Chapter 5

Hydrochemistry, Salinity Distribution, and Trace Constituents: Implications for Salinity Sources, Geochemical Evolution, and Flow Systems Characterization, Gulf Coast Aquifer, Texas

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Introduction

Groundwater is a valuable resource to the fast growing communities along the Texas Gulf Coast. Recurrent drought conditions, historical and current overpumping of the aquifer in excess of natural replenishment through recharge, and limited availability place an ever increasing demand on this resource. Over 1.1 million acre-feet of groundwater are annually used from the Gulf Coast aquifer in Texas. The Gulf Coast aquifer extends over 430 miles from the Texas-Louisiana border in the northeast to Texas-Mexico border in the south. The Gulf Coast aquifer is comprised of fluvial-deltaic sediments that thin in the outcrop areas and progressively thicken to several thousand feet near the coast. Repeated sea-level changes and natural subsidence of the basin due to sediment loading produced a complex set of discontinuous bodies of sand, silt, clay, and gravel in the Gulf Coast. Lateral and vertical discontinuity and interfingering of these sand and clay bodies compartmentalize the flow systems with potential for little hydraulic interconnection between them. Furthermore, numerous growth faults that occur parallel to the coast exert additional complexity to the groundwater flow system. Significant quantities of groundwater occur in the Gulf Coast aquifer in sections where sands are dominant. However, some of this resource is not directly usable due to its moderate to high salinity. In most of the outcrop, groundwater is generally fresh. Groundwater increases in salinity at depth and along flow paths towards the coast. Groundwater salinity also increases from the northern humid areas to the southern semi-tropical and semi-arid areas of the Texas Gulf Coast.

Groundwater pumping in the Gulf Coast aquifer caused water-level declines of more than 350 feet in some areas, produced compaction of clay and shale beds contained within the aquifer materials, and subsequently caused land-surface subsidence in or near the cones of depression. Salt domes that pierce through the aquifer at different depths affect groundwater salinity in their vicinity. In addition, formation brines from the deeper subsurface may flow upward along faults or due to an increase in hydraulic pressure gradients affecting groundwater composition in

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shallow aquifers. A lowering of the hydraulic gradient due to over-pumping in areas near the coast may locally cause saltwater intrusion. In this paper, we will (1) describe spatial and depth distributions of salinity; (2) identify sources and geochemical processes that gave rise to this salinity; (3) describe spatial and depth distributions of arsenic and identify its origin; (4) describe spatial and depth distributions of alpha, beta, and radon-222 activities and identify their origin; and (5) evaluate changes in groundwater salinity with water-level declines in or near the cones of depression. We discuss each of the above topics under separate sections.

Stratigraphy and Mineralogy

The Gulf Coast aquifer in Texas consists of five hydrostratigraphic units (from oldest to youngest): (1) the Catahoula Tuff or Sandstone, (2) the Jasper aquifer, (3) the Burkeville confining system, (4) the Evangeline aquifer, and (5) the Chicot aquifer (Baker, 1979). The Catahoula Tuff or Sandstone mainly consists of pyroclastic and tuffaceous sandstone; the Jasper aquifer mainly contains the Fleming and the Oakville formations, consisting of interbedded sand and clay; the Burkeville confining system consists mainly of silt and clay; the Evangeline aquifer has a high sand-clay ratio and contains sand beds tens of feet thick; and the Chicot aquifer contains sand, clay, and gravel (Baker, 1979).

Sediments of the Gulf Coast aquifer were deposited in a fluvial-deltaic or shallow marine environment (Sellards and others, 1932). Repeated sea-level transgression and regression and basin subsidence caused development of cyclic sedimentary deposits composed of discontinuous sand, silt, clay, and gravel (Sellards and others, 1932; Kasmarek and Robinson, 2004). Most of the sediments of the Gulf Coast aquifer thicken towards the Gulf of Mexico. Faults that remained active during sedimentation (growth faults) contributed to additional sediment thickness over short lateral distances (Verbeek and others, 1979). Kreitler and others (1977) observed appreciable vertical displacement and abrupt thickening of the Alta Loma Sand, placed at the base of the Chicot aquifer in Harris and Galveston counties, which they attributed to faults. They suggested that the fault zone that occurs between Harris and Galveston counties acts as a partial hydrologic barrier separating the two partially independent flow systems and controlling groundwater composition between these two counties. In addition, complexity of the Gulf Coast aquifer is further advanced by numerous clay layers less than six feet thick contained within the water-bearing units of the sand beds that retard vertical movement locally and may provide different hydraulic heads to each sand bed (Gabrysch, 1984).

Numerous salt domes occur in the Gulf Coast aquifer (Beckman and Williamson, 1990), some of which pierce through the shallow aquifers and reach near the land surface (Hamlin, *this volume*). Morton and others (1983) reported that salt domes are abundant along the northern part and nearly absent along the southern part of the Texas Gulf Coast.

In order to explain geochemical conditions for paragenesis of diagenetic minerals in the Oakville Formation sand, Galloway (1982) postulated three hydrogeologic regimes: (1) the meteoric regime that surrounds the basin margins where surface water infiltrates into the permeable strata and moves in response to gravitation heads; (2) the elisian or compactional regime that expels upward to outward connate water contained within the fine-grained sediments caused by compressible or lithostatic stresses; and (3) the abyssal regime in the deep core of the basin fill

that provides significant volumes of water due to permeability reduction by compaction, cementation, and mineral dehydration reactions. Of these three regimes, the meteoric regime is most dynamic, with several geochemical trends observed along flow paths: bicarbonate increases moderately, chloride and total dissolved solids increase markedly, sodium to calcium ratios increase with a reduction in calcium concentrations, pH decreases gradually, and Eh commonly decreases abruptly. Galloway (1982) suggested that uranium mineralization in the Oakville Formation and underlying Catahoula aquifers was caused by migration of compactional fluids along deep-seated growth faults.

