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Research paper

Hydrogeochemical assessment of groundwater in transboundary aquifers along the US-Mexico border and drinking water quality implications for Texas *colonias*

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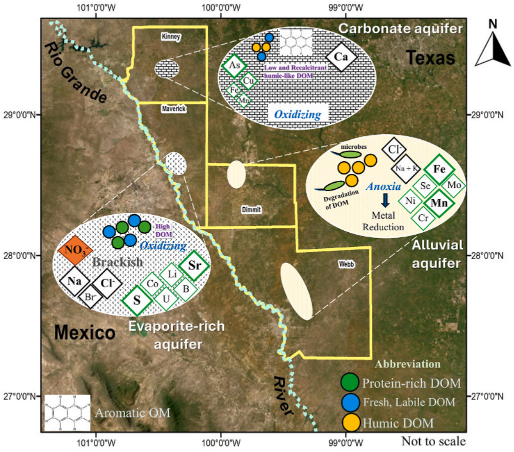
HIGHLIGHTS

- *Colonias* along the US-Mexico border in Texas rely on transboundary groundwater.
- Study reveals evaporite-rich, carbonate, and alluvial aquifer-water interactions.
- Insights on trace elements, and REE distribution for redox state in groundwater.
- Distinct signatures of DOM in oxidizing karst and reducing alluvial aquifer.
- Majority of trace toxic elements concentration were below the safe limits.

GRAPHICAL ABSTRACT



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ABSTRACT

The groundwater resources in transboundary aquifers are crucial to the development of involved nations. A unified governance strategy based on scientific data is essential for the management of transboundary aquifers. This study presents a comprehensive geochemical analysis of the groundwater quality of private wells along the US-Mexico border in Texas across three transboundary aquifer types. The concentrations of dissolved major ions, trace, and rare earth elements (REE) were measured, and the dissolved organic matter was spectroscopically characterized to evaluate the prevailing water-rock interactions, biogeochemical reactions, and anthropogenic contamination in the groundwater and their susceptibility to future contamination. Groundwater samples were collected from private wells ($n = 22$) from four representative counties within a section of the Texas-Mexico

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border (Maverick, Kinney, Dimmit, and Webb Counties). Three distinct aquifer types were revealed from the major ion composition, e.g., a carbonate aquifer within Kinney County (a part of Edwards-Trinity aquifer), an alluvial aquifer with prevailing reducing conditions within Dimmit and Webb Counties (a part of Carrizo-Wilcox aquifer), and an evaporite-rich aquifer within Maverick County. The concentrations of trace elements in the groundwater of each aquifer type were below the MCL of USEPA, however, excessive Sr concentrations were evident mostly in the evaporite-rich aquifer. Our results indicate dissolution of evaporites, and possible anthropogenic contamination may be responsible for the degradation of groundwater quality in Maverick County, raising concern for the viability of the aquifer in the future.

1. Introduction

Transboundary aquifers are defined as aquifers transected by an international border, shared between two or more countries, and serve as a vital freshwater resource for the residents of involved countries. The transboundary aquifers spanning the border between Mexico and United States (U.S.) are the main drinking water resource for inhabitants in the border counties, comprising 10% of the Texas population. Around 23% of the border residents live under the federal poverty line, and 25% lack health insurance (Border Report Section 3 – Population and Demographics of the Texas-Mexico Border Region) who rely on privately owned groundwater wells. These private wells are never monitored by national and regional monitoring programs (Jepson and Vandewalle, 2016). Thus, threats facing the freshwater resources within the transboundary aquifers of the US-Mexico border region have the potential to destabilize further the health of the communities. The Texas-Mexico border is experiencing rapid population growth with a 13.4% increase between 2007 and 2017 (National Center for Health Statistics, 2017) that developed a growing interest in the joint management of the Texas-Mexico transboundary aquifers (Sanchez and Eckstein, 2020). Along with the population growth, the border cities are experiencing an increase in industrial activities which overexploit the region's transboundary aquifers and introduce further uncertainty regarding the water quality and long-term viability of the aquifer's freshwater resources (Border Report Section 3 – Population and Demographics of the Texas-Mexico Border Region).

Salinization of groundwater is common in the arid southern and western regions of Texas due to the process of evapotranspiration (Richter and Kreitler, 1987) and mixing of saline water from seepage from saline plumes, oil-field brines, seawater intrusion (Abd-Elhamid and Javadi, 2011; Arjdal et al., 2024; Konikow and Reilly, 1999), and evaporite dissolution (Chaudhuri and Ale, 2014; McCoy T.W., 1991). The excessive withdrawal of groundwater may induce infiltration of surface-derived recharge that are rich in labile (bio-available) organic matter which may alter groundwater quality (Biazar, 2005; Harvey et al., 2002; Mahlknecht et al., 2023; Neumann et al., 2010; Pathak et al., 2022a, 2022b). Bio-available (labile) dissolved organic matter (DOM) acts as an energy source for microbially mediated redox reactions driving the mobilization of redox-sensitive trace elements in groundwater (Hasan et al., 2007; Kulkarni et al., 2017, 2018a, 2018b; Varner et al., 2022, 2024; Zheng et al., 2004). The chemical reactivity of DOM is often regulated by the molecular structure and the presence of reactive functional groups. These properties are related to the source of organic matter. Therefore, the chemical characterization of DOM provides valuable insights into the properties of the DOM [i.e., source, chemical reactivity, humification, and the extent of decomposition] and helps in understanding the role of microbial metabolisms and the coupled biogeochemical reactions that determine the mobility of contaminants within aquifers (Fuentes-Rivas et al., 2023; Jaouadi et al., 2019). In general, DOM serves as a prominent electron donor to facilitate the reduction of redox-sensitive entities such as O_2, NO_3^-, Fe^{3+}, $Mn^{4+,}$ and SO_4^{2-} in the groundwater (Bethke et al., 2011). Based on the thermodynamic ladder, after the O_2 is exhausted, other electron acceptors are utilized in the order of thermodynamic favorability ($O_2 \rightarrow NO_3^- \rightarrow Fe^{3+} \rightarrow SO_4^{2-} \rightarrow$ Methanogenesis). The DO concentrations can distinguish the aerobic (O_2 has primary electron acceptor) zone from the other redox zones. However, we can use the concentrations of redox couples to comment on the possible redox conditions of the aquifer. Reduction of oxyanions i.e., SO_4^{2-} may actually sequesters trace elements (As) from the solution by As-sulfide coprecipitation. However, the lower abundance of such oxyanions i.e., NO_3^-, and SO_4^{2-} in the groundwater indicates reducing conditions based on the order of most favored electron acceptors which may eventually influence mobilization of trace elements. Therefore microbial interaction of DOM and resultant redox condition play a critical role in mobilizing associated trace elements in groundwater (Buschmann and Berg, 2009; Filter et al., 2024; Gao et al., 2021; Nickson et al., 1998; Pathak et al., 2022b; Riedel et al., 2022; Varner et al., 2024). In alluvial aquifers, DOM commonly drives reducing conditions in the groundwater and fuels the microbially mediated reductive dissolution of contaminants or trace elements (i.e., As, Fe, Mn, Mo) from the aquifer sediment into the groundwater (Bhattacharya et al., 1997; Hou et al., 2020; Huang et al., 2022, 2023; Nickson et al., 1998; Pathak et al., 2022b; Varner et al., 2024).

The natural abundance of rare earth elements (REEs) in the groundwater can improve the holistic understanding of a groundwater system that is often linked hydro-geologically to heterogeneous aquifer systems and surface waters (Noack et al., 2014). The REEs comprise the lanthanide elements in the periodic table ($z = 57$ to 71) between Lanthanum (La) and Lutetium (Lu) (i.e., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) (Cendón et al., 2022). As per the USGS classification of REE, the lighter REEs (LREE) comprise the elements between La and Gd in the periodic table, however, heavy REEs (HREE) comprise the elements between Tb and Lu in the periodic table. The unique and chemically coherent behavior of REE (e.g., similar valence, ionic radii, trivalent redox state except for Ce^{4+} and Eu^{2+}) make them useful tracers for investigating the bulk composition of source rocks, water-rock interactions, and mixing signatures in groundwater along the flow path (Bau and Moller, 1993; Cendón et al., 2022; Johannesson et al., 1999; Johannesson et al., 1997a, 1997b; Smedley P. L., 1991; Taylor and McLennan, 1985). Under the variable pH and redox conditions of the aquifer, REEs participate in adsorption-desorption reactions and preferential fractionation into HREE and LREE species between dissolved and solid phases (aquifer sediment) (Bau and Moller, 1993; Guo et al., 2010; Johannesson et al., 2005; Johannesson and Lyons, 1995; Liu et al., 2016; Tang and Johannesson, 2006). The distribution of HREE and LREE in groundwater, coupled with the shale normalized Ce anomaly (Ce/Ce*) signature, provide valuable insights into the potential redox states in the aquifer (Bau and Dulski, 1996; Braun et al., 1990; De Baar H. J. W. et al., 1988; Dia et al., 2000; Liu et al., 2016).

The lithology within the aquifer has a significant control on the groundwater chemistry due to water-rock interactions, which become enhanced under longer residence times of groundwater (Nordstrom et al., 1989; Verma et al., 2019; Walter et al., 2017). Some of the major transboundary aquifers along the US-Mexico border in Texas include carbonate rock-dominated Edwards-Trinity aquifer and alluvial deposits of the Carrizo-Wilcox aquifer. The regional shallow groundwater in the border region, which is not associated with any major aquifer, is commonly characterized by local pockets of brackish water, derived from the dissolution of evaporite rocks. The ongoing unconventional oil and gas production (e.g., shale fracking) in parts of the border region may perpetuate groundwater contamination from disposal activities, injection of fracture fluids or brines, and the leaching of industrial effluents (Hildenbrand et al., 2017). Furthermore, agricultural activities such as the runoff of fertilizer-rich irrigation (Burow et al., 2010; Gómez et al., 2017; Grizzetti et al., 2011; Gutiérrez et al., 2018; Hansen et al., 2017; Ochoa-Rivero et al., 2023; Rupert, 2008), and wastewater from industrial effluent, leakage from septic tanks, sewage (Izbicki et al., 2015; McArthur et al., 2012, 2016; Wakida and Lerner, 2005) may provide excess NO_3^-, and fresh organic matter that regulates the geochemical processes degrading the groundwater quality; as evident in parts of the US-Mexico transboundary aquifers (Islam, 2023; Sanchez et al., 2016) and northern Mexico (Gómez et al., 2017; Ochoa-Rivero et al., 2023).

