The lower TDS water in the Delaware Basin has greater potential to be treated and reused,

including agricultural irrigation as discussed in section ‘[Produced water reuse potential in the Permian Basin](#)’. In addition to basin-wide comparison, the TDS values also were analyzed within each geo-structural region by formation as a proxy for depth (Table 2). The mean, quartiles, and ranges for TDS for samples from each formation within the three geo-structural regions, are presented in Table 2. The formations are not perfectly horizontal, but are generally oriented such that increasing formation age correlates with increases in depth below land surface. The data shown in Table 1 were classified into three groups based on similarities in TDS histograms: group 1 includes those from the Artesia and San Andres formations; group 2 includes those from the Delaware Mountain Group and Leonardian age formations, and group 3 includes those from Wolfcampian, Pennsylvanian, Devonian, and

Table 2 Permian basin total dissolved solids (TDS, mg/L) statistics

Statistic	Geological formation							
	Artesia	San Andres	Delaware	Leonardian	Wolfcamp	Pennsylvanian	Devonian	Ordovician
Delaware Basin								
Min	2.38E+03	4.46E+03	2.01E+03	8.70E+02	3.39E+03	6.66E+02	5.49E+03	1.84E+03
Quartile 1	1.57E+04	2.63E+04	1.95E+05	1.38E+05	2.64E+04	1.17E+04	2.14E+04	2.33E+04
Mean	8.53E+04	7.63E+04	2.25E+05	1.58E+05	7.11E+04	7.03E+04	7.51E+04	9.28E+04
Quartile 3	1.38E+05	1.21E+05	2.76E+05	1.95E+05	1.08E+05	1.16E+05	1.13E+05	1.42E+05
Max	3.82E+05	3.27E+05	3.84E+05	3.13E+05	1.87E+05	2.37E+05	2.77E+05	2.65E+05
Count	318	63	275	622	43	136	87	30
Central Basin Platform								
Min	2.62E+03	4.74E+03	–	1.98E+03	1.47E+04	6.30E+03	1.14E+03	2.83E+03
Quartile 1	1.62E+04	1.28E+04	–	6.89E+04	1.28E+05	6.49E+04	4.48E+04	4.61E+04
Mean	7.38E+04	6.36E+04	–	1.27E+05	1.54E+05	1.01E+05	1.15E+05	9.01E+04
Quartile 2	9.98E+04	8.64E+04	–	1.69E+05	1.96E+05	1.36E+05	1.80E+05	1.22E+05
Max	3.73E+05	3.93E+05	–	3.81E+05	2.41E+05	2.17E+05	3.77E+05	3.48E+05
Count	518	292	–	460	37	150	215	265
Northwest Shelf								
Min	4.11E+03	2.78E+03	3.16E+04	2.00E+03	1.16E+03	1.75E+03	1.05E+03	7.04E+04
Quartile 1	1.17E+05	1.72E+05	6.03E+04	3.75E+04	5.97E+04	5.25E+04	4.78E+04	7.04E+04
Mean	2.05E+05	1.96E+05	1.32E+05	1.18E+05	8.99E+04	9.25E+04	6.42E+04	1.68E+05
Quartile 2	3.09E+05	2.47E+05	2.11E+05	2.04E+05	1.17E+05	1.18E+05	7.35E+04	2.64E+05
Max	3.85E+05	3.52E+05	2.12E+05	2.97E+05	2.98E+05	3.98E+05	2.24E+05	2.64E+05
Count	70	266	5	265	253	189	322	3

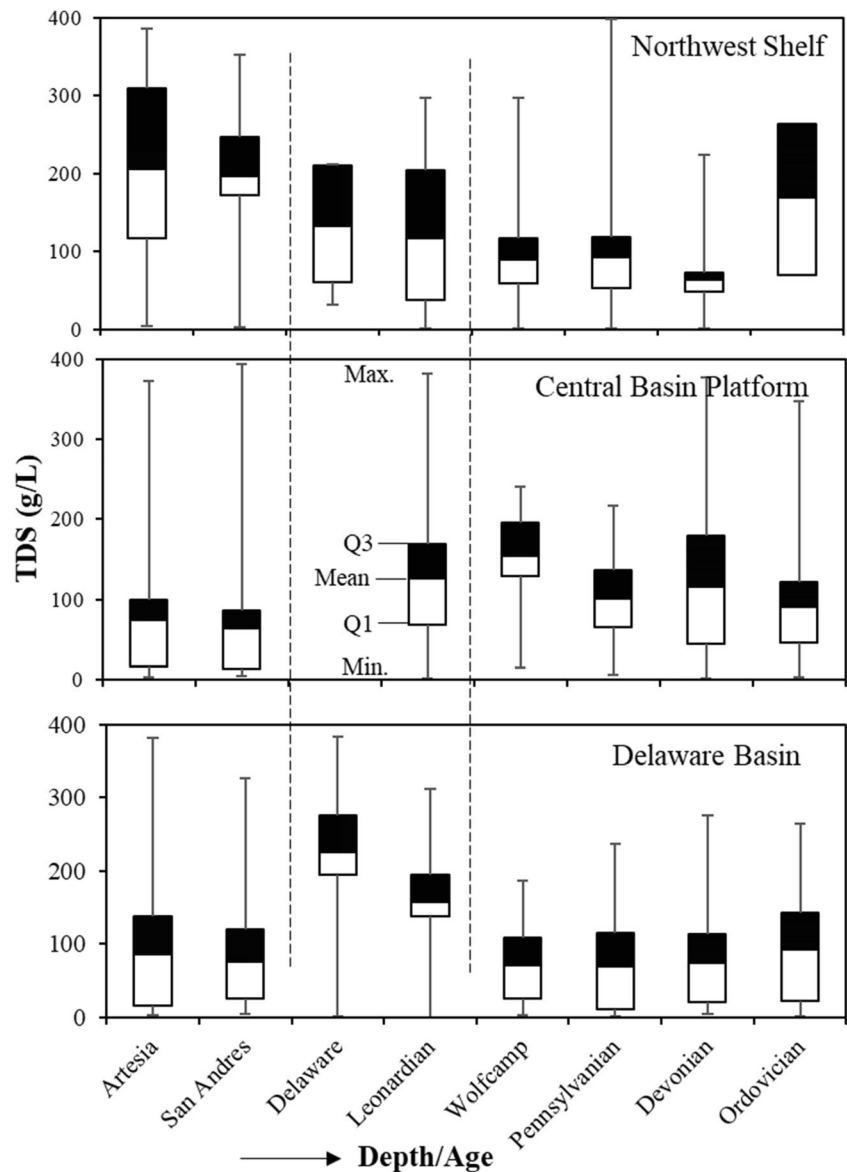
Ordovician formations (Table 1). The group 2 results were notably different from those of group 1. TDS values were more frequently larger within the Delaware Basin and Central Basin, yet smaller within the Northwest Shelf.