Mineralogical compositions of the Miocene-Pliocene sandstones that form the Gulf Coast aquifers in Texas are poorly known. However, numerous investigations have been carried out to determine mineralogical compositions of the Oligocene sandstones from the Frio and the Catahoula formations (Loucks and others, 1979; Galloway, 1982). Quartz percentage in these sandstones increases from 20 to 60 percent at the southern part of the Texas Gulf Coast to 50 to 85 percent at the northern part of the Texas Gulf Coast (Lindquist, 1977; Loucks and others, 1981). Feldspar decreases from 20 to 50 percent to 10 to 30 percent in the same direction. Sandstones along the lower coast are rich in volcanic and carbonate rocks occasionally containing caliche fragments (Lindquist, 1977). Carbonate rock fragments decrease and metamorphic rock fragments increase towards the middle coast. Volcanic rocks dominate again in the upper coast (Lindquist, 1977). McBride and others (1968) suggest that the lower Catahoula Formation in northern Fayette County contains mainly tuff, with volcanic conglomerate and sandstones dominant in the mid-section. Bentonite and alteration products of volcanic glass (zeolite, calcium-montmorrilonite, and chalcedony) are widespread throughout the formation. Caliches are common near the surface, which suggests that the land surface was occasionally exposed to soil forming processes (McBride and others, 1968). Hoel (1982) observed that the Goliad Formation is genetically and compositionally similar to the Catahoula and the Oakville sandstones and contains a large proportion of orthoclase and plagioclase feldspars and volcanic rock fragments, particularly south of the San Patricio-Refugio county line. Sellards and others (1932) report that the Goliad Sand in South Texas is cemented by caliche containing more than 30 percent calcium carbonate. Gabrysch and Bonnet (1975) analyzed the mineralogical composition of the clay beds and observed montmorillonite to be the main constituent of the clay with minor amounts of illite, chlorite, and kaolinite.
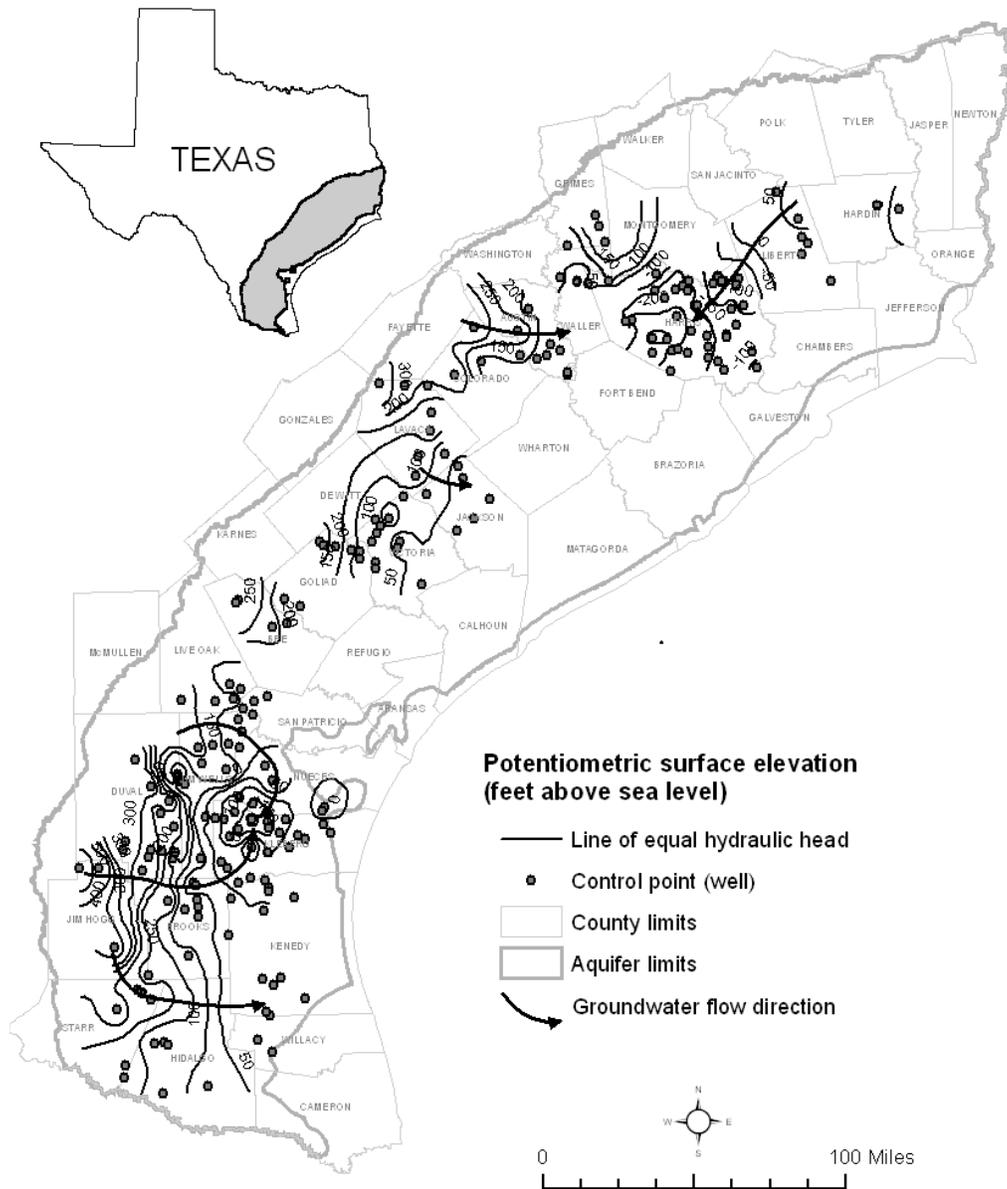
Water Levels and Regional Groundwater Flow

A water table is generally a subdued replica of the land surface. Under topographic highs where recharge occurs, water levels occur at shallow depths under unconfined conditions. Recharge waters in the outcrop are typically fresh and reflect composition of the rainwater, except in arid and semi-arid areas, where rainwater dissolves salts from the soils and percolates to the groundwater in the outcrop. As the aquifer dips beneath lower permeability sediments, groundwater becomes confined under increasing hydrostatic pressure due to the presence of impermeable fine-grained clays and silts. In topographic lows (discharge areas), groundwater flow is directed upward as a result of artesian pressure exceeding local hydrostatic pressure. Groundwater becomes more saline in the deeper subsurface and in discharge areas due to its long residence time and continued reaction with the aquifer minerals.

Water-level maps for the Chicot, Evangeline, and the Jasper aquifers show that regional groundwater flow is directed east towards the Gulf of Mexico (Figures 5-1, 5-2, and 5-3). We note that groundwater pumping has caused significant water-level decline in parts of the Gulf Coast aquifer (Figures 5-1 and 5-2). For example, water-level measurements from 2001 to 2005 show the presence of large cones of depression in Harris and Kleberg counties (Figure 5-2). Major cones of depression change regional groundwater flow direction wherein groundwater from the outcrop is diverted towards the center of the cone as opposed to allowing it to flow towards the Gulf of Mexico (Figures 5-1 and 5-2). Hydrographs of selected wells from areas
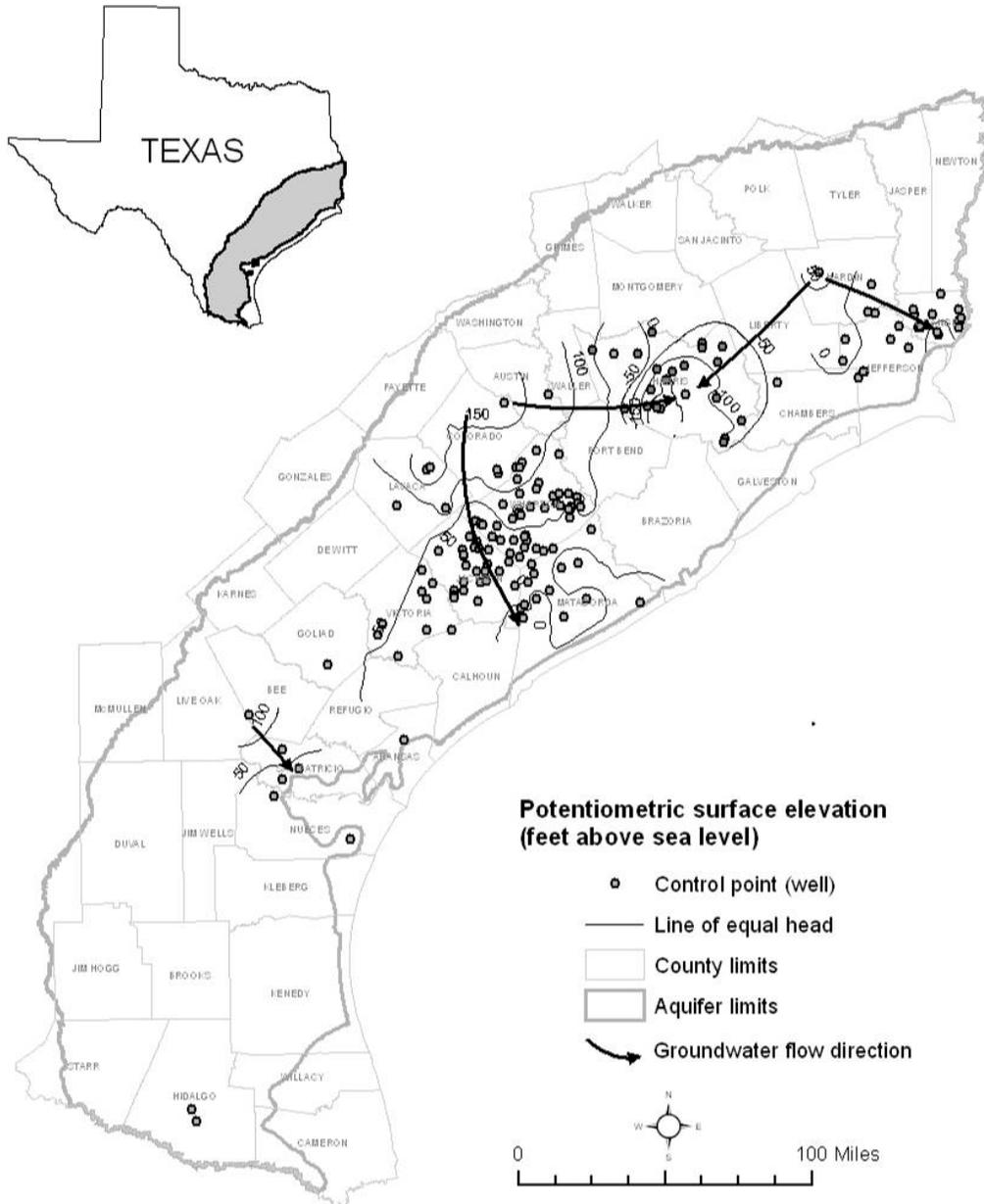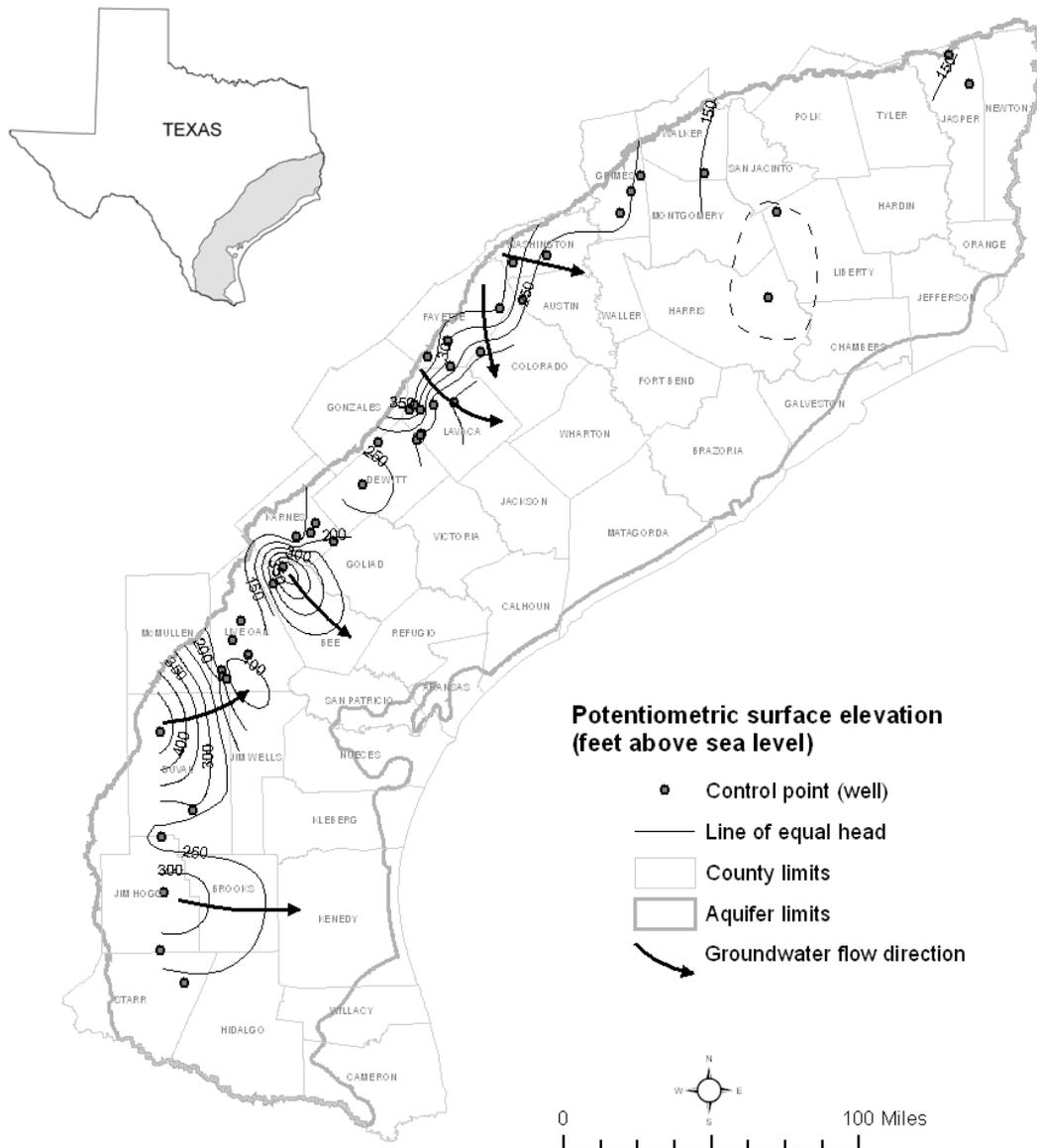