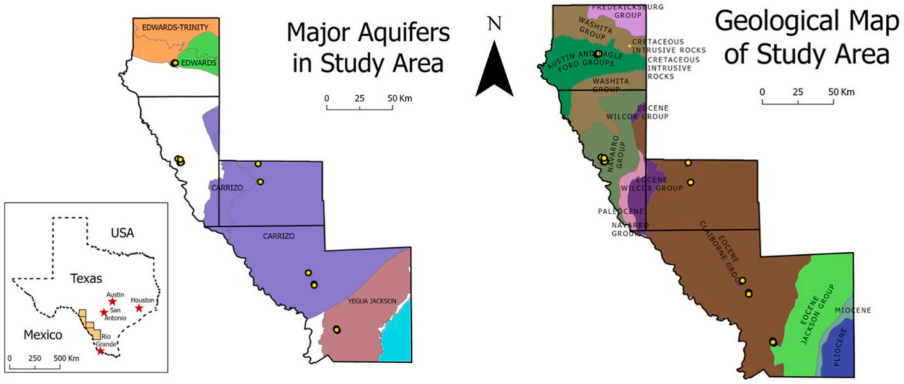
Interpretation of the regional historical groundwater data (n ~1500) from the USGS database (McMahon et al., 2016; Stanton et al., 2017) along a section of the US-Mexico border shows that the concentration of dissolved trace elements is typically below the Maximum Contamination Level (MCL) assigned by US Environmental Protection Agency (USEPA) (EPA). However, occasional occurrences of arsenic (As) and lead (Pb) enrichment (>MCL) indicate contaminant hotspots and raise concerns about future water quality under rapidly changing climate, water demand, and land-use patterns. However, this historical database does not provide any information about the prevalent bio-geochemical processes within these aquifers that may mobilize such contaminants and jeopardize groundwater quality in the future. Moreover private wells of the border region among the '*colonias*' were never been monitored for water quality. To resolve such limitations, in this study, our objectivity is to employ a multi-proxy geochemical investigation to understand the occurrence, distribution, and geochemical processes responsible for mobilizing trace elements and REEs in groundwater monitored from privately owned wells of a few representative counties within a section of the US-Mexico border in Texas.

2. Study area

A total of 22 private wells were sampled for groundwater from Kinney, Maverick, Dimmit, and Webb Counties along a section of the Texas-Mexico border (Fig. 1). The groundwater samples were collected from, a) Kinney County (n = 4; 257–452 m bgl depths) from the Edwards-Trinity karst aquifer, b) Maverick County (n = 8; 61–92 m bgl depths; no major aquifer defined) c) Webb & Dimmit County (n = 10; 122–198 m bgl depths) from the Carrizo-Wilcox alluvial aquifer. It is to be noted that the total number of samples used in this study (n = 22) is not sufficient to describe the entire spatial spread of the aquifers. However, these samples were chosen as representative data points from each county where *colonias* rely on this groundwater for drinking. The overall groundwater flow is from north to south crossing the US-Mexico border (Texas Water Development Board Groundwater Database), however the local flowpaths may be different due to possible connections between and within the aquifers under the conditions of excessive irrigation withdrawal (Sanchez et al., 2016). The detailed lithological description of the study area is marked in Fig. 1. The Edwards-Trinity (Plateau) karst aquifer is one of the largest aquifers in the state of Texas, composed of predominantly limestone and some dolostone of the lower Cretaceous age and quartz sands (Chaudhuri and Ale, 2014). It is a crucial freshwater resource for the inhabitants in south-central Texas (Sanchez et al., 2016). The Edwards-Trinity groundwater is typically considered hard water, with total dissolved solids (TDS) concentrations ranging between 400 and 1000 mg/L. The Carrizo-Wilcox aquifer, another prolific aquifer in Texas used majorly for irrigation, is composed of Tertiary-age sand interbedded with gravel, silt, clay, and lignite (Chaudhuri and Ale, 2014) which were deposited in a fluvio-deltaic environment (Hamlin, 1983; Mace et al., 1999). Based on the USGS database it is evident that, in Kinney County, the groundwater flow is driven by recharge from the Edwards Plateau, moving southwest toward the Rio Grande. In Webb, Maverick, and Dimmitt counties, groundwater flow is primarily influenced by the Carrizo-Wilcox Aquifer, generally moving southeast toward the Rio Grande. In specific areas, local geological features such as faults and intensive irrigation pumping may disrupt regional groundwater flow pattern by replacing with several local-to intermediate-scale flow systems with a tendency to generate cones of depression around the pumping. High TDS values are common in the western and southern regions of the Carrizo–Wilcox aquifer and in the north-western parts of the Edwards-Trinity (plateau) aquifer (Chaudhuri and Ale, 2014; Reutter and Dunn, 2000) due to the localized anthropogenic contamination potentially induced by irrigation return flow or unregulated oil-field brine disposal activities (Chaudhuri and Ale, 2014; McCoy T.W., 1991).

3. Methodology

The collection of groundwater samples (~61–452 m bgl depth ranges) followed the USGS groundwater sampling protocol. Each well was pumped for around 30 min until the physical parameters (pH, specific conductance, and temperature) were stabilized to ensure that the sampled groundwater was derived from the aquifer itself. A set of sub-samples of groundwaters was prepared from each sampling location for subsequent analyses, (i) unfiltered unacidified sample for



Lithological Description of Sampling Locations

Kinney County	Maverick County	Dimmit County	Webb County
▪ Quaternary Holocene alluvium, floodplain deposits. ▪ Cretaceous Gulfian Eagle Ford Group, shale, siltstone, and limestone, 22 – 60 m	▪ Pliocene caliche-cemented gravel, ~ 10 m ▪ Cretaceous Gulfian Navarro group, clay, sandstone, siltstone limestone, ~ 82m ▪ Mudstone (82-86 m), sandstone (~266 m)	▪ Tertiary Eocene Claiborne Group, El Pico Clay, clay, sandstone, and coal, ~270 m ▪ Bigford formation, clay, sandstone and lgnite, cross bedded, ~243 m	▪ Tertiary Eocene Claiborne Group, Laredo formation, sandstone and clay, ~ 189m ▪ Yegua formation, clay and sandstone, chert, calcareous, cross bedded, ~122 m.

Fig. 1. Figure showing the hydrogeology and locations of representative groundwater samples (white circles) collected from four counties among the *Colonias*. Adjoining transboundary aquifer types within a section of the Texas-Mexico border region in Texas are highlighted.

measurements of pH, conductivity, and temperature, (ii) 0.22-μm filtered and unacidified sample for measurements of major anions, (iii) 0.45-μm filtered samples a) acidified with 0.2% v/v ultrapure HNO_3 for measurements of major cations, and, b) acidified with 2% v/v ultrapure HNO_3 for REEs and trace elements measurements, (iv) 0.22-μm filtered sample acidified with 0.2% v/v ultrapure HCl, for measurements of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN), (v) 0.22-μm filtered and unacidified sample for measurement of UV–Vis absorbance and fluorescence spectroscopic properties. All the prepared sub-sample sets of groundwater were preserved in the pre-acid rinsed HDPE narrow-mouth bottles in the dark at 4 °C until the analysis was conducted.

The pH, temperature, and specific conductance were measured in the water samples in the field immediately upon collection using a HACH Pocket Pro + Tester (HACH Catalog # 9532800). Major anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) and cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were measured using the Thermo Scientific Dionex Integrion High-Pressure Ion Chromatography and Dionex Aquion Ion Chromatography systems respectively at the University of Texas at San Antonio (UTSA), Department of Earth and Planetary Sciences, Institute for Water Research, Sustainability and Policy (UTSA-IWRSP). Dissolved NO_3^--N concentrations were recalculated from the measured NO_3^- dataset in the present groundwater samples. Anions were eluted with 20 mM Potassium Hydroxide solution using Dionex IonPac AS18 (4 × 50 mm) separator column, and cations were eluted isocratic with 20 mM Methanosulfonic acid using Dionex IonPac CS12A (4 × 50 mm) separator column. The concentrations of trace elements (B, P, S, Cr, Fe, Mn, Cu, Co, Ni, As, Se, Sr, Mo, Cd, U) were measured in the 2% v/v HNO_3 acidified water samples with Ga as the internal standard for drift correction using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent ICP-MS 7500 cx; Santa Clara, CA) at the Spectroscopy and Biophysics Core at the University of Nebraska, Lincoln following the protocol described in (Malinouski et al., 2014). The REEs were measured in the same set of acidified water samples with Bi as the internal standard. The analytical uncertainty of the major ions and trace elements lies within <5%. The shale normalized (SN) Ce anomaly (Ce/Ce*) of the water samples was calculated following the mathematical expression of (De Baar et al., 1983; Bau and Dulski, 1996; Noack et al., 2014)

$$Ce \Big/ Ce^*_{SN} = \frac{2^*[Ce]_{SN}}{(La)_{SN} + (Pr)_{SN}}$$

where Ce^*_{SN} are interpolated values based on the measured concentrations of the neighbor elements of Ce, that include Lanthanum (La), and Praseodymium (Pr).