Statistical parameters including minimum, Q1 (25%-percentile), Q3 (75%-percentile), and maximum were used to observe and compare the trends with respect to the mean TDS (Fig. 3). Interestingly, the minimum values in each formation within each of the three geo-structural regions contained some relatively low TDS values (i.e., ~1 to ~15 g/L). Figure 3 shows that the trend of mean TDS values for the Delaware Basin increased from group 1 to 2, and then decreased from group 2 to 3. The Central Basin mean TDS also increased from group 1 to 2 including the elevated values in the Leonardian and Wolfcamp, but the decrease in group 3 in the underlying the Wolfcamp was much less significant compared to the Delaware Basin. However, the mean, Q1, and Q3 of TDS decreased continuously with depth in the Northwest Shelf except in Ordovician Formations. These results quantify the TDS variability, and likely have implications for salinity sources and/or fluid flow history. The lower salinity in these groups of the Delaware Basin and Central Basin Platform could be due to influx of low salinity meteoric water. Higher salinity in the Northwest Shelf likely corresponds to areas where dissolution of evaporite minerals by meteoric waters

has been active (Barnaby et al. 2004; Saller and Stueber 2018; Siegel and Anderholm 1994).

The contour maps in Fig. 4 illustrate the spatial distribution of PW TDS as well as the high degree of spatial variability and uncertainty for the different geologic formations in each of the three geo-structural regions. The kriging outputs were classified into five classes corresponding to potential PW reuse and desalination technologies (Fig. 4): 0–8 g/L (e.g., brackish reverse osmosis, nanofiltration, electrodialysis, and electrodialysis reversal), 8–25 and 25–40 g/L (e.g., seawater reverse osmosis, brackish water reverse osmosis, and electrodialysis), 40–70 g/L (e.g., mechanical vapor compression, mechanical effect distillation, and multi-stage flash), and > 70 g/L (e.g., forward osmosis, membrane distillation, and other new thermal desalination techniques; Geza et al. 2018; Ma et al. 2018; Xu et al. 2016). TDS in PW was generally greater than 70 g/L in all three geo-structural regions. The standard error was greater than 25 g/L for nearly all of the mapped areas due to spatial heterogeneity in the samples, which analogously characterizes the geochemical heterogeneity of the formation waters—for example, samples with greater than 100 g/L TDS often were located not far from locations where samples were collected that had TDS values less than 25 g/L. The areas in the younger/shallower formations (i.e., Artesia and San Andres) that did have lower salinity likely corresponded with

Fig. 3 Box and whisker statistical plots of the total dissolved solids (TDS) in the three geo-structural regions as a function of age and/or depth of each formation. Groups are separated by dashed lines with groups 1 to 3 from left to right



the location of the Permian Reef structures at the northern boundary of the Delaware Basin, which may allow for higher permeability and in-flux of meteoric water. This boundary area also had lower salinity in the Devonian of group 3. Alternatively, pervasive use of water flooding as a technique to improve oil extraction in the Permian Basin also can produce large variations in TDS within a small area. These results confirm variability of salinity existed both with depth and laterally throughout the geo-structural regions. The majority of the study area was dominated by the higher values of TDS.

Examination of solute composition indicated that Na and Cl were generally the dominant ions throughout the study area; however, Ca, Mg, HCO_3 , and SO_4 also were major components of the TDS. Figure 5 indicates relative distribution (normalized g/L) of Ca, Na, Cl, Mg, HCO_3 , and SO_4 by formations in the three geo-structural regions. The graphs of ions

were prepared by taking the geometric mean of each constituent and normalizing the results to 100% in each geo-structural region (referred to as a “center” in compositional data analysis methods). The distribution trends of Ca, Na, Cl, and Mg with depth were generally consistent with the salinity. Figure 5a shows that Ca, Na, and Cl are elevated in group 1 of Northwest Shelf, and then decrease with increasing age and/or depth. In the Delaware Basin, they peak in group 2, with significantly lower percentages in all formations above and below. For the Central Basin Platform, they peak in the Wolfcamp, just below group 2, with percentage declines in group 3 that are less significant than were observed for the Delaware Basin. Brines that obtained their salinity through the dissolution of evaporite minerals (e.g., halite) are more likely to exhibit more Na than Ca; conversely, brines which are ancient evaporated seawaters tend to exhibit high relative