Figure 5-1. Water-level elevations and regional groundwater flow directions in the Chicot aquifer (includes water-level measurements from 2001 to 2005).

84

Figure 5-2. **Water-level elevations and regional groundwater flow directions in the Evangeline aquifer (includes water-level measurements from 2001 to 2005).**

where land-surface subsidence has occurred show that water levels in some of these wells have since recovered but with no significant rebounding of the land-surface (Kasmarek and Robinson, 2004). Kasmarek and Robinson (2004) reported that water levels in the aquifers had declined by as much as 350 feet by 1977 in the Houston area and caused subsequent land-surface subsidence. Land-surface subsidence in excess of ten feet was reported for Baytown and the Houston Ship Channel area in southwestern Harris County (Harris-Galveston Coastal Subsidence District, 1998). Land-surface subsides as pumping causes expulsion of water from the interbedded clay in sandstones and shale beds. Similarly, in Wharton and Jackson counties, water levels have

Figure 5-3. Water-level elevations and regional groundwater flow directions in the Jasper aquifer (includes water-level measurements from 2001 to 2005).

declined by more than 50 feet (Chowdhury and others, 2004). Farther south in Kleberg County, water levels have declined historically by as much as 200 feet (Shafer and Baker, 1973).

Groundwater Composition

Groundwater composition commonly retains unique chemical signatures of a flow system. These diagnostic signatures help define groundwater flow behavior as groundwater moves from the recharge areas in the outcrop, downward to the deeper subsurface, and upward to the discharge

areas near the coast. Differences in groundwater composition along flow paths help us interpret and verify flow systems, identify water sourced under various recharge conditions, and understand geochemical evolution of the water. Final groundwater composition ultimately depends on a multitude of factors that may include hydraulic characteristics and mineralogy of the aquifer materials, relative rates of mineral dissolution and precipitation reactions, cation exchanges, mixing of waters of various origins, redox reactions, and groundwater residence times in the aquifer.

Major Elements

Major elements consisting of calcium, sodium, potassium, magnesium, bicarbonate, chloride, and sulfate typically comprise more than ninety-five percent of the groundwater composition. These elements are non-conservative as they participate in and are subject to changes in concentrations due to geochemical reactions. Major elements in groundwater are derived from solute concentrations in the precipitation, water-rock interactions in the soil zone above the water table, and mineral reactions in the saturated zone below the water table. Progress or extent of chemical reactions along flow paths can therefore be identified by observing changes in absolute concentrations or relative element ratios from their initial compositions in the outcrop. In most cases, groundwater movement down flow paths follows a sequence of geochemical reactions that may provide information on chemical maturity and relative residence times of the ground water (Herczeg and Edmunds, 2000). Molar ratios of several elements including Na/Cl, SO_4/Cl, Mg/Ca, K/Na, Ca/Na, and Ca+Mg/SO_4 ratios are used to determine geochemical evolution of groundwater (Richter and Kreitler, 1991; Herczeg and Edmunds, 2000; Cartwright and others, 2004).

Methods

We analyzed chemical compositions of about six hundred groundwater samples from the Texas Water Development Board's (TWDB) groundwater database. For this study, we considered samples collected during 2001 through 2005. This time period was chosen because extensive sampling of the Gulf Coast aquifer was undertaken during this period and this dataset should adequately represent current groundwater compositions in the Gulf Coast aquifer. However, adequate sample coverage was missing for Harris County during 2001 through 2005. Therefore, we included additional samples analyzed during 1997 to increase sample coverage for Harris County. All groundwater samples were analyzed by ion chromatography-mass spectrometry (ICP-MS) for major and trace elements at the Lower Colorado River Authority's Environmental Laboratory.

We described groundwater salinity based on total dissolved solids (TDS) concentration of the waters: fresh (less than 1,000 milligrams per liter [mg/l]), slightly saline (1,000 to 3,000 mg/l), moderately saline (3,000 to 10,000 mg/l), very saline (10,000 to 35,000 mg/l), and brine (greater than 35,000 mg/l) (Winslow and Kister, 1956). TDS represents the total amount of solids that remain in water after the sample is evaporated to dryness. Salinity essentially means the same as total dissolved solids. We plotted the major elements and their ratios for identifying geochemical processes and identify sources of salinity. We plotted groundwater compositions into Piper diagrams to group groundwater into distinct water types or chemical facies (Piper, 1944).

Results

Groundwater composition in the Gulf Coast aquifer in Texas is highly variable. Groundwater composition is generally fresh in the outcrop and becomes more saline near the coast. Of the six hundred samples that we analyzed, we observed that about seventy percent of the samples in the Chicot and the Evangeline aquifers and eighty-five percent of the samples in the Jasper aquifer have fresh water. Nearly all of the remaining samples are slightly saline (Table 5-1).

Table 5-1.   Water quality types in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Water quality (percent total)		
	Fresh	Slightly saline	Moderately saline
Chicot	72	26	2
Evangeline	70	28	2
Jasper	85	13	1

Groundwater is relatively more saline in the central and southern parts compared to the northern part of the Gulf Coast aquifer (Figures 5-4, 5-5, and 5-6).