The DOC concentrations in water samples, measured as non-purgeable organic carbon (NPOC) and total dissolved nitrogen (TDN) concentrations were analyzed by thermic oxidation using Shimadzu TOC/TN Analyzer at the UTSA. Characterization of DOM was done by measuring UV–Vis absorbance (240 nm–450 nm) and fluorescence (300 nm–600 nm) using a 1 cm pathlength quartz cuvette on Horiba Aqualog Benchtop fluorometer at the UTSA-IWRSP. The detailed methods for spectroscopic characterization of DOM are described in (Kulkarni et al., 2017). Briefly, fluorescence emission spectra were collected in signal to reference (S:R) mode from 300 nm to 600 nm range with an increment of 3.28 nm (instrument default). The emission spectra were corrected for the inner filter effect (Ohno, 2002) and normalized for the Raman effect using the emission intensity at 350 nm for 18.3 MΩ cm Milli-Q ultra-pure water. An ultrapure water blank spectra was substracted from the sample spectra. The 1st and 2nd order Rayleigh scattering bands were excised (Stedmon and Bro, 2008). All the corrections were performed using drEEM 0.6.6 toolbox (https://dreem.openfluor.org/). Various fluorescence indices and peak intenseities were extracted from the corrected fluorescence spectra.

The humification index (HIX) indicates the content of humic substance and the degree of humification (Ohno, 2002) of the organic matter which is determined by the ratio of the emission (em) spectra peak area between 435 and 480 nm to the peak area between 300 and 345 nm at an excitation wavelength of 254 nm (Zsolnay, 2003). The ratio of recently produced DOM to decomposed humic-like DOM provides the freshness index (β:α) (Fellman et al., 2010). At 310 nm, an indication of recently produced DOM (β) is observed along an emission of 380 nm. However, more decomposed DOM (α) is observed by the maximum emission intensity between 420 and 435 nm (Parlanti et al., 2000). The fluorescence index (FI) was determined by the ratio of fluorescence intensities at 470 nm and 520 nm emission and 370 nm excitation. The FI provides an indication of whether the DOM is terrestrially sourced (FI < 1.4) or microbially produced (FI > 1.7) (McKnight et al., 2001). The specific UV absorbance of water at a given wavelength of 254 nm ($SUVA_{254}$) (Weishaar et al., 2003) was determined as Abs_{254} over the DOC concentration and is indicative of the aromaticity of DOC in water (Ohno, 2002).

Principal Components Analysis (PCA) is useful for reducing the dimensionality of large datasets and transforming sets of variables into principal components, or PCs, to provide relationships between the variables (Jackson, 1991). The measure of PCs associated variance is represented by the eigen values and loadings define the participation of original variables in the PCs. Here, PCA was performed on the geochemical dataset of groundwater, including the inorganic and organic parameters (32 variables), using Origin Pro® 2024 software to explain the relationships between the variables. Following the criteria of Cattell and Jaspers (1967) PCs with eigen values > 1 (i.e., 7 PC's) were retained. In the PCA analysis, varimax rotation option has been used and the data were Kaiser log normalized. The Kaiser–Meyer–Olkin (KMO) test and Berlett's test of sphericity on the correlation matrix of variables was run for understanding the validity of PCA analysis. The PCA was constructed from a correlation matrix with z-score standardized data to give a value between −1 and + 1 (mean = 0 and SD = 1) for each variable. Two PCs were selected based on the highest eigenvalues (i.e., 13.8, 4.9). Fig. S1 summarizes the PCA results including the loadings, eigen values and percentage of variances elucidated by each principal component (PC). The supporting correlation matrix table of the variables included in the PCA is provided in Fig. S2. The groundwater samples, the variables used in the PCA analysis, and the analytical dataset are provided in Tables 1 and 2 and supporting data Tables S1–S4.

4. Results

4.1. Chemical constituents of groundwater in the transboundary aquifers

The groundwater samples showed overall circumneutral to slightly alkaline pH ranging between 6.4 and 8.5. A comparatively alkaline pH (i.e., pH 7.6 and pH 8.5) was evident in Dimmit County groundwater (Fig. S4). However, a few point sources of lower pH (i.e., pH 6.4) were reported in the groundwater type of Maverick County. The representative groundwater samples from Maverick (n = 8) and the majority of Webb & Dimmit County (n = 6 out of 10) showed higher specific conductivity values ranging between 1012 and 1970 μS/cm (Table 1). Contrastingly, one sample from Kinney County reported a much higher specific conductivity value than the other measured samples (3000 μS/cm).

Webb & Dimmit Counties groundwater were considered representative of an alluvial siliciclastic aquifer and therefore presented together in results and discussion section. The major cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (F^-, Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, Br^-) in the groundwater samples of variable transboundary aquifer types in the study region showed wide distributions (Table 1). The alluvial aquifer comprising Webb & Dimmit County documented Ca-Mg-SO_4 type groundwater with a wide distribution of major ions. The evaporite-rich aquifer comprising Maverick County showed (Na-K-Cl-SO_4) groundwater type along with higher Li and Br^- concentrations. Whereas the karst aquifer comprising Kinney County (n = 3) showed Ca-rich groundwater type (Fig. 2b)

Table 1
Major ion abundances in the groundwater samples from representative counties. Due to their similarities, the inorganic parameters from Dimmit County and Webb County are grouped and reported together. All ionic concentrations are in mg/L.

Category	Parameter	Webb & Dimmit (n = 10)	Kinney (n = 3)	Maverick (n = 8)
General	pH	7.5 ± 0.5 (7.0–8.5)	7.4 ± 0.4 (6.7–7.7)	6.8 ± 0.3 (6.4–7.1)
	Temperature (°C)	28.4 ± 0.8 (27–29.5)	26.5 ± 1.6 (24.7–27.9)	30.9 ± 3.05 (28.0–36.0)
	Conductivity (μS/cm)	1103 ± 495 (513–1970)	473 ± 12 (460–480)	1504 ± 161 (1184–1669)
Cations (mg/L)	Li^+	0.2 ± 0.1 (bdl – 0.28)	(bdl – 0.12)	0.8 ± 0.2 (0.6–1.0)
	Na^+	153 ± 93 (66–311)	4 ± 0.2 (3.8–4.3)	3007 ± 628 (2260–3765)
	NH_4^+	(bdl – 1.0)	bdl	(bdl – 0.35)
	K^+	5.5 ± 2.0 (3.3–8.8)	0.8 ± 0.05 (0.7–0.8)	14 ± 4 (9–18)
	Mg^{2+}	25 ± 13 (9–44)	6 ± 0.2 (5.5–5.8)	58 ± 22 (27–81)
	Ca^{2+}	72 ± 25 (24–113)	86 ± 2 (84–88)	157 ± 51 (86–216)
Anions (mg/L)	F^-	0.6 ± 0.2 (0.2–1.0)	0.2 ± 0.1 (0.1–0.4)	3.6 ± 2.5 (2–9)
	Cl^-	128 ± 68 (27–237)	17 ± 14 (9–33)	4198 ± 1253 (2504–5479)
	NO_2^-	bdl	(bdl - 1.63)	bdl
	Br^-	2.5 ± 1.6 (bdl – 4.5)	bdl	15.1 ± 20.7 (3.4–61.0)
	SO_4^{2-}	258 ± 186 (24–658)	12 ± 4 (9–17)	1812 ± 251 (1357–2028)
	NO_3^--N	2.2 ± 1.3 (bdl – 5)	1 ± 0.06 (1.0–1.2)	5 ± 1 (3–6)

Bdl – Below detection limit (<0.01 mg/L).

Table 2
Dissolved organic matter (DOM) spectroscopic parameters in the groundwater samples from each county. Due to their similarities, the DOM parameters from Webb and Dimmit County are grouped and reported together. Results in ***bold italics*** indicate statistical differences ($p < 0.05$) among one or more groups interpreted by the Mann-Whitney-Wilcoxon Test.

Category	Parameter	Webb & Dimmit ($n = 10$)	Kinney ($n = 3$)	Maverick ($n = 8$)
Concentrations (mg/L)	DOC	2.85 ± 2.12 (0.61–8.30)	0.74 ± 0.07 (0.66–0.81)	[a] ***4.02 ± 2.17 (2.63 – 9.17)***
	TDN	0.92 ± 1.45 (0.00–4.68)	2.04 ± 0.12 (1.94–2.17)	[b] ***3.24 ± 0.70 (2.20 – 4.30)***
Fluorescence and Absorbance Indices	FI	[c] ***1.73 ± 0.18 (1.50 – 2.05)***	1.40 ± 0.39 (0.97–1.73)	[c] ***1.72 ± 0.20 (0.87 – 1.61)***
	β:α	0.96 ± 0.12 (0.81–1.24)	0.96 ± 0.12 (0.83–1.08)	[d] ***1.11 ± 0.18 (0.87 – 1.61)***
	BIX	1.02 ± 0.13 (0.92–1.36)	0.84 ± 0.15 (0.70–0.99)	1.23 ± 0.26 (0.87–1.61)
	HIX	0.67 ± 0.09 (0.51–0.83)	0.54 ± 0.11 (0.41–0.61)	0.59 ± 0.12 (0.33–0.70)
	$SUVA_{254}$ ($L.mg^{-1}.m^{-1}$)	0.68 ± 0.74 (0.01–2.25)	2.00 ± 1.99 (0.74–4.30)	0.89 ± 1.35 (0.09–4.16)
Peak Intensities	T	0.10 ± 0.05 (0.01–0.18)	0.08 ± 0.10 (0.00–0.20)	[e] ***0.33 ± 0.36 (0.07 – 1.07)***
	A	0.23 ± 0.08 (0.10–0.35)	0.11 ± 0.08 (0.02–0.17)	0.37 ± 0.41 (0.13–1.37)
	M	0.14 ± 0.05 (0.06–0.20)	0.06 ± 0.04 (0.01–0.09)	0.28 ± 0.29 (0.10–0.99)
	C	0.12 ± 0.05 (0.04–0.18)	0.05 ± 0.04 (0.01–0.09)	0.22 ± 0.28 (0.07–0.89)

[a] DOC in Maverick county is statistically higher than that in Webb & Dimmit counties (p <0.001).
[b] TDN in Maverick county is statistically higher than that in Kinney county ($p = 0.0272$).
[c] Fluorescence index (FI) in Webb & Dimmit is statistically higher than that in Kinney ($p = 0.038$) and Maverick ($p = 0.05$) counties.
[d] Freshness index (β:α) in Maverick county is statistically higher than that in Webb & Dimmit counties ($p = 0.039$).
[e] Intensity of fluorescence peak T in Maverick county is statistically higher than that in Webb & Dimmit ($p = 0.047$).

except for one outlier sample (KC4) showing much higher abundances for all major ions (Tables S1 and S2). The NH_4^+ in all samples remained below detection levels (<0.01 mg/L) except for one sample from Maverick County (0.35 mg/L), and one sample from Webb County (1 mg/L). Concentrations of F^- exceeded the US Environmental Protection Agency's maximum contaminant level (USEPA, 2014, MCL) of 4 mg/L in only two groundwater samples from Maverick County. On average, NO_3-N concentrations were highest in Maverick County groundwater samples (5 mg/L) although much lower than the USEPA MCL of 10 mg/L (Table 1).