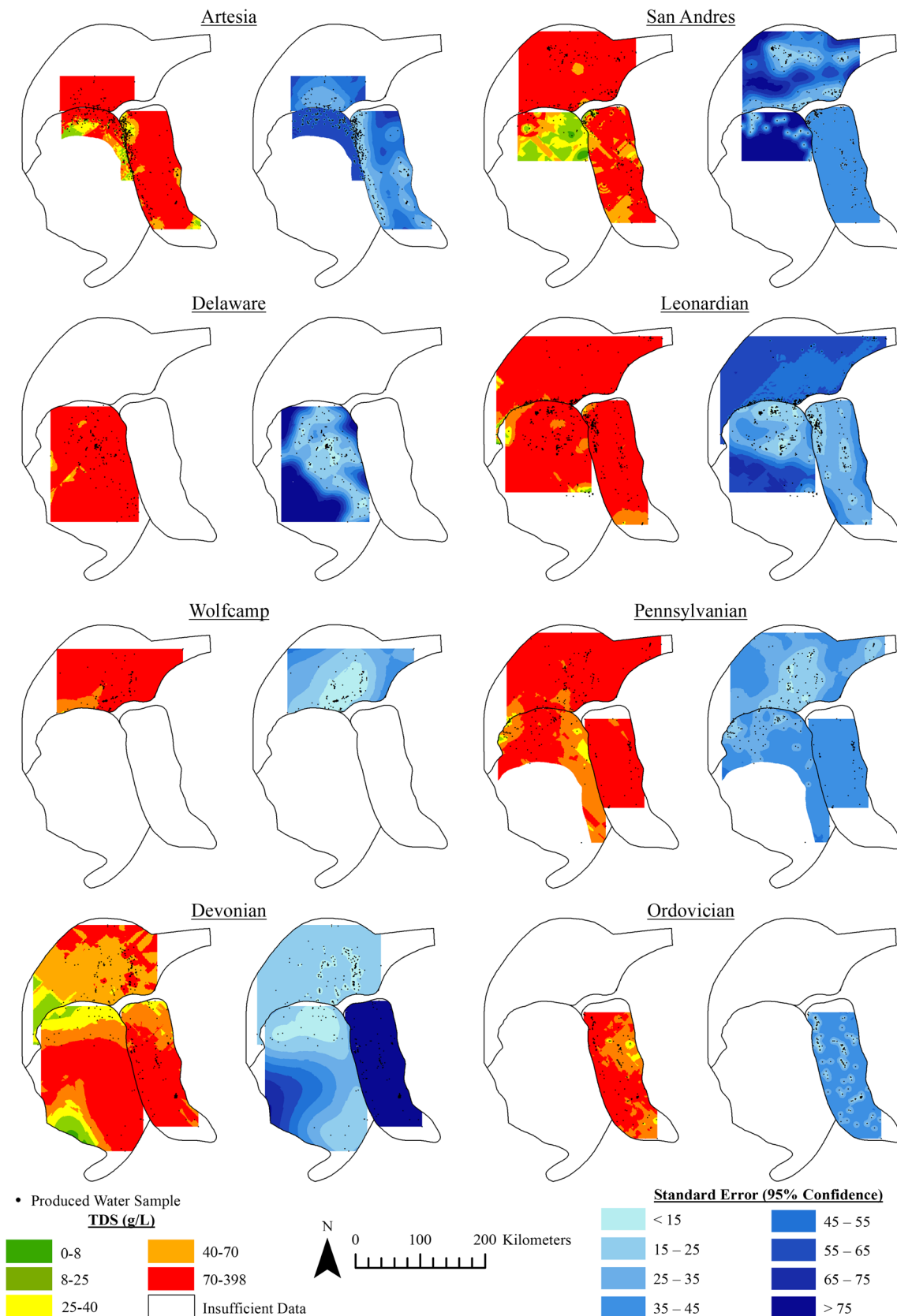
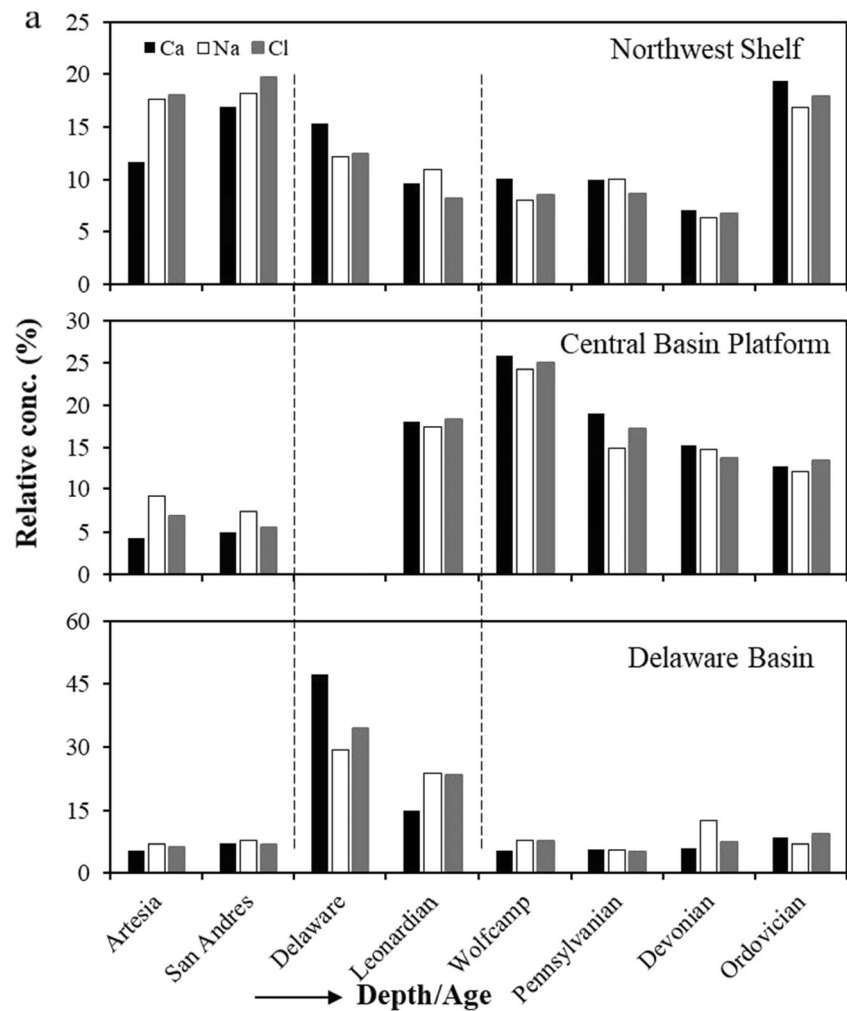


Fig. 4 Kriged contour maps of TDS from Guadalupian to Ordovician age and/or depth formations in the three geo-structural regions of the Northwest Shelf (top), Central Basin Platform (lower right) and Delaware Basin (lower left)

Fig. 5 Relative abundances of **a** Na, Cl, and Ca (geometric mean values for each constituent were normalized to 100%) in the three geo-structural regions as a function of age and/or depth of each Formation, and relative abundances of **b** Mg, HCO₃, and SO₄ (geometric mean values for each constituent were normalized to 100%) in the three geo-structural regions as a function of age and/or depth of each formation. Groups are separated by dashed lines with groups 1 to 3 from left to right



abundances of Ca to Na (Kharaka and Hanor 2014). The cause of the observed Na, Ca, and Cl variability in water chemistry could be due to infiltration of meteoric water, use of water-flooding in older conventional oil reservoirs, and the interactions with Formation rocks including evaporate deposits.