In order to better understand geochemical processes that gave rise to groundwater salinity, we examined spatial distribution of the major elements across the Gulf Coast aquifer. Details on this distribution are presented elsewhere (Chowdhury and others, in prep.). We observed that bicarbonate concentrations generally increase along flow paths with an abrupt increase in their concentration along the coast in Matagorda and Brazoria counties (Figure 5-7). To the south, bicarbonate shows a decrease along flow paths in Kenedy and Cameron counties. Sulfate concentrations do not vary significantly along flowpaths, but higher concentrations of sulfate occur in the south than the northern part of the Gulf Coast aquifer (Figure 5-8). Sodium and chloride concentrations increase along flow paths, and their concentrations significantly increase in the southern part of the Gulf Coast aquifer (Figures 5-9 and 5-10).

We used molar ratios of Na/Cl to determine sources of Na ions and identify geochemical processes that affect Na concentrations. Halite contains Na and Cl in equal concentrations. Therefore, groundwater affected by halite dissolution should typically contain molar Na/Cl ratios equal to 1 unless the ratio is affected by cation exchange reactions. Molar Na/Cl ratios in sea water is about 0.85 and the ratio in deep-basin brines is less than 0.5 (Richter and Kreitler, 1991). In the Gulf Coast aquifer, we observe that the molar Na/Cl ratios range from 0.49 to 5.98 (1.77 ± 0.94), 0.4 to 10.95 (2.03 ± 1.57), and 0.6 to 41.94 (3.58 ± 5.48) for the Chicot, Evangeline, and Jasper aquifers, respectively. Molar ratios of Na/Cl increase from the shallower to the deeper aquifers which is probably caused by progressive cation exchanges and/or mixing of saline water from the deeper subsurface (Table 5-2). Variability in the Na/Cl ratios increases with depth, as reflected by increases in standard deviations from the Chicot to the Jasper aquifers. Spatial distributions of molar Na/Cl ratios indicate that several samples, particularly in the northern part of the Gulf Coast aquifer in the vicinity of the salt diapers, have molar Na/Cl ratios close to 1 (Figure 5-11). Most of the groundwater in the Gulf Coast aquifer has molar Na/Cl ratios that vary from 1 to 4 (Figure 5-11).
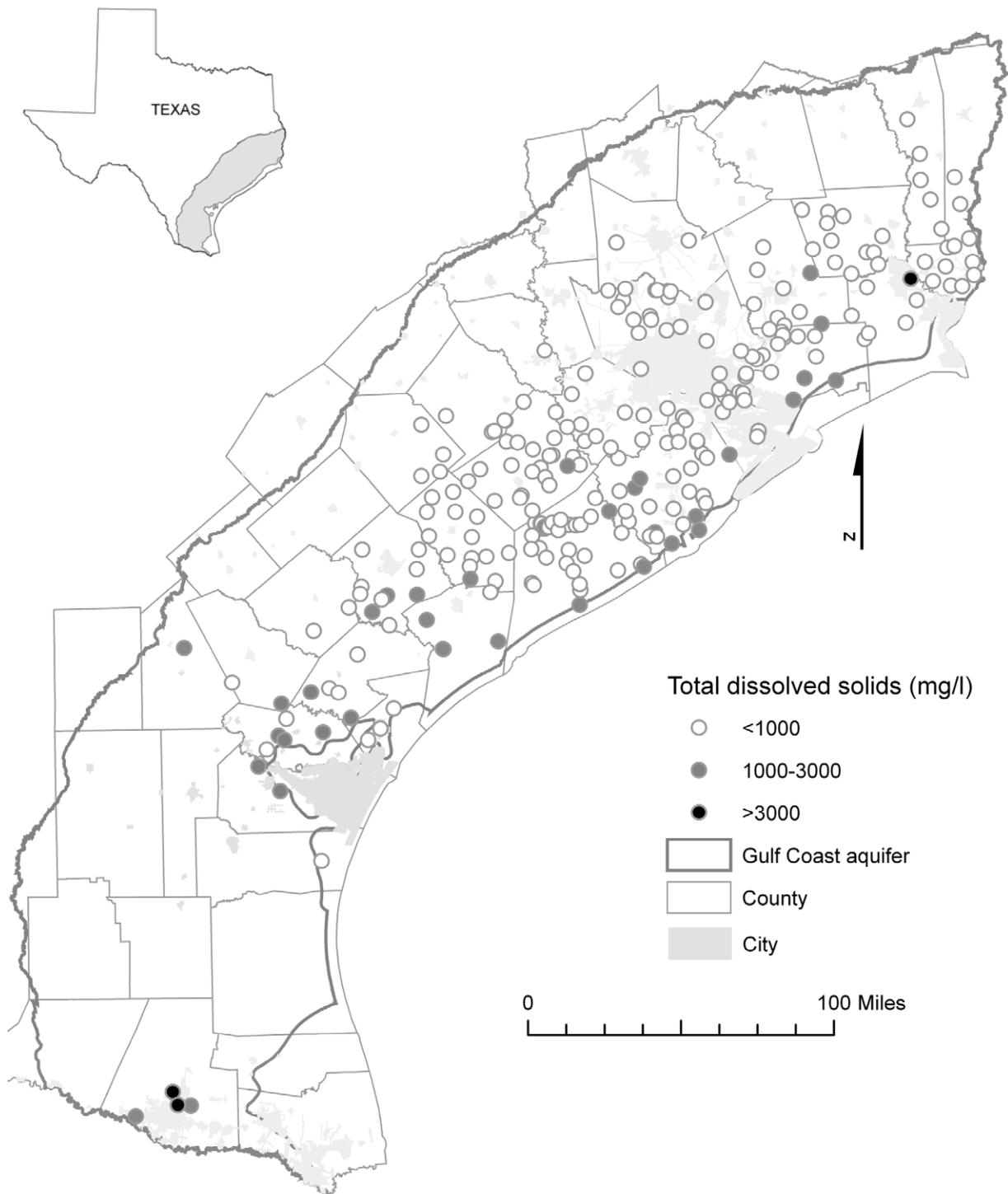
Figure 5-4. Distribution of total dissolved solids concentrations in the Chicot aquifer.
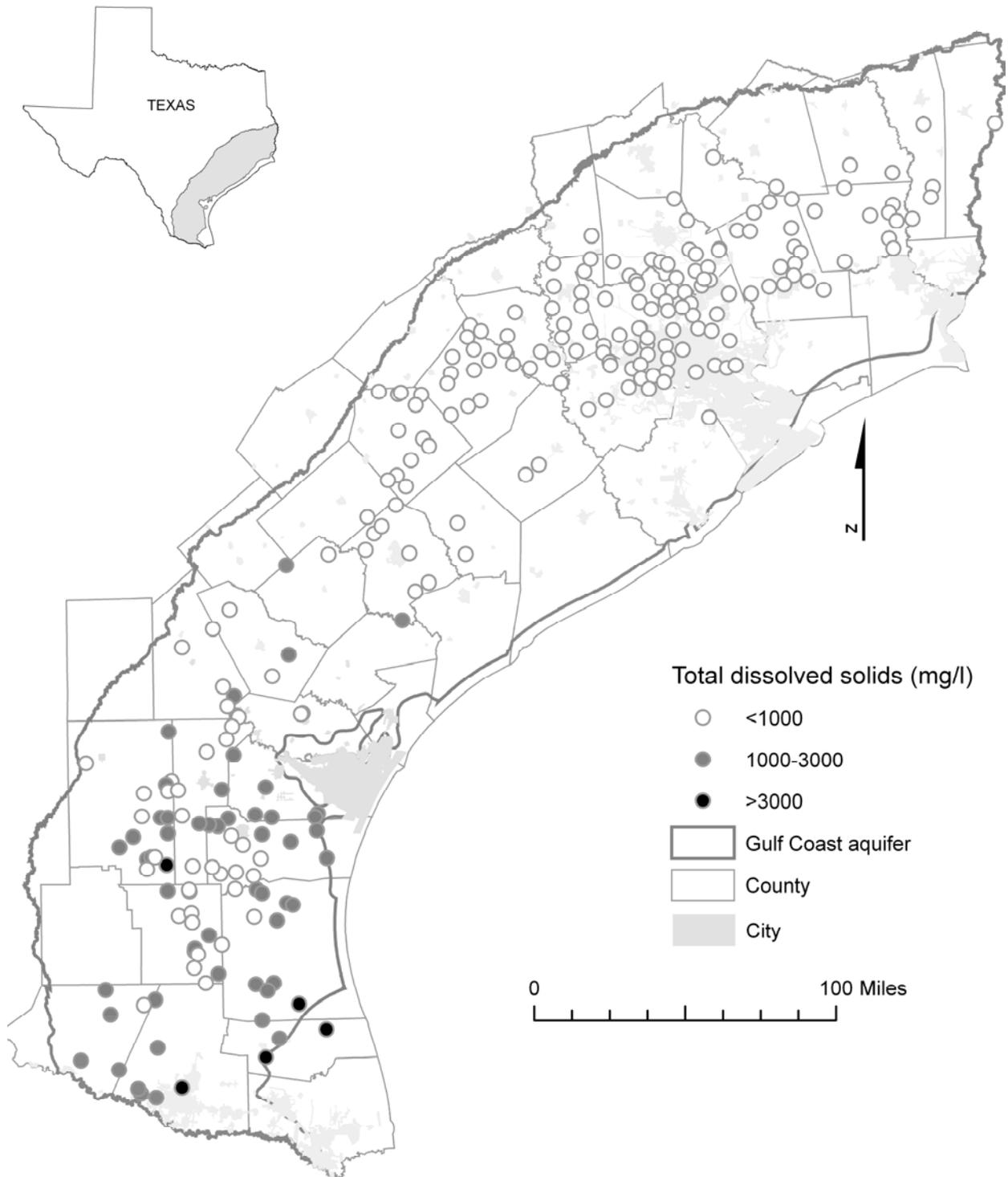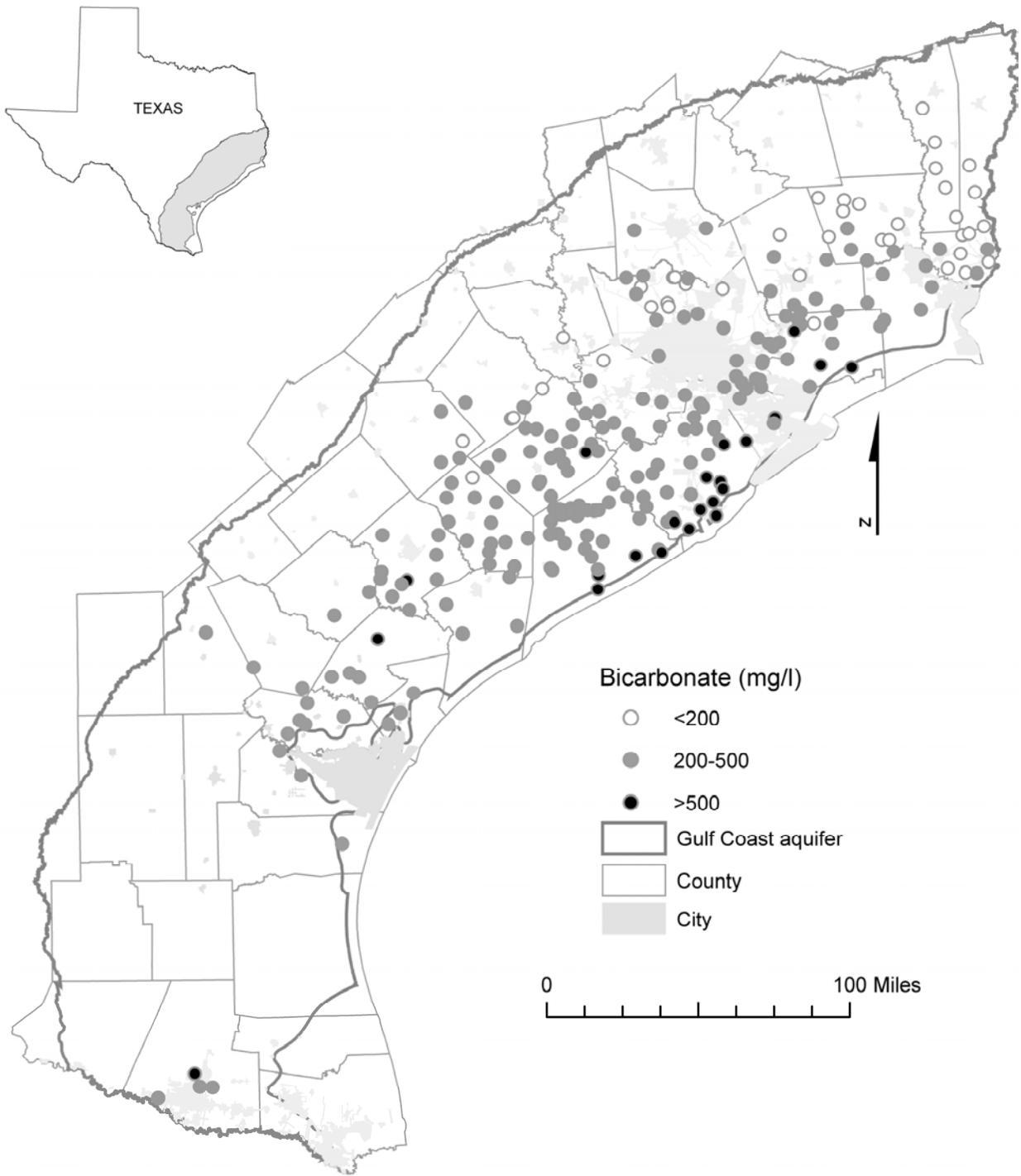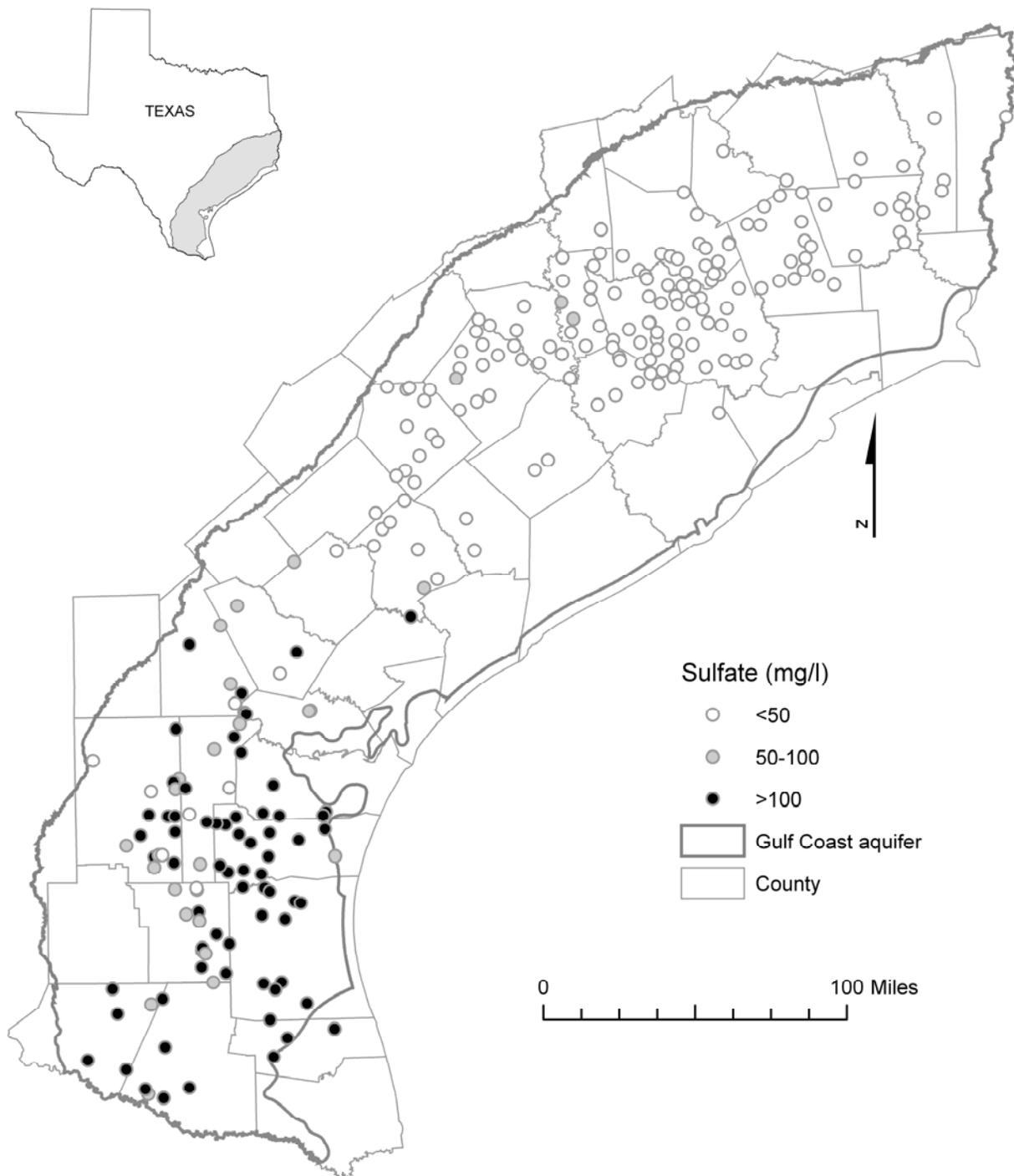
Figure 5-5. Distribution of total dissolved solids concentrations in the Evangeline aquifer.
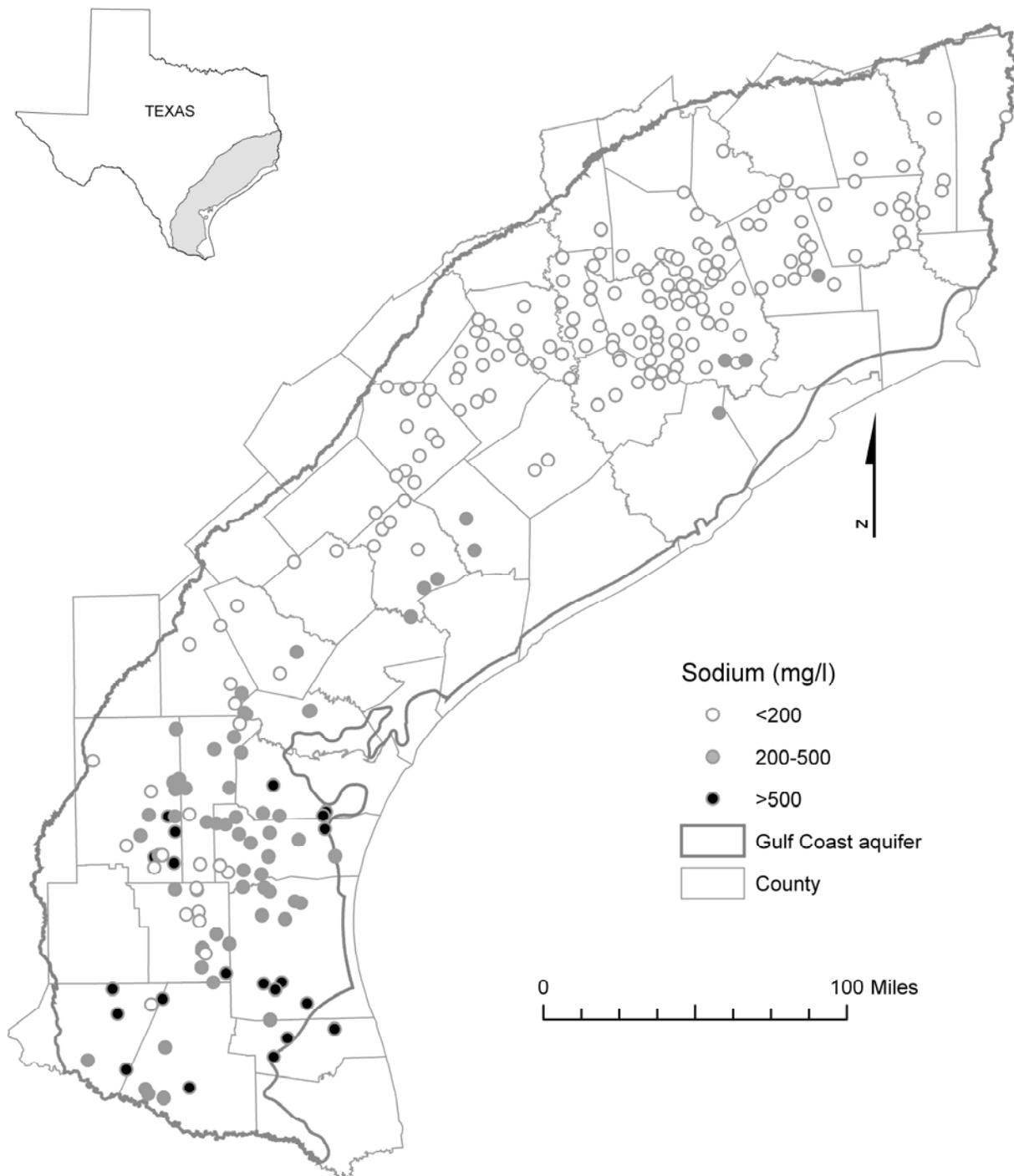
Figure 5-6. Distribution of total dissolved solids concentrations in the Jasper aquifer.