The groundwater samples contained variable concentrations of trace elements, although most (except for Sr in Maverick County) were below the respective MCL of USEPA (USEPA, 2014, MCL) assigned for National Primary Drinking Water Regulations. The evaporite-rich aquifer in Maverick County showed comparatively higher B (7.4 ± 0.7 mg/L), Sr (15 ± 3 mg/L), Co (0.2 ± 0.1 μg/L), U (1.1 ± 0.1 μg/L) Mn (10 ± 9 μg/L), and S (562 ± 76 mg/L) concentrations (Fig. 3, Table S3). The karst aquifer (Kinney County) water contained comparatively higher As concentrations (0.6 ± 0.2 μg/L) although below MCL of 10 μg/L. The alluvial aquifer in Webb & Dimmit County showed comparatively higher Cu (13 ± 9 μg/L), Ni (0.7 ± 0.6 μg/L), Cr (1.6 ± 2.6 μg/L), Mo (3 ± 2 μg/L), Se (0.4 ± 0.1 μg/L), Fe (130 ± 189 μg/L), and Cd (0.06 ± 0.08 μg/L) concentrations with wide ranges of abundances documented for some of the redox-sensitive trace elements (Fig. 3, Table S3).

Total REE abundance (ΣREE) in groundwater reported a similar distribution in Maverick, Webb & Dimmit and Kinney County (i.e., 1.4

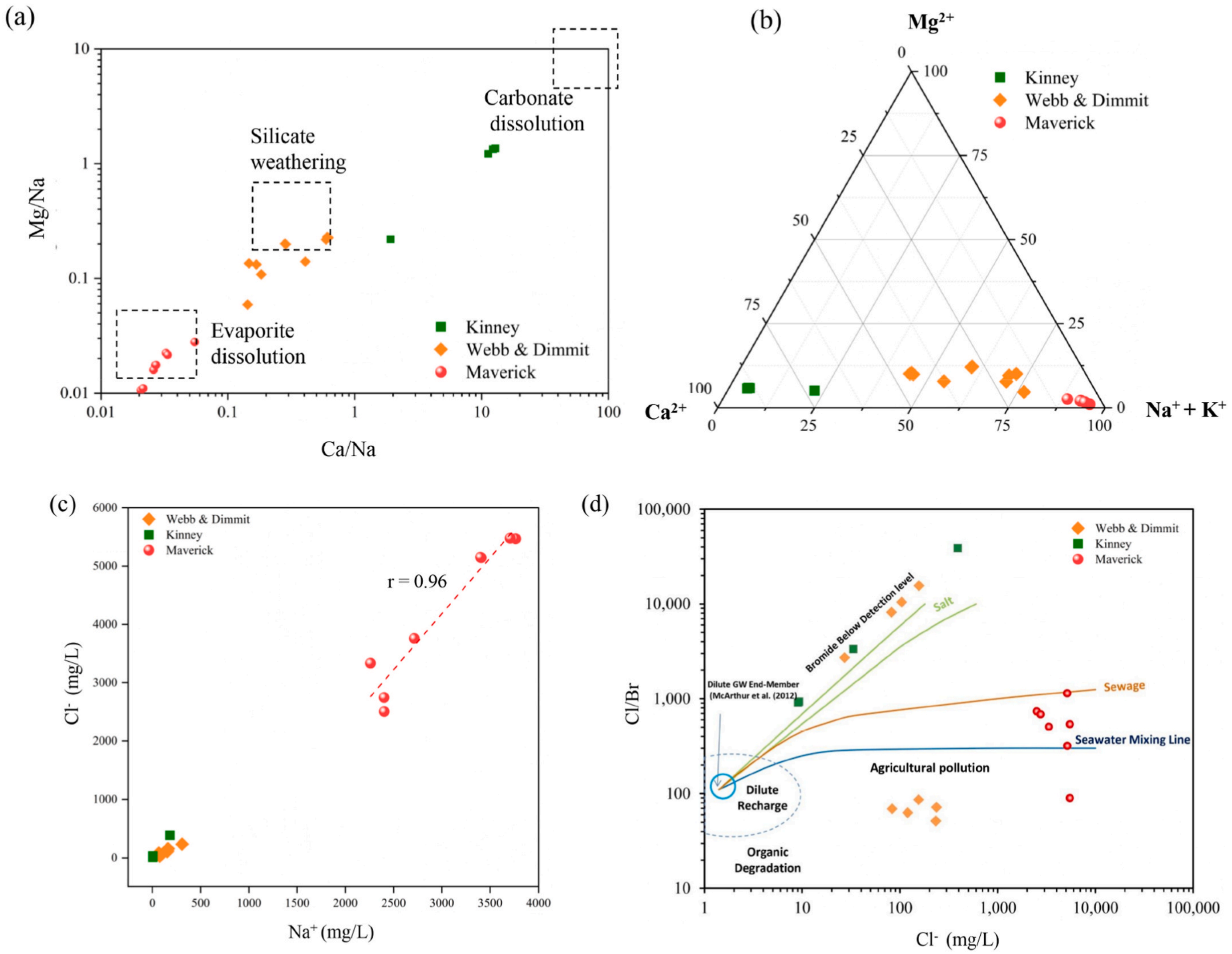


Fig. 2. a) Bivariate plot of Ca/Na and Mg/Na (molar ratio) shows the prevailing chemical weathering possibilities of the aquifer minerals in groundwater samples, b) Ternary diagram showing major cation compositions of the categorized groundwater samples, c) Correlation plot between Na^+ and Cl^- indicating an effect of evaporite (halite) dissolution in Maverick County, and d) Cl^-/Br^- mass ratio in groundwater samples plotted along with sea water mixing, agricultural pollution, sewage contamination, and salt dissolution lines (Alcalá and Custodio, 2008; Davis et al., 1998, 2004; Knappett et al., 2016, 2018; Kulkarni et al., 2018a; McArthur et al., 2012; Vengosh and Pankratov, 1998). Note that Kinney and Dimmit County groundwater samples are displayed in Fig. 2d considering their Br^- concentrations being ~0.01 mg/L which is the instrument detection level.

± 0.04 ng/L, 1.3 ± 0.2 ng/L, 1.4 ± 0.004 ng/L respectively). The REE abundance in the present groundwater samples was normalized concerning the North American Shale Composite (NASC) to remove the Oddo-Harkins effect (McLennan, 1989, 1994). The Shale normalized (SN) groundwater data was defined as Water/NASC which showed enrichment in heavy (atomic number 65 to 71) REEs (HREE) over light (atomic number 57 to 64) REEs (LREE) in all the counties with HREE/LREE values ranging between 4 and 5.87. The Ce anomaly [Ce/Ce*](De Baar et al., 1983; Bau and Dulski, 1996) was calculated for the shale-normalized groundwater REE data which documented overall low positive values in all the counties. The lowest positive Ce anomaly (Ce/Ce*) was recorded in Kinney County groundwater (Ce/Ce* = 0.11), and the highest positive Ce anomaly was in Webb & Dimmit County groundwater (Ce/Ce* = 0.35).

4.2. *Spectroscopic properties of dissolved organic matter*

The DOC and TDN, along with the absorbance and fluorescence characteristics of the chromophoric DOM were measured in the groundwater samples for each county (Fig. 5, Table 2). In general, the DOM properties were similar among the samples, specifically in the Webb & Dimmit Counties groundwater which were considered representative of an alluvial siliciclastic aquifer and therefore presented together in this section. However, a few observable differences in the organic matter quality may be influenced by the respective aquifer properties (i.e., alluvial, karst, evaporite-rich) and may reflect the prevailing biogeochemical processes in each aquifer type. The DOC concentrations were highest in the Maverick County groundwater samples (4 ± 2 mg/L), followed by the Webb & Dimmit County samples (3 ± 2 mg/L), and were lowest in the Kinney County groundwaters (0.7 ± 0.1 mg/L). On the other hand, the TDN concentrations were lowest in the Webb & Dimmit County groundwater (0.9 ± 1 mg/L) and were relatively elevated in the Kinney and Maverick County groundwater samples (2.0 ± 0.1 mg/L and 3.0 ± 0.7 mg/L, respectively).