Classification of produced water

Figure 6 presents the spatial distribution of different types of water based on the classification of Davidson (2003). The PW was classified into different types at lower confidence without availability of isotope data, because only TDS and Cl/SO₄ were used in the criteria for classifications. Over 3,500 samples were classified—1,017 in the Delaware Basin, 1,515 in the Central Basin Platform, and 1,010 in the Northwest Shelf. The fraction of waters classified as fresh meteoric was the highest in the Northwest Shelf and Central Basin Platform. While the Delaware Basin had the largest percentage as paleoseawater brine, it also had a significant percentage of fresh meteoric samples. Each type of water was further divided into three groups representing the three groups of

formations, as previously defined and in Table 1, with depth as used in the interpretation of salinity (Fig. 6). Water classified as fresh meteoric from group 3 formations was found across the study area and suggests deep transport of meteoric water in the western and northern reaches of the study area, agreeing with studies by Barnaby et al. (2004) and Saller and Stueber (2018). Conversely, water classified as fresh meteoric from group 1 formations was located along the Permian Reef structures located at the structural boundaries of the geo-structural regions, which suggests they serve as an important water recharge location for meteoric water. Similarly, water classified as paleoseawater brines from groups 1 and 3 in the Northwest Shelf and Central Basin Platform was spatially distributed. However, in group 2, paleoseawater brines were clustered more in the Delaware Basin, which is supported by the elevated TDS as previously noted (Fig. 3). Such results suggest that there are paleoseawater brines, which are found in overlying and underlying Formations, that have yet to be displaced by meteoric water. The results indicate that the fresh meteoric waters (e.g., with lower salinity) had migrated to varying degrees into many of these Formations, which could

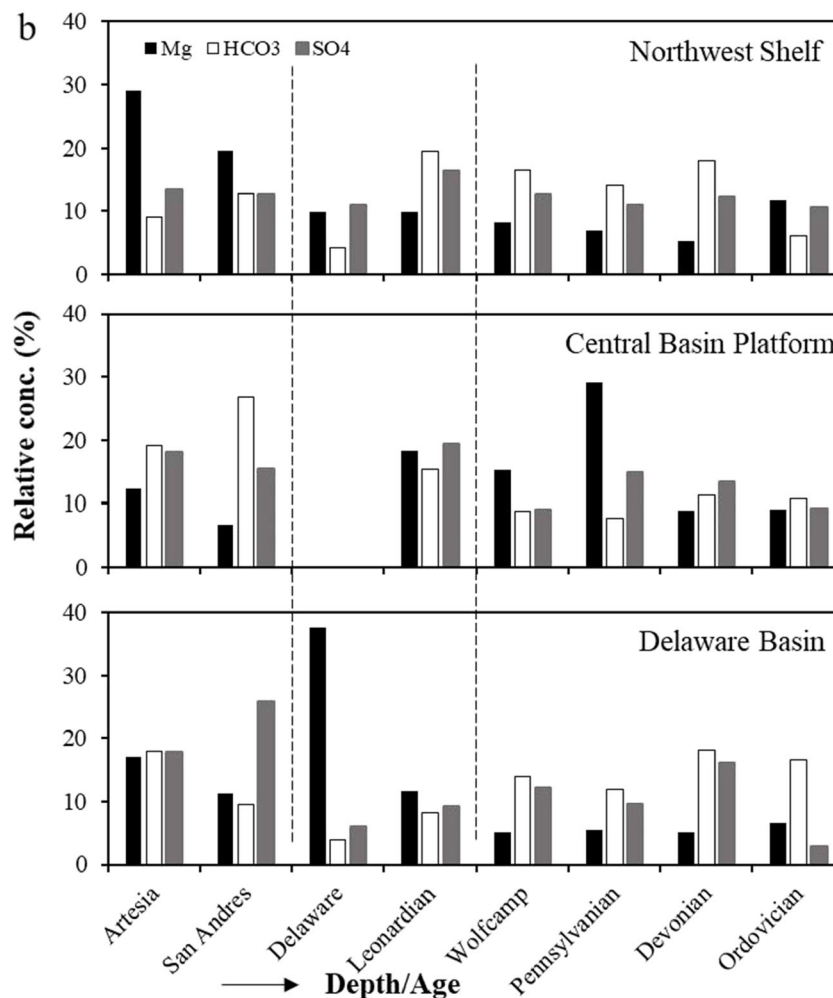


Fig. 5 (continued)