Figure 5-7. Distribution of bicarbonate concentrations in the Chicot aquifer.

TEXAS

Sulfate (mg/l)

○ <50

● 50-100

● >100

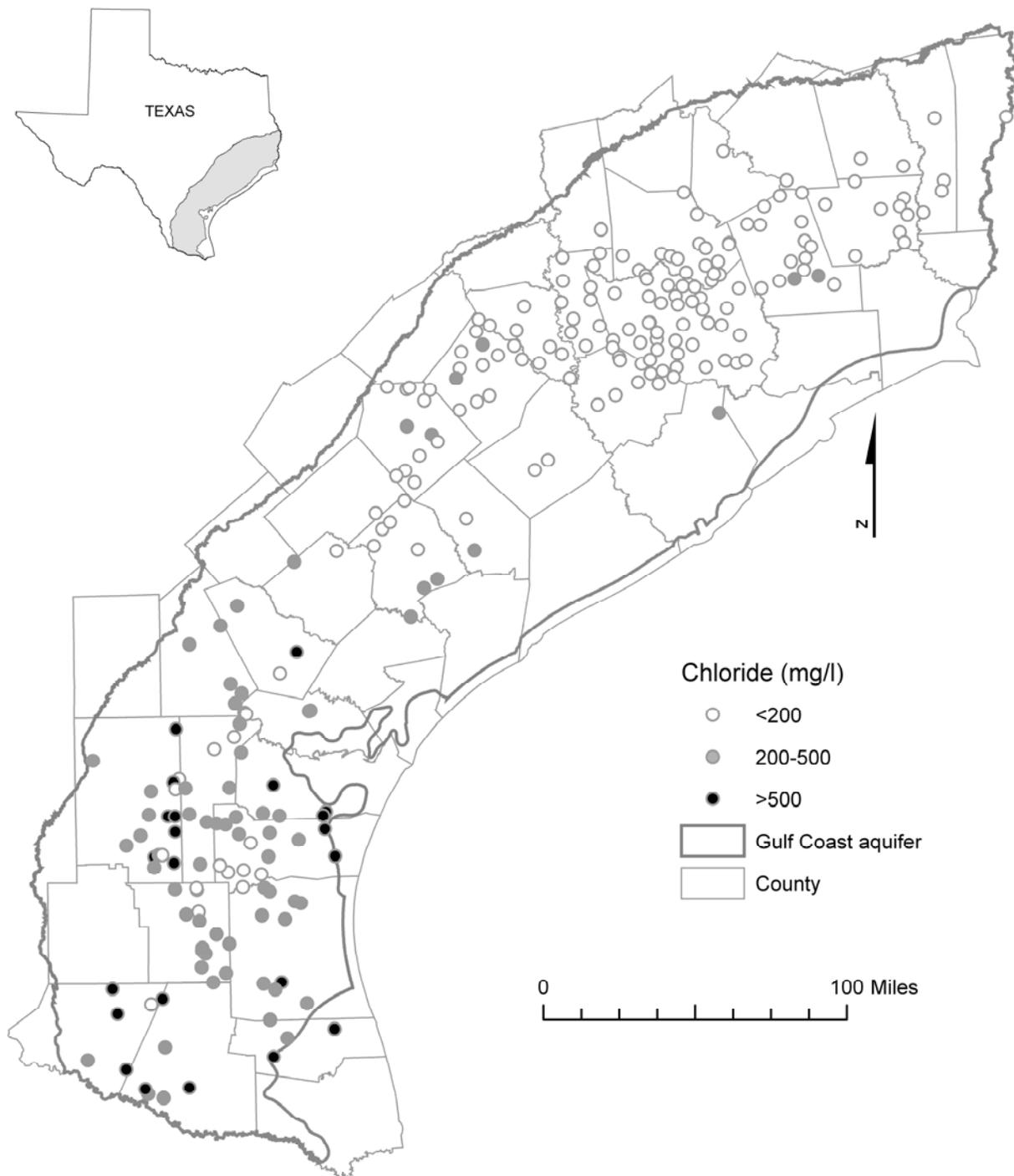☐ Gulf Coast aquifer

☐ County

0   100 Miles

Figure 5-8.   Distribution of sulfate concentrations in the Evangeline aquifer.

Figure 5-9. Distribution of sodium concentrations in the Evangeline aquifer.