The average fluorescence indices (FI) in Kinney County groundwaters showed a lower value (FI = 1.4) than that of Dimmit & Webb and Maverick Counties (FI = 1.73 and 1.72, respectively). Furthermore, Maverick County groundwater contained the highest values for freshness index (β:α = 1.11) and biological index (BIX = 1.23). The

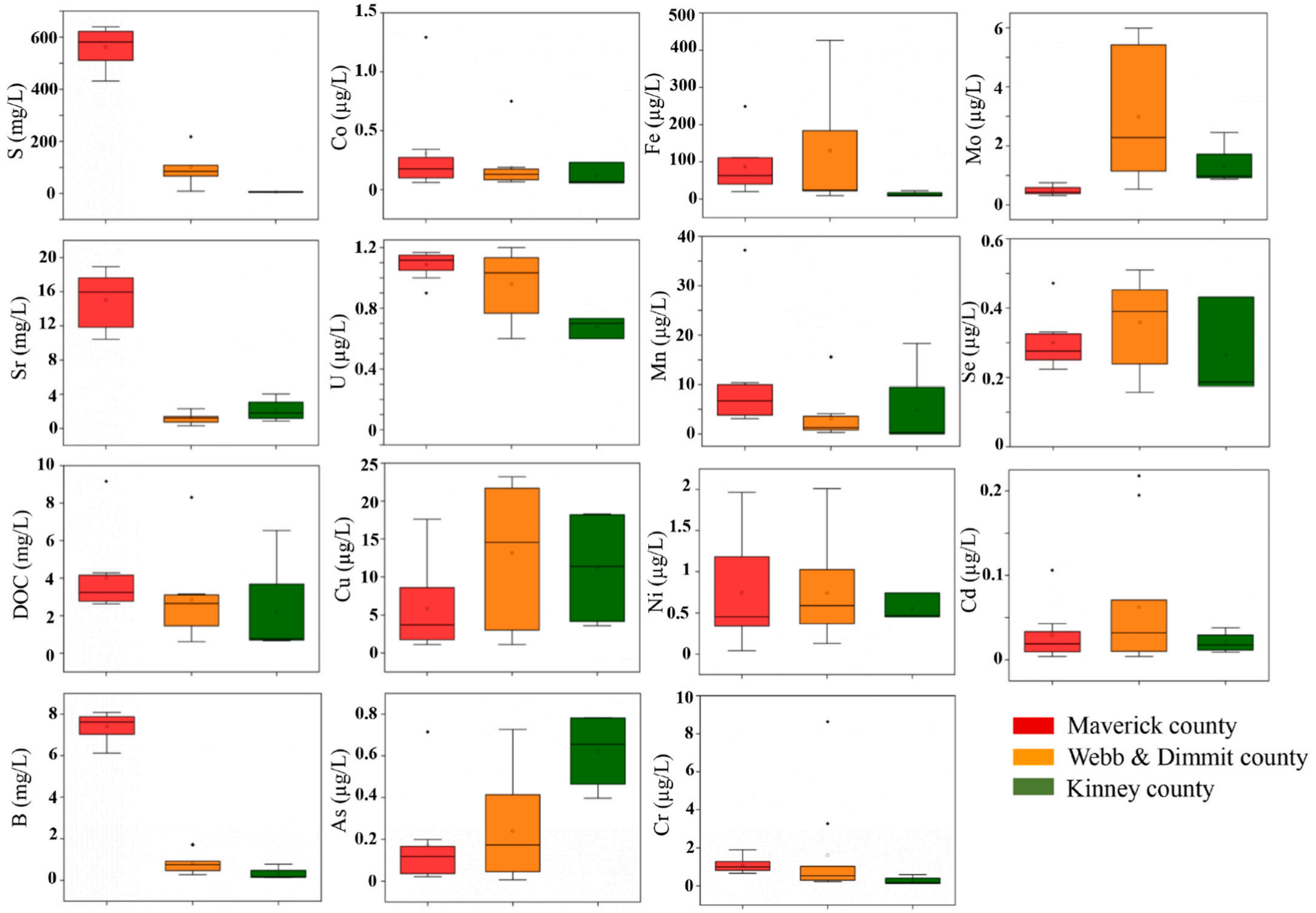


Fig. 3. Boxplots showing the concentrations of trace elements in groundwater samples. The safe limits for the dissolved concentrations of these trace elements according to the World Health Organization (WHO) are, 70 µg/L (Mo), 15 µg/L (U), 400 µg/L (Mn), 10 µg/L (Se), 2 mg/L (Cu), 70 µg/L (Ni), 3 µg/L (Cd), 500 µg/L (B), 10 µg/L (As), 50 µg/L (Cr). However, the safe limits for the dissolved concentrations of these trace elements according to the United States Environmental Protection Agency (USEPA) are, 4 mg/L (Sr), 30 µg/L (U), 1.3 mg/L (Cu), 1.0 mg/L (Cr), 40 µg/L (Mo), 10 µg/L (As), 50 µg/L (Se), 5 µg/L (Cd).

humification index (HIX) was slightly higher in Webb & Dimmit County groundwater (HIX = 0.67) as compared to that of Kinney and Maverick Counties (HIX = 0.54 and 0.59, respectively) (Table 2). Similarly, the SUVA$_{254}$, which provides a measure of aromaticity of DOM, was lowest in the Webb & Dimmit County groundwater (0.68 ± 0.74 L mg^{-1}.m^{-1}), highest in Kinney (2.00 ± 1.99 L mg^{-1}.m^{-1}) and moderate in Maverick County (0.89 ± 1.35 L mg^{-1}.m^{-1}) groundwater samples.

The four peaks identified in the excitation and emission spectra of the groundwater samples included peak A (terrestrial humic-like), peak T (protein-like), peak C (terrestrial fulvic-like), and peak M (microbially produced, humic-like) (Coble et al., 1998) (Table 2, Fig. 5). In general, Maverick County groundwater showed the highest signatures for each peak, likely due to the higher abundance of DOC. Notably, the abundance of peak T, which represents protein-like compounds, was markedly higher in the Maverick County groundwater as opposed to other locations (Table 2). However, taking the ratio of the individual peak to the sum of all peaks yields the relative proportions of these components in each sample. For example, this demonstrates that the Maverick County groundwater primarily consists of humic-like organic matter (peak A = 30%) followed by protein-like (peak T = 28%), microbially produced (peak M = 23%), and fulvic-like organic matter (peak C = 19%). Likewise, the groundwater from Kinney County showed the same distribution with decreasing proportions of peaks A, T, M, and C (36%, 26%, 20%, and 18%, respectively). The organic matter character in the Webb & Dimmit County groundwater had higher humic- and fulvic-like signatures with the highest proportion of peak A (40%) followed by peaks M, C, and T (24%, 20%, and 16%, respectively) (Table 2, Fig. 5).

4.3. Principal Component Analysis of the dataset

The PCA analysis yielded seven PCs with eigen values > 1 explaining around 89.3 % of the total variance of the dataset (Fig. 6, S1). Among the PCs, PC1 and PC2 accounting for 43.3 % and 15.4 % of total variance, respectively, are predominantly responsible for controlling the geochemistry of groundwater. The calculated Kaiser–Meyer–Olkin (KMO) index value for the present set of variables is 0.811 which indicates the adequacy of sampling of each observed variables for the analysis. Berlett's test of sphericity on the correlation matrix of variables is documented significant at $p < 0.05$ ($p = 3.62E-08$); indicating PCA can accomplish a momentous reduction of the dimensionality of the original dataset or the factor analysis is appropriate.

The PCA analysis revealed that in PC1, temperature, specific conductivity, U, Mn, DOC, Ca^{2+}, Cl^-, Li^+, Sr, Na^+, SO_4^{2-}, Br^-, TDN, B, S, NO_3-N, F^-, K^+, Mg^{2+}, β:α (Freshness Index) had high positive factors loading and while BIX (Biological Index) had comparatively lower positive factors loading. In PC2, Co, Cd, Fe, As, Mo had high positive factor loadings, while Ni, Cu, Cr had comperatively lower positive factor loadings. In PC2, P, and Se had high negative factor loading values, while HIX (Humification Index) had lower negative factor loading. The correlation and degree of association between the variables of PC1 and

PC2 were demonstrated in a bivariate plot (Fig. 6; Fig. S2). Using the loading scores for PC1 and PC2, the data for sample type were projected as points on a score plot. Groundwater geochemical data and DOM characteristics of Maverick County were grouped along the positive PC1 axis, dominated by major ions and oxidative trace elements. In contrast, the Kinney County dataset was grouped along the negative PC1 axis with no prominent ionic/elemental enrichment. The Webb & Dimmit County groundwater data were grouped both along the positive and negative PC2 axes and partly along the negative PC1 axis; dominated by widely variable redox-sensitive trace elements.

5. Discussion

5.1. *Chemical weathering and anthropogenic inputs*

The major ion abundance in groundwater is predominantly regulated by the sediment-water interaction processes in the aquifer which may further be altered by the mixing influences from surface-derived sources (Mukherjee and Fryar, 2008; Pathak et al., 2022b). The sediment-water interaction processes in the aquifer depend on the residence time of groundwater and aquifer host lithology. To understand the differential chemical weathering processes in the transboundary aquifers, Ca/Na vs. Mg/Na molar ratios (modified after Gaillardet et al., 1999; Mukherjee and Fryar, 2008) of the groundwaters samples (Fig. 2a) were used. The Kinney County groundwater samples plotted adjacent to the zone of carbonate dissolution and showed enrichment in Ca^{2+} (Fig. 2a and b) due to the dissolution of limestone from the aquifer (Chaudhuri and Ale, 2014; Humphrey and Díaz, 2003). This pointed towards the predominant influence of carbonate rock weathering and is consistent with the karst geology of the Edwards-Trinity aquifer (Chaudhuri and Ale, 2014). The groundwater from Webb & Dimmit counties plotted between the silicate and evaporite weathering zones (Fig. 2a) and showed enrichment of monovalent cations ($Na^{+} + K^{+}$) (Fig. 2b) that are typical of silicate weathering. It is consistent with the prior geological data in this region which suggests that this aquifer (Carrizo-Wilcox) is predominantly composed of alluvial deposits and siliciclastic sediments (Chaudhuri and Ale, 2014; Hamlin, 1983; Mace et al., 1999), attributing to silicate weathering as a prominent process in controlling the groundwater chemistry. Only samples from Maverick County exhibited peculiar evaporite dissolution signatures i.e., enrichment of Na^{+} and Cl^{-} ions (Lambert, 1983; Wang et al., 2019) (Fig. 2b and c). This is attributed to the localized evaporite (e.g. halite) deposits in the region. Based on major ion chemistry, it is inferred that the groundwaters sampled in this study undergo distinct geochemical weathering processes based on the hydrogeological setting.