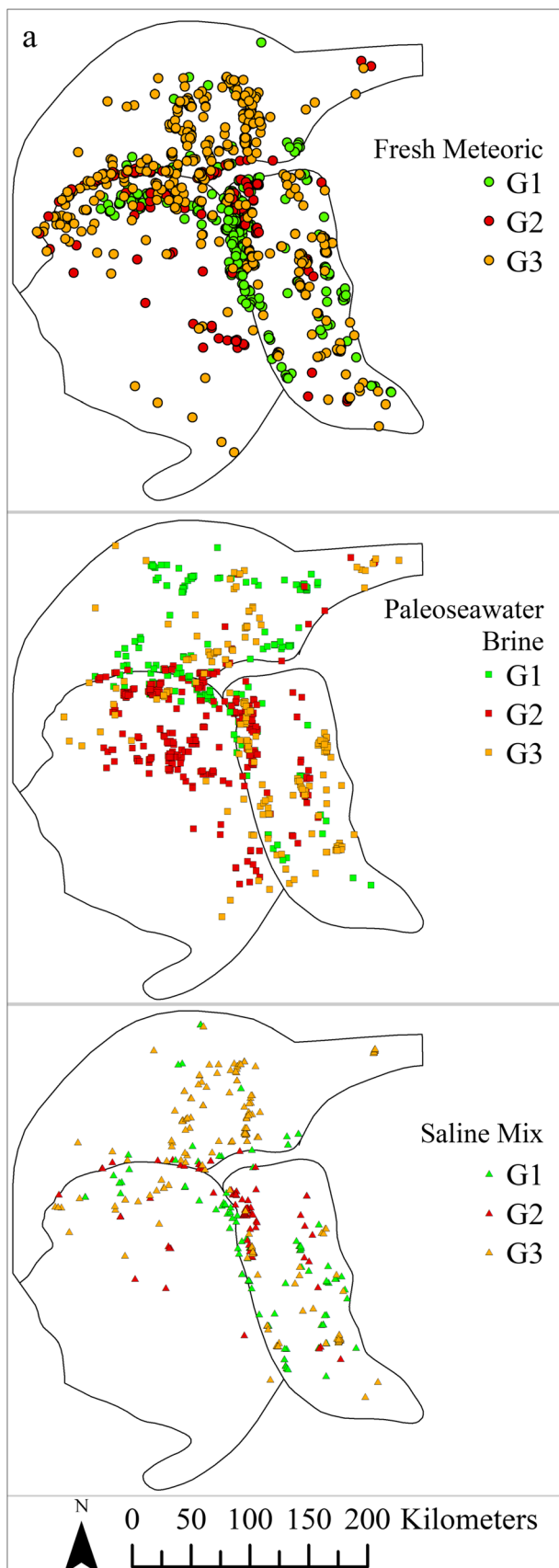
be due to water flooding and/or tilting and uplifting during the Laramide Orogeny (55–50 million years ago) and Basin and Range extension (25–10 million years ago) leading to subhydrostatic pressures in more permeable units (Engle et al. 2016; Senger and Fogg 1987).

In addition to spatial distribution of water types, the fractions of water types in the three geo-structural regions are shown as a function of age and/or depth in Fig. 6b. Approximately 65–76% of the samples in group 1 formations were classified as fresh meteoric in the Delaware Basin and Central Basin Platform, whereas data classified as paleoseawater brine comprised close to 80% in these group 1 formations of the Northwest Shelf. Occurrences of fresh meteoric waters in the Central Basin Platform were comparable to paleoseawater brine in groups 2 and 3, except for Wolfcamp. In the Delaware Basin and Northwest Shelf, a large percentage of samples was of fresh meteoric type in the group 3 formations, except in the oldest formation. These spatial distributions of water type can be used to identify regions to target for reuse even though water volume estimations are not provided. Additional data (e.g., formation

thickness and porosity) and site specific investigation would be required to support volume determination for these water types.

Origin of produced water

In previous investigations of brines from the Permian Basin, Engle et al. (2016) noted that use of traditional Na-Cl-Br plots for interpretation of brine origin is unduly influenced by spurious correlations. Thus, an ilr analysis of Na-Cl-Br was applied, following Engle and Rowan (2013). Figures 7 and 8 show zones in ilr scatter plots to examine where and how different water constituents might have originated. In Fig. 7, the x-axis corresponds to the partitioning (or lack thereof) of Br into the halite mineral structure relative to Na and Cl. Because halite dissolution produces Br-poor fluid, the data will move to the right on this axis; thus, brines derived from evaporated seawater will exhibit low values as Br is retained in the solution once halite saturation occurs. Conversely, meteoric water which gained its salinity through dissolution of primary halite (Br-poor), will exhibit high values on this axis.



◀ **Fig. 6** **a** Fractional areal distribution and location of different types of produced water in the three geo-structural regions. G1: group 1 formations, G2: group 2 formations, G3: group 3 formations. **b** Distribution of samples by water types from Guadalupian to Ordovician age formations in the three geo-structural regions as a function of age and/or depth of each formation. Sample (%) indicates fraction of samples of each water type in each formation. Groups are separated by dashed lines with groups 1 to 3 from left to right

Brines of both origins are known to exist in the study area (Barnaby et al. 2004; Engle and Blondes 2014; Saller and Stueber 2018). The Fig. 7 y-axis is simply a natural log molar ratio of Na/Cl; thus, waters resulting from dissolved halite approach zero (as the log of 1 is 0), while evaporated seawaters will start slightly negative and decrease with increased evaporation. Seawater evaporation will concentrate Br relative to Na and Cl, which are preferentially lost due to halite precipitation, and will move to the left on the y-axis. Results from the Northwest Shelf and Central Basin Platform suggest that most of the waters gained their salinity from halite dissolution, except for those from group 2 (Wolfcamp), which differs with the results from the local brine classification scheme (Davidson 2003), but agrees with prior publications on the origin of salinity in the Northwest Shelf (Barnaby et al. 2004; Siegel and Anderholm 1994). This apparent discrepancy is likely due to the fact that meteoric waters that dissolve large quantities of Cl-rich salts (e.g., halite and sylvite; both of which are present across much of the study area) will exhibit high TDS values and high Cl/SO₄ ratios; these meteoric waters would be classified incorrectly as brines under the brine classification scheme.

Data from the Delaware Basin indicate that most are derived from paleoseawater with the exception of a few samples from Pennsylvanian-age reservoirs and the Delaware Group. Notably, samples from the Delaware Basin tend to plot further down the seawater evaporation pathway than for the other two areas. These same samples also exhibit the highest TDS of group 2 waters in the study area (mean > 200 g/L; Fig. 3), and have high relative Ca and Mg contents relative to Na (Fig. 5a), which suggests they are highly evolved brines (Kharaka and Hanor 2014). This may indicate that, due to the exceptional depth in the Delaware Basin (the deepest region of the entire Permian) and the low permeability of these Formations, west–east topographically- driven groundwater flow and meteoric influx is limited. This allows for some of the saline fluids to remain more or less intact, especially in group 2 of the Delaware Basin. This interpretation also agrees with a recent conceptual model for west–east meteoric flow concentrated across the Northwest Shelf down into the Central Basin Platform (Saller and Stueber 2018).