94

Figure 5-10. Distribution of chloride concentrations in the Evangeline aquifer.

95

Table 5-2.   Concentrations of Na/Cl ratios in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Molar Na/Cl ratios				
	Range	Mean	Median	Standard deviation	Number of samples
Chicot	0.49 - 5.98	1.77	1.56	0.94	240
Evangeline	0.4 - 10.95	2.03	1.61	1.57	258
Jasper	0.6 - 41.94	3.58	2.23	5.48	98
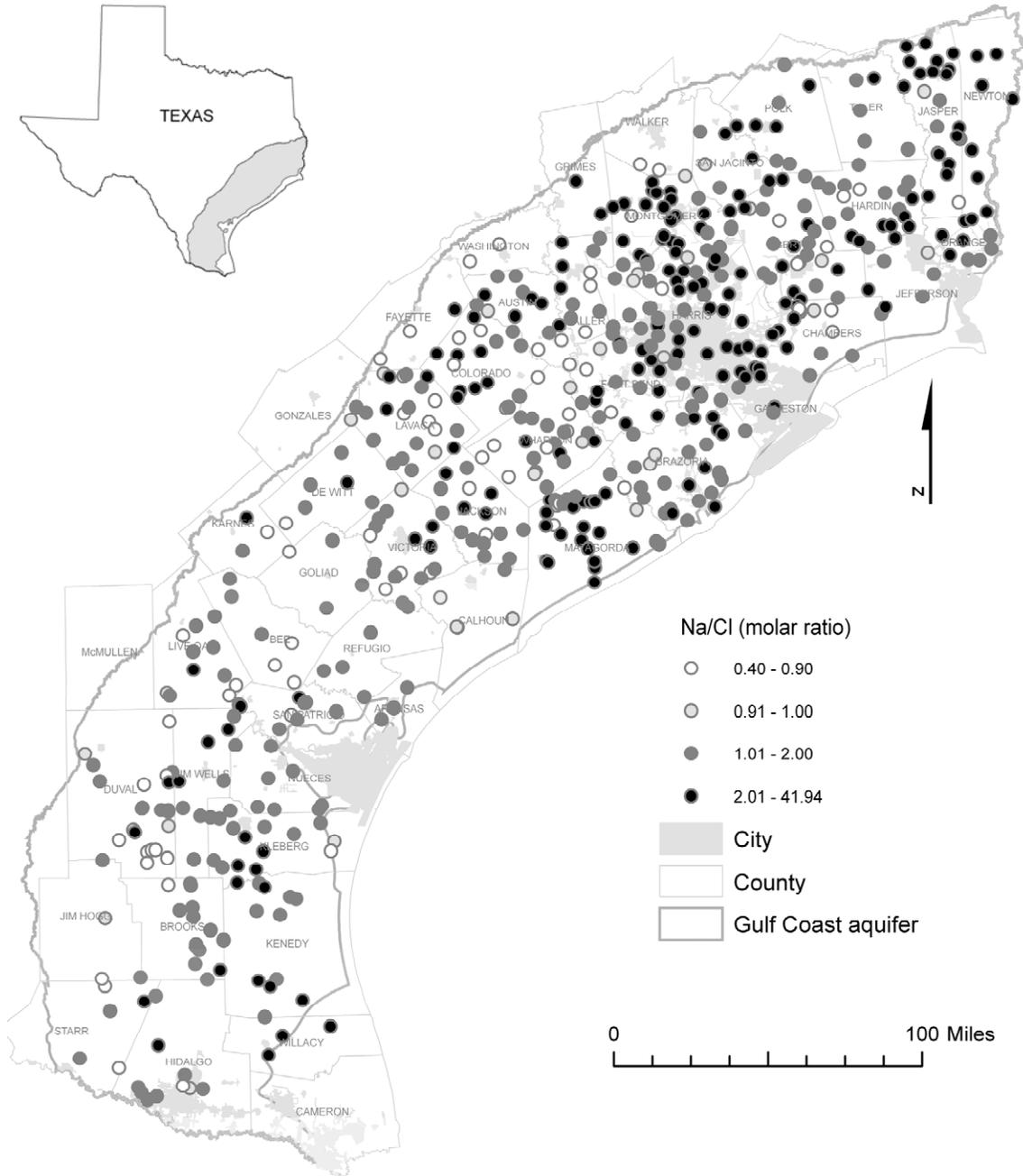
Figure 5-11. Distribution of Na/Cl molar ratios in the Gulf Coast aquifer of Texas.

96

We used Piper diagrams to group groundwater from the Chicot, Evangeline, and Jasper aquifers into distinct chemical types. We observed that the analyzed samples in the Gulf Coast aquifer are mainly composed of Ca-HCO_3, Ca-Na-HCO_3-Cl, and Na-HCO_3 type waters (Figure 5-12). Numerous samples fall along a straight line from the calcium to the sodium end of the cation triangle (Figure 5-9). Groundwater in the outcrop areas in the northern part are more commonly Ca-HCO_3 types that evolve into mixed Ca-Na-HCO_3-Cl water along regional flow paths and to Na-HCO_3 water in the discharge areas near the coast. Groundwater composition in the central and the southern parts of the Gulf Coast aquifer changes to Na-Cl-HCO_3 or Na-Cl-SO_4 water along regional flow paths (Figures, 5-7, 5-8, 5-9, and 5-10). Relatively more samples from the Evangeline aquifer have higher concentrations of sulfate, sodium, and chloride (Figure 5-12b).

We used cross-plots of various ions to identify their sources. Plots of sodium and bicarbonate and sodium and calcium for 17 groundwater samples from Harris and Galveston counties show a correlation coefficient of 0.82 between sodium and bicarbonate and a correlation coefficient of -0.66 between sodium and calcium (Figures 5-13a and 5-13b). Bivariate plots of Na and Cl show good correlation coefficients of 0.85 and 0.87 for the Chicot and Jasper aquifers, respectively, and a moderate correlation coefficient of 0.59 for the Evangeline aquifer (Figures 5-14b, 5-15b, and 5-16b). Plots of Na/Cl ratios versus Cl show a decrease in Na/Cl ratios at higher Cl concentrations in a small number of samples (Figures 5-14c, 5-15c, and 5-16c). Plots of excess sodium from sources other than halite (Na-Cl) and excess calcium and magnesium (Ca+Mg-$0.5HCO_3$-SO_4) from sources other than carbonate and gypsum show near perfect correlation coefficients ($r^2 = 0.95$, $r^2 = 0.98$, and $r^2 = 0.98$ for the Chicot, Evangeline, and Jasper aquifers, respectively; Figures 5-14d, 5-15d, and 5-16d).

Groundwater composition shows no trends in salinity changes with well depths (Figures 5-14a, 5-15a, and 5-16a). Many wells in the Chicot, Evangeline, and Jasper aquifers have groundwater compositions containing low dissolved solids (less than 300 mg/l) at depths of more than 2,000 feet.

Discussion

Salinity differences from the northern to the southern parts of the Gulf Coast aquifer are probably caused by several processes including recharge under different climatic conditions, variation in lithologic composition, ion-exchange reactions, saltwater intrusion, and retention of residual connate water. For example, annual average rainfall in the northern part of the Gulf Coast aquifer is about 56 inches, while in the central and the southern parts of the Gulf Coast aquifer annual rainfall gradually decreases to about 18 inches (Chowdhury and Mace, 2004). A higher evaporation rate in the central and southern parts of the aquifer, frequent occurrences of caliches, and salt accumulation in the soils further reduce potential for fresh rainwater infiltration into the groundwater. Therefore, it is no coincidence that the groundwater in the southern parts of the Gulf Coast aquifer has higher concentrations of sodium, chloride, and sulfate. In addition, differences in mineralogical compositions of the aquifer materials between the northern and the southern parts of the Gulf Coast contributed to varying groundwater composition. For example, sandstone compositions in the northern part are more commonly quartz arenite, while to the south, sandstone compositions are more likely arkosic and greywackes containing abundant feldspar and rock fragments. Varying chemical stability of the aquifer minerals will produce