Analysis of the Cl/Br mass ratio revealed that the groundwater from Webb County may experienced recharge from evaporative irrigation return flow as indicated by Cl/Br < 100 and Cl > 100 mg/L (Fig. 2d). Whereas the groundwater samples from Maverick County with $100 <$ Cl/Br > 1000 and Cl > 1000 mg/L, plot above the sea-water mixing line and below the sewage contamination line (Fig. 2d). Since both Cl and Br behave conservatively in most of the natural waters and undergo negligible ion exchange reactions and adsorption-desorption cycles at low temperatures (Alcalá and Custodio, 2008; Davis et al., 1998, 2004; McArthur et al., 2012; Vengosh and Pankratov, 1998), the Cl/Br mass ratios have been used as an indicator to determine the groundwater source and chemical evolution (Alcalá and Custodio, 2008; Cartwright et al., 2006; Davis et al., 1998, 2004; Katz et al., 2011; Knappett et al., 2016, 2018, 2016; Kulkarni et al., 2018a; Li et al., 2016, 2019; McArthur et al., 2012; Panno et al., 2006; Vengosh and Pankratov, 1998). The end members shown in Fig. 2d (e.g., dilute recharge zone, organic matter degradation, evaporative recharge zone characterized by agricultural pollution, seawater mixing line, sewage and salt lines) are adopted from the prior literature (Alcalá and Custodio, 2008; Davis et al., 1998, 2004; Katz et al., 2011; Knappett et al., 2016, 2018; Kulkarni et al., 2018a; McArthur et al., 2012; Vengosh and Pankratov, 1998). In an evaporative setting or the aquifer influenced by evaporative recharge (agricultural pollution), the concentration of Cl and Br increases proportionately until halite precipitates and certain residual Cl/Br ~ 50 is maintained (Davis et al., 1998; McCaffrey et al., 1987) in the solution. The abundance of Br in Webb County groundwater samples does not appear to be solely influenced by organic matter degradation as Br is not enriched compared to Cl in those samples (Brown et al., 1958; Davis et al., 1998; Hite and Cheng, 1996; Long and Gudramovics, 1983). Additionally, the Cl^{-} abundance appears to correlate positively with NO_3^{-}-N concentration in groundwater in Webb & Dimmit County (Fig. S3, $r = 0.8$; $p < 0.05$) with however, no samples showing NO_3^{-}-N values $>$ MCL of 10 mg/L. It has been well documented that NO_3^{-} concentrations in the groundwater can result from wastewater mixing (leakage of sewage, septic tank, industrial effluent) (Izbicki et al., 2015; McArthur et al., 2012, 2016; Wakida and Lerner, 2005) and N-fertilizer-rich agricultural runoff (Burow et al., 2010; Grizzetti et al., 2011; Gutiérrez et al., 2018; Hansen et al., 2017; Rupert, 2008). Under oxidizing aquifer conditions, such NO_3^{-} tends to accumulate in the groundwater due to a lack of microbial nitrate reduction (Pathak et al., 2022b) or artificial mixing during samping. While the strong positive correlation between the Cl^{-} and NO_3^{-} (NO_3^{-}-N) in Webb & Dimmit County groundwater samples (Fig. S3) pointed towards the agricultural runoff influx to the aquifer, further analysis is required including detailed nutrient analyses. It is important to mention here that, an expectation of the widespread presence of anthropogenic pollution in long-screen wells (i.e., >100–200 m depths) is rather unlikely provided that fact that it carries the mixing of groundwaters of different ages from multiple depths in the stratified aquifer. Therefore the abundance of NO_3^{-}-N in such groundwater may be locally derived due to higher permeability of the superficial horizons.

The Maverick County groundwater samples appear to be much more saline or brackish with much higher Na^{+} and Cl^{-} concentrations (Fig. 2c) (Table 1). The Cl/Br mass ratio in Maverick County samples plot below the sewage contamination line and above seawater mixing line (Fig. 2d). This indicates that the chemistry of the groundwater in Maverick County is regulated by salt (e.g. halite) dissolution, which has also been observed in other aquifers in the USA and globally (Dutton, 1989; Fisher and Mullican, 1997; Herczeg et al., 2001; Jia et al., 2017; Johnson, 1982, 2008; Lambert, 1983; Wang et al., 2019). Only a few data points plot very close to the sewage line (Fig. 2d) indicating that there may be some point sources of anthropogenic wastewater influx in this aquifer. However, it is important to be noted that the sewage line shown for reference in Fig. 2d was adopted from (McArthur et al., 2012) and it was specifically developed using sewage water samples from Bangladesh and Vietnam; which might vary for other study areas. Hence interpreting the influence of sewage water in Maverick County groundwater shall be used with caution for the data presented in this study.

NH_4^{+} in groundwater can be oxidized to NO_2^{-}/NO_3^{-} during freshwater recharge (Kulkarni et al., 2018a) increasing groundwater NO_3^{-} concentration. In our study, only a few samples from Maverick county showed higher NO_3^{-} concentrations, which has cretaceous geology and includes sandstone, limestone, and potential evaporite lithology. In such instances, nitrogenous organic matter oxidation to release those levels of NO_3^{-} seem unlikely or cannot be inferred accurately without further investigation (e.g., $\delta^{15}N$ isotopic signatures). Therefore we hypothesize potential point sources anthropogenic contamination by mixing of N-rich irrigation return flow and/or sewage water may drive such contrasting high NO_3^{-} values in a few Maverick county groundwater. A few prior studies have linked the mixing of oilfield brine with groundwater (Akob et al., 2016; Cozzarelli et al., 2017; Lauer et al., 2016) and the resulting chemistry. It is suggested that the oilfield brine containing a lower Br^{-} concentration than the seawater ($Br^{-} \sim 67$ mg/L) could maintain a lower Br^{-} and higher Cl/Br mass ratio in the resulting water. In Maverick County groundwater samples, the average Br^{-} concentration is 13 mg/L, much lower than the seawater, indicating seawater intrusion may not be a significant process. Further, the data indicated that the Cl/Br mass ratio correlates positively with trace elements like B, Sr, and Li which are often present in higher concentration in the oilfield brine (Akob et al., 2016; Blondes et al., 2018; Cozzarelli et al., 2017; Dresel and Rose, 2010; Lester et al., 2015). The localized oilfield exploration, brine disposal activities, and their connection to the groundwater contamination have been documented in southern, central, and western Texas covering the parts of the Carrizo-Wilcox aquifer, and north-western parts of Edwards-Trinity aquifer (Anaya, 2004; Chaudhuri and Ale, 2014; Hudak and Wachal, 2001; McCoy, 1991; Walker, 1979), however not specifically in the sampling area of this study. Therefore, further study is needed to fully understand the interrelations between oilfield exploration, brine disposal activities along the border counties, and the groundwater quality in the underlying aquifers.

5.2. Trace elements of human health concern and dissolved organic matter

The observed low trace element abundances (Ni, Cr, Cd, Co, Cu, U, Mn, As, Mn, Se were below the MCL defined by USEPA) EPA (Table S3) in each transboundary aquifers suggested that the groundwater in the study region is overall safe for consumption. In the USGS reports (McMahon et al., 2016; Stanton et al., 2017), frequent zones of arsenic (As) (>10 μg/L) and lead (Pb) enrichment were documented which were absent in our groundwater samples.

In Webb & Dimmit County groundwater samples that were represented by an alluvial siliciclastic aquifer and groundwater chemistry predominantly regulated by silicate weathering and may contain evaporative recharge influences, a higher abundance and co-association of redox-sensitive elements (i.e., Cu, Ni, Mo, Se, Fe, Cd) was found (Figs. 3 and 6, and Table S3). It has been previously shown that in alluvial aquifers, microbial activity on DOM can promote reducing conditions under which many of these redox-sensitive elements tend to mobilize (Bhattacharya et al., 1997; Nickson et al., 1998; Pathak et al., 2022b; Varner et al., 2024; Vega et al., 2020). The average DOC concentration in these samples was 2.85 mg/L which is within the range of natural waters (2–4 mg/L) (Volk et al., 2002). The spectroscopic analyses of the DOM in these groundwater samples showed that the higher fluorescence index (FI) > 1.4, often attributed to microbially-derived DOM highlighting the role of microbial respiration within the aquifer. Microorganisms can utilize various electron acceptors (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, and methanogenesis) across a thermodynamic ladder (Bethke et al., 2011) in the presence of the DOM as an electron donor. When dissolved oxygen (DO) is sufficiently lowered in the aquifer, microbial NO_3^- reduction and metal reduction become the prominent processes and it has been shown that many metal-reducing microbes can mobilize co-occurring trace elements (Mukherjee et al., 2008; Mukherjee and Fryar, 2008; Pathak et al., 2022b; Vega et al., 2020; Zheng et al., 2004). The DOM in these aquifers also appears to be humified, as indicated by higher humification index (HIX) values, which also complements the mobilization of trace elements under partially reducing conditions. Due to low concentrations of trace elements in our samples, there is some uncertainty regarding which specific microbial and chemical reactions may have resulted in the mobilization of these elements. Moreover, considering the fact that vertical redox gradients are often very steep in a stratified alluvial aquifer which can only be addressed by using multi level samplers or nested monitoring wells; lacking in this study of limited representative monitoring. Therefore, a higher number of groundwater sampling from the same aquifer at multidepth intervals with analysis including estimation of electron-donating and accepting moieties in the aquifer would be necessary in the future to better understand the role of DOM and microbes in driving the aquifer redox states and influencing the mobility of trace elements.