Figure 8 scatter plots, prepared using *ilr* transformed coordinates in all formations of three geo-structural regions, showed clustering of water samples at the zone where rocks or minerals rich in Na, Cl, Ca, and SO₄ contributed through dissolution to the water composition. The sample points along

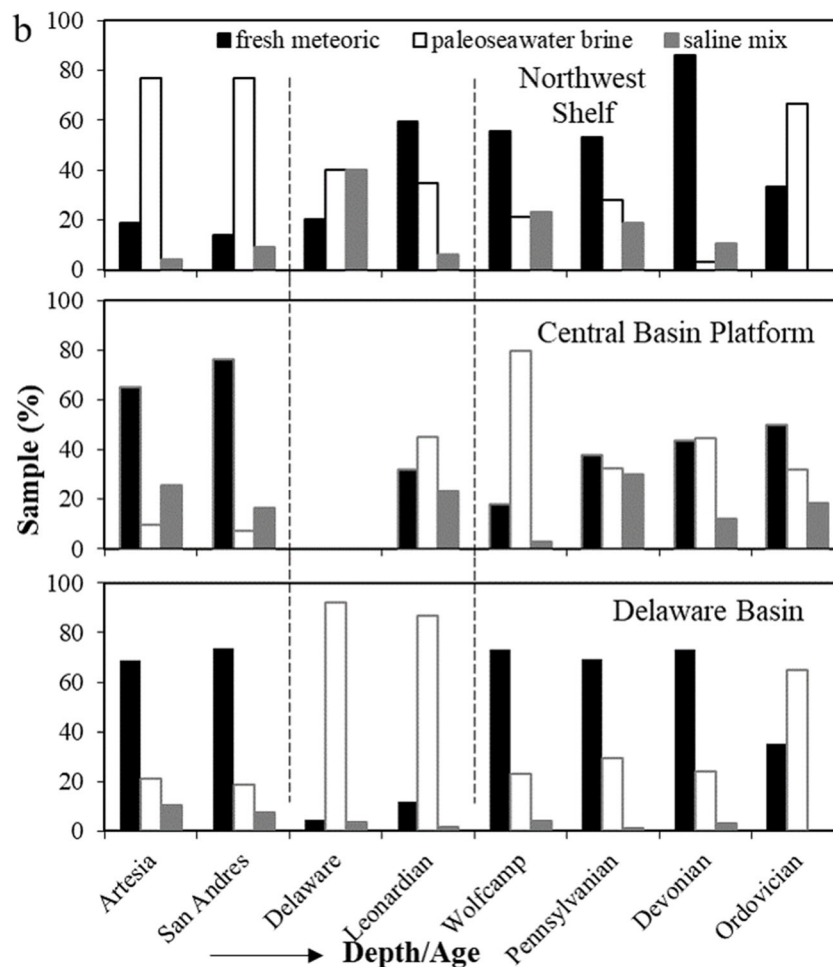


Fig. 6 (continued)

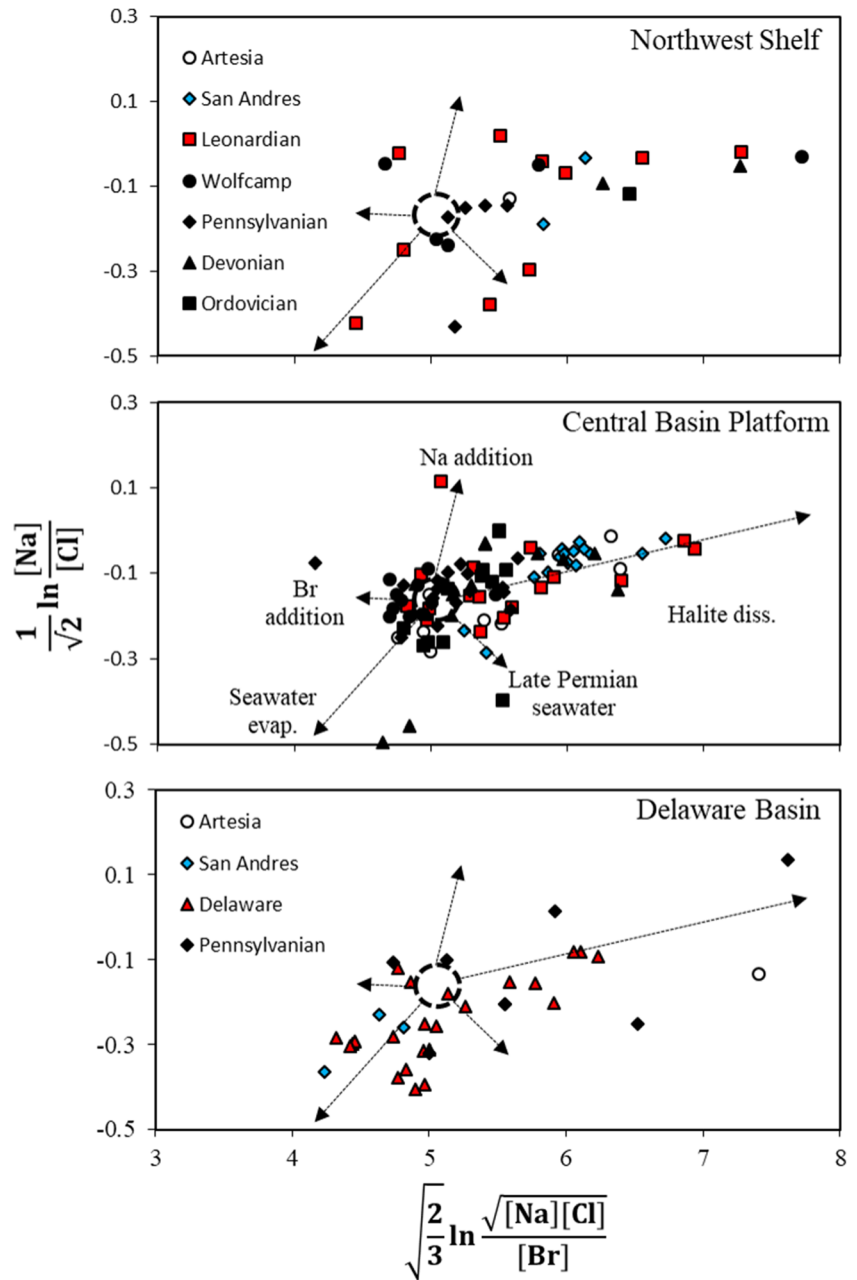
the dashed vertical line oriented at zero value on the horizontal axis indicate the contribution of halite dissolution. The data points deviating from that vertical line with negative values imply the contribution of water constituents mainly from Ca-Cl type minerals (Engle et al. 2016). Although data overplotting makes interpretation difficult, many of the group 1 waters in all three area plots near the 0,0 point suggesting that they are meteoric waters which have gained salinity through halite and anhydrite dissolution. This interpretation is consistent with results from the scatterplot of isometric log ratio transformed Na, Cl, and Br (Fig. 7). In the Central Basin Platform, many of the group 3 waters plot near $x=0$ but exhibit positive values along the y-axis. This is typical of meteoric waters that dissolved evaporites and then underwent SO_4 -reduction. Conversely group 3 waters from the Northwest Shelf and Delaware Basin tend to plot away from $x=0$ as values increase along the y-axis. This trend is consistent with increasing contribution from residual brines that originated as paleoseawater in the basin (Engle et al. 2016). Similar plotting is observed for group 2 water data especially in the Delaware Basin and Northwest Shelf, suggesting many of these waters