The Maverick County groundwater was characterized by enrichment of S, B, Li, Co, Mn, and U along with Sr concentrations as high as 15 ± 3 mg/L. Such high Li and Sr concentrations can be explained as a result of evaporite dissolution as reported in previous studies (Dean, 1987; Hem, 1985; Lindsey et al., 2021; Musgrove, 2021). These trace elements were also found to be positively correlated with other parameters such as DOC, Cl^-, Br^-, Na^+, K^+, NO_3^-, and SO_4^{2-} (Fig. S22) and grouped together in the PCA analysis (Fig. 6). Unlike Webb & Dimmit County samples, a correlation between redox-sensitive elements was not observed in the evaporite-rich Maverick County groundwater samples. Further comparatively higher NO_3^- concentrations in Maverick County pointed towards relatively more oxidizing conditions and potential anthropogenic influx of NO_3^- (i.e., N-fertilizer-rich agricultural runoff) in the aquifer. Interestingly, these samples contained on average 4 mg/L of DOC which is more than ~2 mg/L in Webb & Dimmit County samples. The optical properties of DOM in these samples also revealed the presence of fresh, labile OM indicated by higher intensities of freshness index (β:α), biological index (BIX), and peak T values (Fig. 5, Table 2), which would further support influx from surface-derived organic matter such as agricultural runoff. Despite higher DOC concentrations, the redox conditions in this aquifer appear to be oxidizing. This would imply that the available electron donor (DOC) is not being utilized by the microorganisms. One of the plausible causes could be the high salinity of this groundwater may inhibit the microbial processes (Servais et al., 2019; Yannarell and Paerl, 2007). Alternatively, higher NO_3^- remains in this groundwater type may indicate restricted NO_3^--reducing microbial processes under high salinity in the aquifer (AbuBakr, 2020; Dinçer and Kargi, 2001; Rivett et al., 2008; Rysgaard Soren. et al., 1999).

The groundwater samples from Kinney County represented predominant carbonate dissolution in a typical karst hydrogeological setting. Based on the PCA results, these samples were grouped along negative PC1 and showed a lower association with most of the redox-sensitive trace elements (Fig. 6). Except for the highest As concentrations (although below the MCL) compared to the groundwater from other counties, these samples exhibit lower trace element concentrations as well as very low DOC concentrations (Fig. 3). The mobilization of Fe and Mn is commonly driven by the microbially mediated reductive dissolution of Fe/Mn-oxyhydroxides coupled with the degradation of DOM under reducing conditions (Bhattacharya et al., 1997; Nickson et al., 1998; Pathak et al., 2022b, 2022c; Zheng et al., 2004). The lowest concentrations of Fe and Mn were found in these samples which indicated the oxidizing conditions in the aquifer that are typical in karst hydrogeological settings. The DOM in these samples appeared to be moderately humified, aromatic, and containing less labile organic matter necessary for microbial respiration. This finding is consistent with typical karst aquifers where recharge is faster and shorter reaction time for the humification of the organic matter carried by the water (Lechleitner et al., 2017; Simon et al., 2010). Unlike an alluvial aquifer where reducing conditions can be prevalent, and the sediments contain significant proportions of redox-sensitive trace elements like Fe, and Mn (oxides and hydroxides) along with other trace elements and metalloids, a karst aquifer is predominantly composed of carbonate rock that typically do not incorporate higher concentrations of redox-sensitive trace elements and metalloids. Therefore, any exceptionally high concentrations of heavy metals in karst aquifer water can be easily interpreted as anthropogenic contamination. In our samples, no such contamination is apparent.

5.3. Distribution of light and heavy REEs in groundwater

All groundwater samples in the present study irrespective of the characteristic aquifer types showed HREE enrichment (Fig. 4a) which pointed towards either the sequestration of LREE onto the aquifer sediments i.e., commonly in Fe/Mn oxy-hydroxide phases (Liu et al., 2016), or due to the formation of stronger carbonate aqueous complexes of HREE inhibiting their adsorption onto sediments (Johannesson et al., 1996, 1999).

The use of Ce anomalies is employed to understand the aquifer redox state controlling the distribution of dissolved solutes (Bau and Dulski, 1996; Braun et al., 1990; De Baar H. J. W. et al., 1988; Dia et al., 2000;

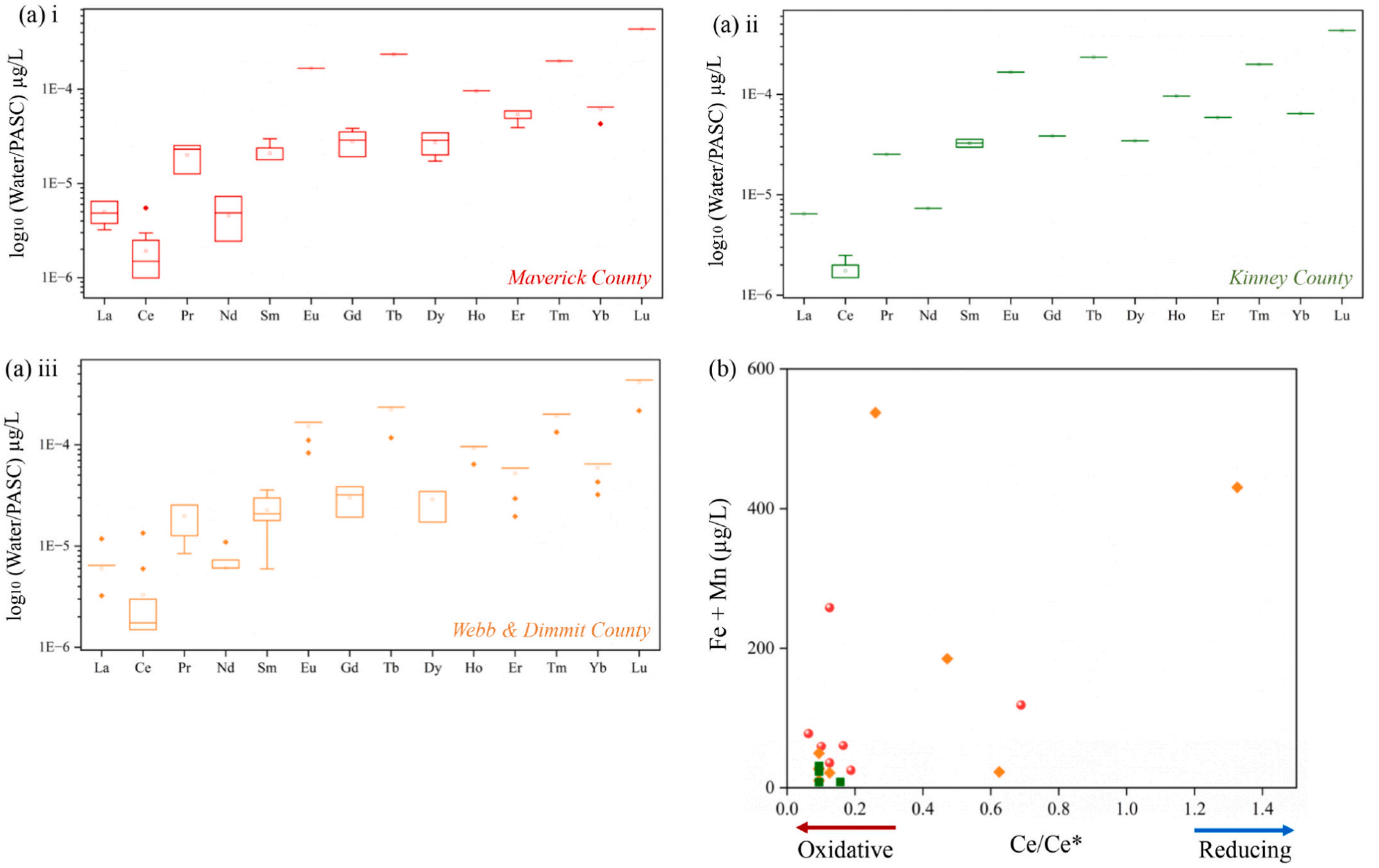


Fig. 4. a) Distribution of shale normalized LREE and HREE in groundwater samples from representative counties (a(i), a(ii) and a(iii)) within a section of the US-Mexico border in Texas, and b) Correlation between Ce/Ce* and redox-sensitive trace element (Fe + Mn) concentrations in groundwater showing most samples representing oxidizing conditions within the aquifer.

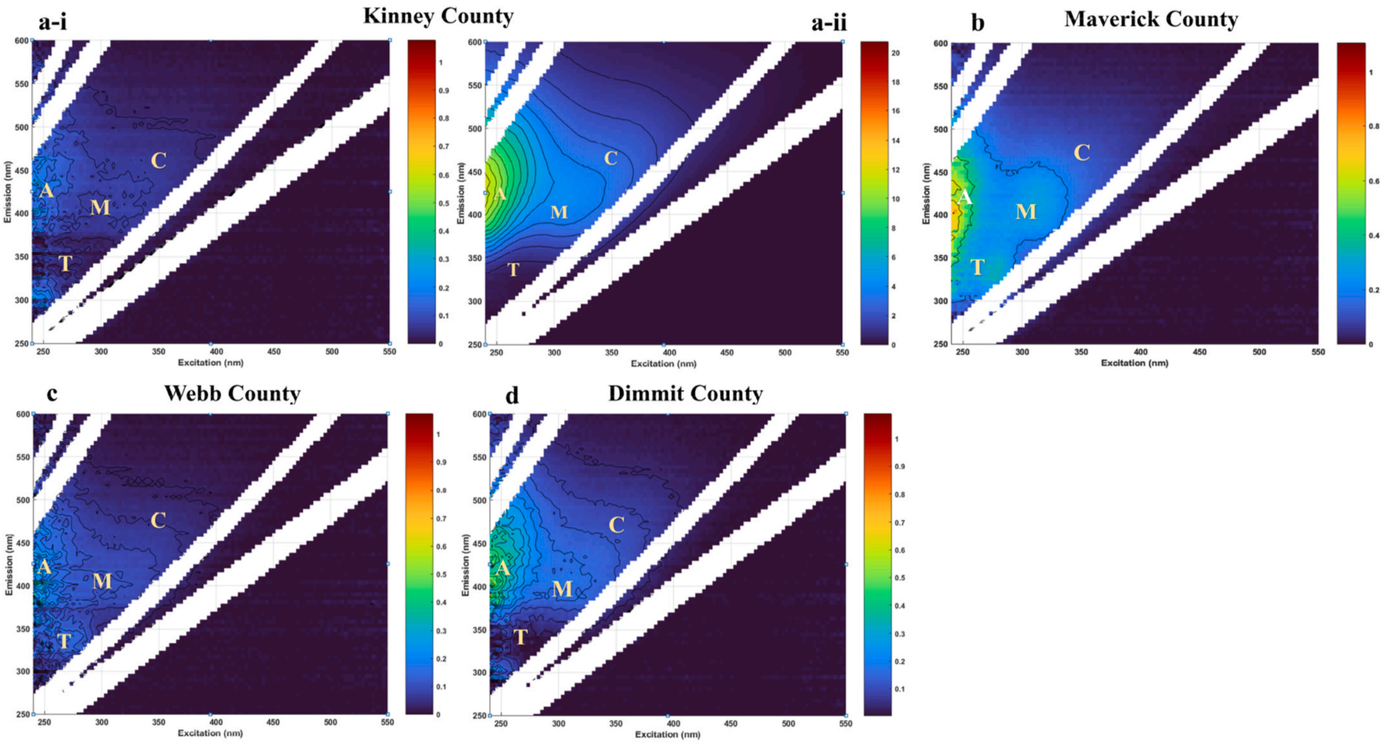


Fig. 5. Representative excitation-emission matrices (EEM) after 1st and 2nd order Rayleigh and Raman scatter correction following (Bahram et al., 2007) from groundwater sample categories; a-i, a-ii) Kinney County, b) Maverick County, c-d) Webb & Dimmit County.