are residual brines of paleoseawater origin, that have yet to be displaced by meteoric waters. In the Central Basin Platform, all waters, including group 2, are more centered around the 0,0 point, suggesting that meteoric inflow has been more uniformly significant here than in the Northwest Shelf and Delaware Basin.

Produced water reuse potential in the Permian Basin

The average TDS of PW in the Permian Basin is approximately 90 g/L, mostly in the range of 20 g/L but up to 200 g/L or more. Composition and magnitude of the salinity of the formation brines tend to be the limiting factors for beneficial reuse of unconventional oil and gas wastewater (Kondash et al. 2017). Treatment technologies are available to treat the PW to desired water quality standards for beneficial use, but may not be currently economically feasible depending on the location and quality of PW (Zemlick et al. 2018). There is lower TDS water in the Delaware, Devonian, and Leonardian regions (e.g., less than 8,000 mg/L as identified in the Kriged contour maps of Fig. 4) that has greater potential

Fig. 7 Scatter plots of isometric log ratio transformation of Na, Cl, and Br in the three geo-structural regions

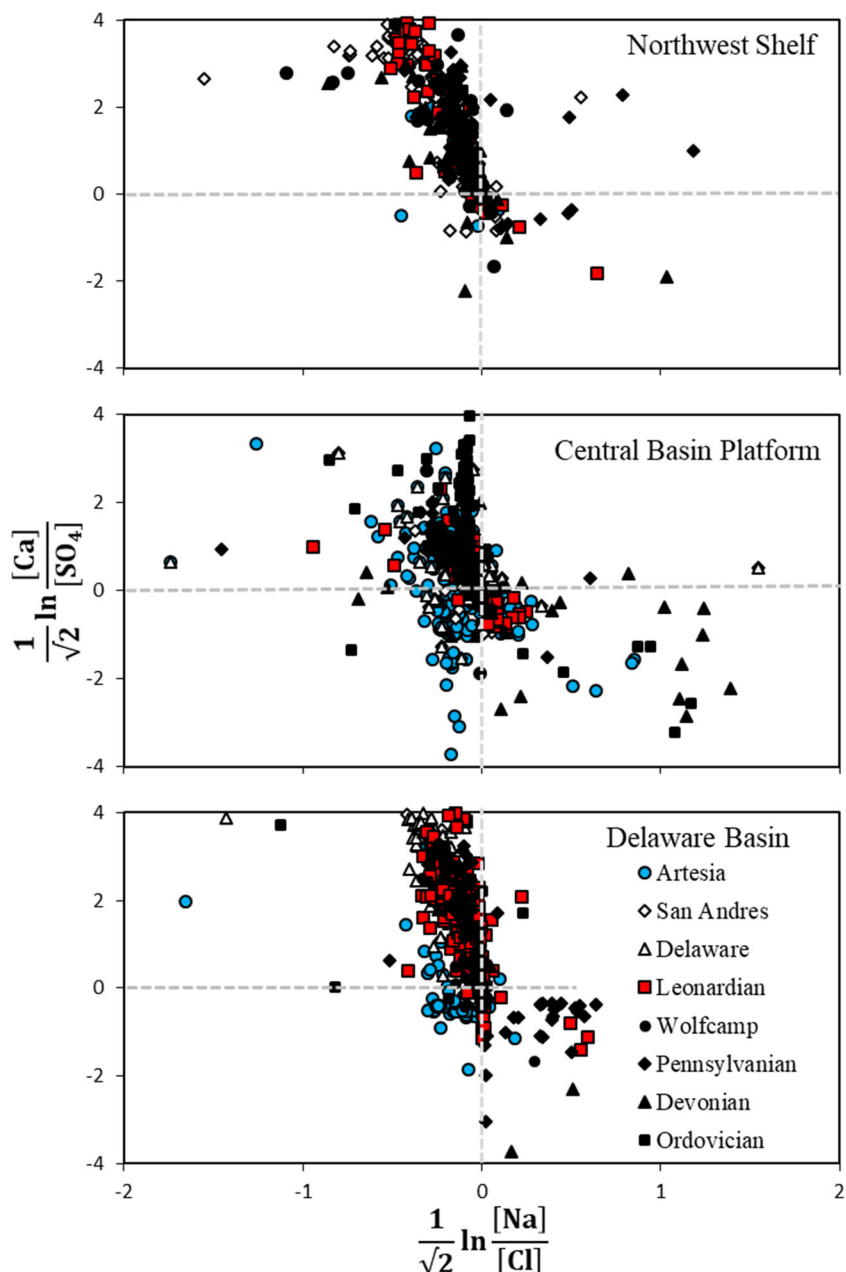


to be treated and reused for various applications, including agricultural irrigation. However, unless treated, water with TDS >2 g/L has severe restrictions on use for crop production. To meet irrigation requirements, PW in the Permian Basin has to be treated through extensive pretreatment and desalination processes to remove suspended solids, TDS, boron, chloride, radionuclides, petroleum hydrocarbons, trace metals, and organic compounds. Additionally, the proportion of Na to Ca and Mg (sodium adsorption ratio) and the concentration of HCO₃ in relation to Ca and Mg must be adjusted (Fipps 2003). Reusing PW for applications in oil and gas or mining industries is more economically feasible than for irrigation. Mining operations use water for mineral extraction and

processing, metal recovery, and dust control (Maupin et al. 2014). Acceptable water quality for mining is 100 g/L TDS, with limited suspended solids, hydrocarbons, radioactive materials, trace metals, and fracturing additives. Upon state and federal permitting, PW in the Permian Basin can be used for potash solution mining with minimal treatment. This would be ideal because New Mexico is the leading producer of potash for the US (Longworth et al. 2013), with 85% of the domestic production of potash in Carlsbad, NM (Willet 2004).

On-site PW reuse for oil and gas exploration and production reduces the need for water transportation (Zemlick et al. 2018). Hydraulic fracturing methods have water quality requirements (Nicot and Scanlon 2012; Scanlon et al. 2017)—

Fig. 8 Scatter plot of isometric log ratios for subcompositions (Na, Cl, Ca, and SO₄) in the three geo-structural regions



for example, cross-link gel systems are impacted by hardness and boron (in the cases of a borate-based cross-linker). During the early stage of shale development, freshwater was required for hydraulic fracturing. With the advances in frac fluid chemistry, “clean brine” with TDS up to 200,000 mg/L can be used for hydraulic fracturing (Scanlon et al. 2017). “Clean brine” requires the removal of suspended solids, organic matter, iron, and sometimes hardness, plus the addition of biocides (bacteria inactivation, reduction of iron and organic levels) to ensure the wells will not be clogged and there is no bacteria growth. Considering the majority of PW in Permian Basin has TDS concentrations less than 200 g/L—e.g., the PW in the Delaware Basin and Central Basin Platform has TDS values