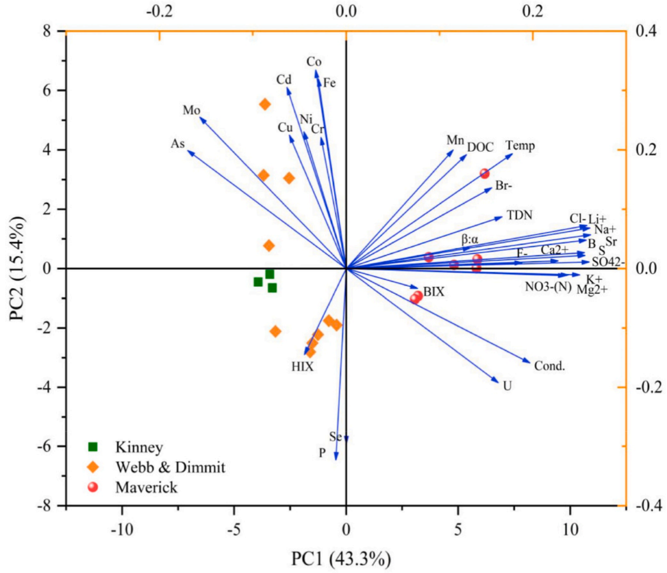


Fig. 6. Graph showing Principal Component Analysis (loadings plot and score plot) depicts the relationships of the chemical and organic constituents in groundwater samples among representative counties.

Liu et al., 2016). Ce(III) is commonly partially scavenged onto the aquifer sediment (rich in Fe/Mn oxy-hydroxide phases) by being converted into Ce(IV) and/or reprecipitation as cerianite (CeO_2) under oxic conditions (Bau, 1999; Braun et al., 1990; Dia et al., 2000), which results in a negative Ce anomaly in the water. Due to the sensitivity of Ce to redox transformations, the shale-normalized Ce anomaly (Ce/Ce*) (Bau and Dulski, 1996) is used as an indirect indicator of the aquifer redox state (Bau, 1999; Braun et al., 1990; Dia et al., 2000; Liu et al., 2016). The high positive Ce anomaly (mean $Ce/Ce^* = 0.35$) was evident in the alluvial aquifer of Webb & Dimmit County, which may indicate a prominent reducing condition in the aquifer (Fig. 4a and b). However, low positive Ce anomaly evident in the majority of Kinney and Maverick County groundwater samples (mean $Ce/Ce^* = 0.11$ and 0.13 respectively) possibly suggested an oxic or sub-oxic condition in the respective aquifer. However, it is important to mention here that accurate determination of the aquifer redox state is challenging and requires multi-level sampling together with the determination of Eh/ORP of the water in the field. Such parameters are lacking in this study which defines the limitation of the present interpretations in terms of assessing the redox state of the aquifer. However, based on the abundance of oxyanions, redox-sensitive trace elements, and signature of Ce anomaly, we tentatively assess the redox condition of the aquifer types in this study which is subject to further verification in future studies.

It is commonly observed that under low pH and oxic conditions in the aquifer, a higher amount of REE is released into the groundwater (Gosselin et al., 1992; Leybourne et al., 2000; Liu et al., 2016). However, in the present study, total REE abundance in the groundwater samples showed less significant spatial variations (Table S4) with no significant correlation with the pH (Fig. S4). Further, the lower abundance of (Fe + Mn) and low positive Ce anomaly in a karst aquifer (Kinney County) water compared to the higher abundance of (Fe + Mn) and high positive Ce anomaly in the alluvial aquifer (Webb & Dimmit County) water further strengthen our interpretation of respective aquifer redox states (Fig. 4b). Additionally a few contrasting higher abundances of (Fe + Mn) in the evaporite-rich aquifer (Maverick County) water irrespective of the prevailing oxidative conditions (evident from low positive Ce/Ce*) may potentially point towards anthropogenic inputs to the aquifer.

5.4. *Sustainability of transboundary aquifers along the US-Mexico border in Texas*

Providing sufficient and safe drinking water to the residents of both nations residing along the US-Mexico border in Texas is a critical challenge in the context of the fast-growing economy of the state and the consequences of global climate change. The sustainability of freshwater resources in fast-growing border regions relies on high-resolution frequent monitoring of the water quality over spatio-temporal intervals, potential risk assessment, and adopting suitable management/mitigation strategies immediately. Many studies have highlighted the need for a comprehensive international groundwater policy for the protection of these transboundary aquifers and the groundwater therein (Dunlap, 2006; Hall and Rogers, 2004; Hardberger, 2004; Mahlknecht et al., 2023; Milanes, 2020; Tapia-Villaseñor and Megdal, 2021). Despite this need, very few studies (Islam, 2023; Sanchez et al., 2016) have carried out detailed hydrogeochemical investigations of these transboundary aquifers. Chemical characterization of groundwater in US aquifers including those in Texas (McMahon et al., 2016; Stanton et al., 2017) provides valuable data, however, the privately owned wells by the residents of border counties largely remain outside of the major monitoring programs of the Federal government. Therefore, it is essential to understand geochemical and anthropogenic processes that control the short- and long-term quality of these freshwater resources in the border region. The present study investigates in detail (using multi-proxy) the groundwater quality from privately owned wells within a section of the border counties of Texas which is lacking till date. Present database provides insights into major ion chemistry, trace elements of human health concerns, distribution of REEs, and natural dissolved organic matter chemical characteristics in the groundwater. In terms of inorganic contaminants, the present database documents overall safe freshwater resources for the border residents in Kinney, Webb & Dimmit counties. However this study reveals a potential concern about contaminant mobilization possibility in the groundwater of Maverick County in the near future considering the characteristics of DOM and Sr abundances > MCL. Although this data explains many underlying processes that control the groundwater quality in the study region, it also highlights the need for further analyses to better understand the role of anthropogenic activities such as the mixing of agricultural runoff and wastewater discharge, oilfield brine disposal on the groundwater quality of transboundary aquifers in this fast-growing region along the US-Mexico border. Climate change impacts (i.e., increasing temperatures and frequent drought episodes) in the southern and southwestern US may further add to the broad implications of this study which should be a matter of future research interest. The present study is limited to representative groundwater sampling over a few transboundary aquifers along a part of the US-Mexico border and based on one time monitoring. However, the continuation of long-term monitoring studies with broadened sampling along the border counties is highly recommended to precisely predict the future vulnerability of groundwater quality to climate change impact.

6. Conclusion

In a rapidly growing region along the US-Mexico border in Texas, groundwater availability and security is a critical issue for sustainable development in both countries. The findings of this study provide the baseline water quality data that the residents of *Colonias* use as a major source of drinking. Detailed geochemical analysis of groundwater from private wells of *Colonias* residents revealed that the groundwater is typically sourced from evaporite-rich, karst, and alluvial aquifer deposits, and the water chemistry is mainly influenced by the water-rock interactions in the aquifer and isolated specific cases by potential anthropogenic inputs. The concentration of trace toxic elements was below the safe limits in most of the groundwaters of the representative counties (Kinney, Webb & Dimmit) monitored in this study which implies overall safer drinking water resources for the *colonias*. However, the concentrations of strontium (Sr) were found to be elevated in evaporite dissolution-affected groundwater of Maverick County which may eventually drive a health concern in the near future. Although Sr is not directly considered as a contaminant in water, long term consumption of Sr rich drinking water may impact on the bone structure and its functionality specially for the infants by slowly partitioning with bone Ca. Therefore further detailed monitoring studies with immediate mitigation strategies need to applied in the Maverick County groundwater. While the distribution of rare earth elements (REEs) across all aquifers did not vary significantly, its relationship with redox-sensitive elements like Fe and Mn showed that except for a few samples from Webb & Dimmit Counties, most groundwater samples were documented oxidizing pointing towards minimal contamination with toxic trace elements. The dissolved organic matter showed a distinct signature with strong humic-like fluorescence in Kinney County representing fresh groundwater in Karst aquifer as well as in Webb & Dimmit Counties representing groundwater from alluvial aquifer deposits, whereas relatively fresh and labile protein-like fluorescence signatures in the Maverick County with brackish groundwater. The findings of this study provide important insights for the better management of groundwater resources across the US-Mexico border and indicate that routine monitoring of these wells will be beneficial to assess future changes in the groundwater quality in this region.

CRediT authorship contribution statement

Pousali Pathak: Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Ruben Olivares:** Visualization, Methodology, Investigation, Conceptualization. **Thomas S. Varner:** Writing – review & editing, Formal analysis. **Harshad V. Kulkarni:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Guadalupe Carmona:** Writing – review & editing. **Cynthia Lima:** Writing – review & editing. **Steven Hollan:** Methodology. **Saugata Datta:** Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsd.2024.101377.

Data availability

Data will be made available on request.

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