below 70 g/L—the potential of using PW for hydraulic fracturing with minimal treatment is very high. Processes to treat PW for fracturing include settling, softening, coagulation and flocculation, media filters, and addition of biocides (Butkovskiy et al. 2017; Kausley et al. 2017). As no desalination process is required, reusing PW for hydraulic fracturing with or without blending has a relatively low cost and more economical benefits than disposing of PW through reinjection. A recent study in the Midland Basin indicated that reuse of PW that had been treated to remove total suspended solids and oil, and it had the addition of chlorine dioxide ranged from 30 to 50% of the costs of sourcing fresh or brackish groundwater and disposing of PW (Scanlon et al. 2017). However, it

should be noted the SO_4 type of PW shown in Fig. 6b for the three geo-structural regions can exceed acceptable SO_4 limits for cross-linked gel fluids (Reyes et al. 2018). Dilution or mixing with low SO_4 PW or selective removal of sulfate through ion exchange or nanofiltration membranes may solve this water quality issue. Reuse of PW will reduce the reliance of the oil and gas industry on freshwater supplies and decrease the water competition with other users (e.g., municipal, agricultural, and environmental), especially in arid regions. Another benefit of PW reuse is the reduced volumes of water injected into non-oil-producing geological formations through saltwater disposal wells that could result in over-pressuring and induced seismicity.

Conclusions

This study characterized the spatial distribution and variability of PW quality in the Delaware Basin, Central Basin Platform, and Northwest Shelf regions of the Permian Basin to support beneficial use-feasibility assessment. The major factors controlling geochemistry and variability of PW were examined with sedimentary rock layers formed during different geological time periods, which was inferred from the analysis of more than 4,000 samples. Upper formations (Guadalupian-age) had lower TDS compared to the Delaware- and Leonardian-age formations in the Delaware Basin and Central Basin Platform. The TDS concentrations of deep formations (Pennsylvanian-Ordovician ages) in these geo-structural regions were similar to Guadalupian-age formations. On the contrary, average TDS of Northwest Shelf waters decreased with increase in depth (Guadalupian-Ordovician ages). The results showed that meteoric waters (with lower salinity) existed even in deep Formations, which could be due to water flooding or recharge that has occurred since tilting and uplifting during the Laramide Orogeny and Basin and Range extension. In addition, the variation in geochemistry of PW was due to (1) Na-Cl waters which acquired their salinity through the dissolution of evaporites; and (2) Na-Ca-Cl waters which are the remnants of evaporated paleoseawater deposited across the basin during the late Permian. The changes in salinity within the study area were consistent with the geological Formation. The salinity variability and water classification based on major ion chemistry suggest significant quantities of meteoric water have migrated into the deeper formations through geologic structures (e.g., reefs), especially at the boundaries of the geo-structural regions and/or has been injected to support oil/gas extraction.

The statistical characterization of TDS also has quantified the water quality variability for considerations of treatment and use. The results of this investigation have identified areas and depths of decreased TDS, which may be considered for various analyses of beneficial use feasibility. The high TDS of

the PW and the extreme variability in water composition challenge reuse feasibility for agricultural irrigation. Given the scarcity of water in the semiarid region of southeastern New Mexico and western Texas, using PW for onsite oil and gas exploration and production (e.g., well drilling and hydraulic fracturing), and/or mining has the most economic feasibility and reduces the demand for freshwater in the region.

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