(a)
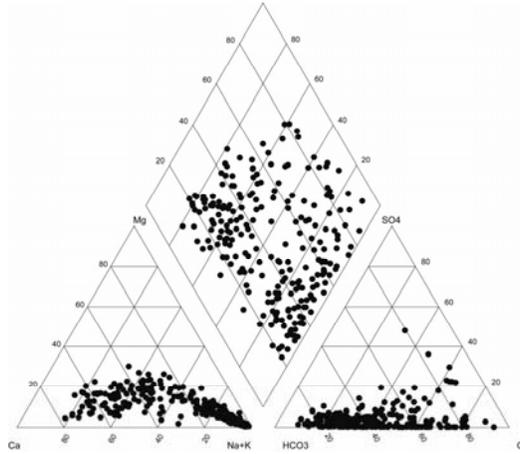
(b)
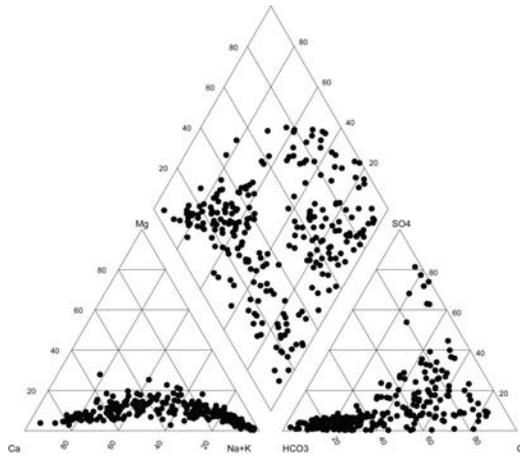
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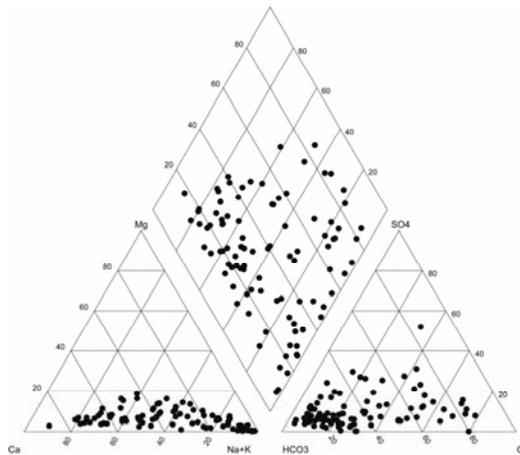
Figure 5-12. Piper diagrams of groundwater composition from the (a) Chicot, (b) Evangeline, and (c) Jasper aquifers.
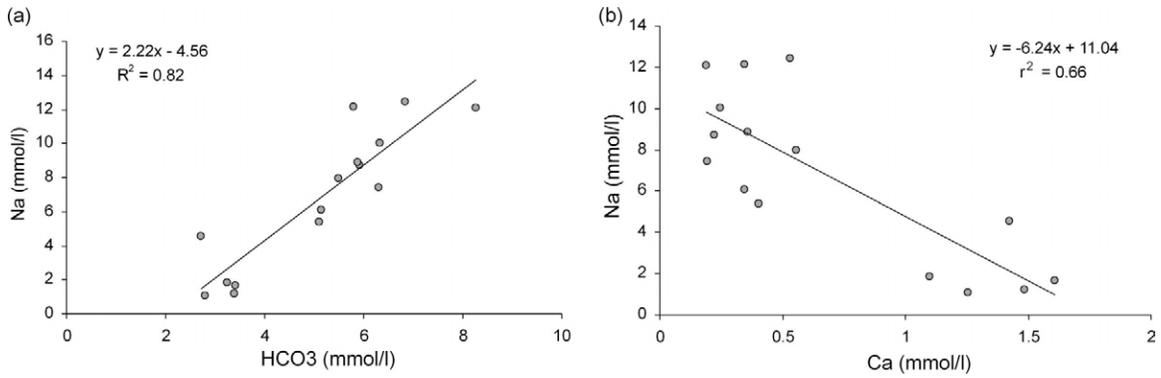
Figure 5-13. Relationships between (a) Na and HCO₃ and (b) Na and Ca in the Chicot aquifer in Harris and Galveston counties.
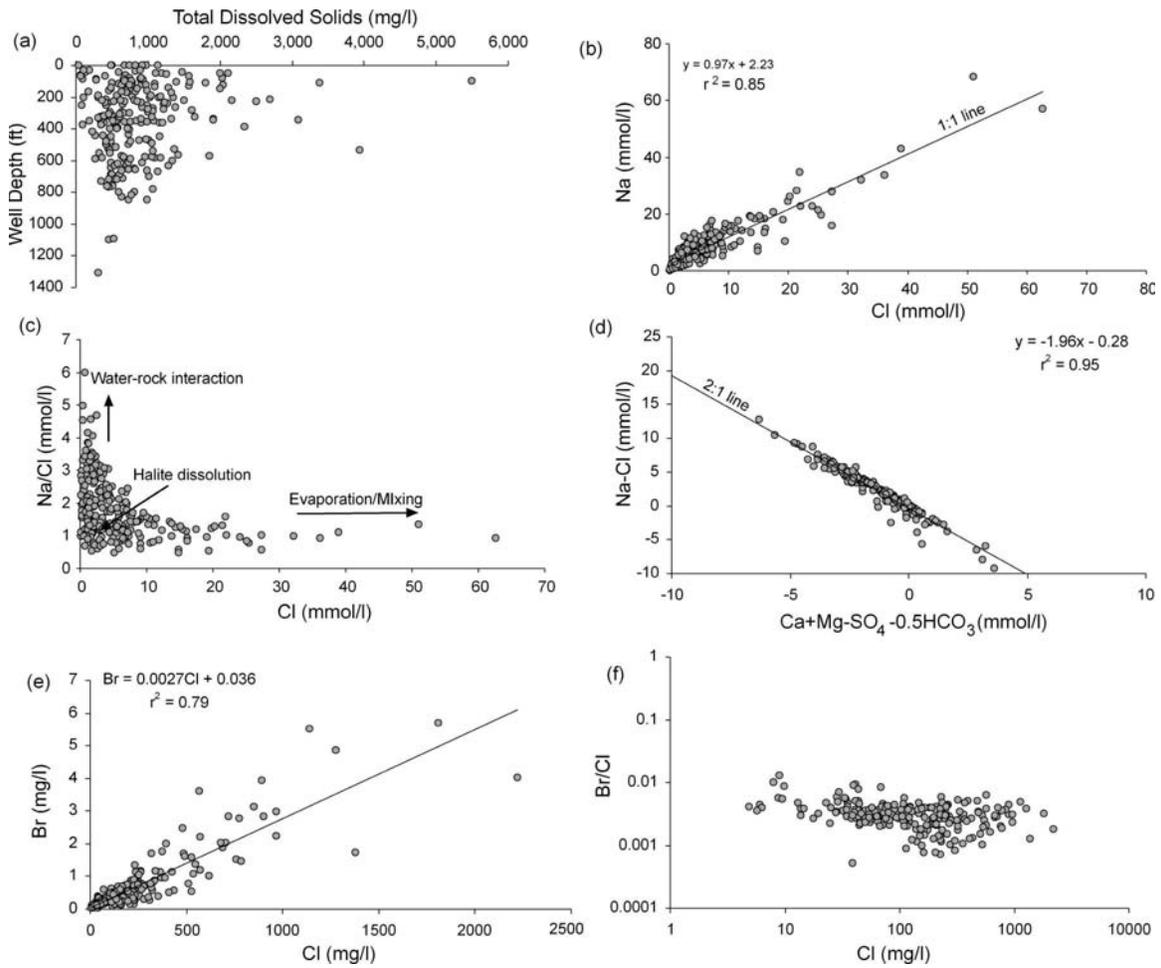

Figure 5-14. Relationships between (a) total dissolved solids and well depth, (b) Na and Cl, (c) Na/Cl and Cl, (d) Na-Cl and Ca+Mg-SO4-0.5HCO3, (e) Br and Cl, and (f) Br/Cl and Cl for the Chicot aquifer.

99

Figure 5-15. Relationships between (a) total dissolved solids and well depth, (b) Na and Cl, (c) Na/Cl and Cl, (d) Na-Cl and Ca+Mg-SO4-0.5HCO3, (e) Br and Cl, and (f) Br/Cl and Cl for the Evangeline aquifer.

different sets of chemical reactions and result in varying concentrations of dissolved solids in the groundwater in these areas.

Fresh meteoric water containing less than 300 mg/l total dissolved solids occurs in numerous wells throughout the Gulf Coast aquifer from near land surface to depths of about 2,000 feet. Such conditions may indicate that dominant quartz composition of the sands inhibited mineral reactions, thus retaining low dissolved solids content of the recharge water. Alternatively, it is possible that fresh meteoric water reached the aquifer at that depth by short-circuiting through faults or permeable sands. Capuano and Lindsay (2004) found that younger recharge water, containing lighter carbon-13 and high percent modern carbon-14 activity, is reaching the Chicot aquifer in Fort Bend, Brazoria, and Matagorda counties where the clayey Beaumont Formation has been cut by more permeable incised valley-fill. However, Noble and others (1996), in their
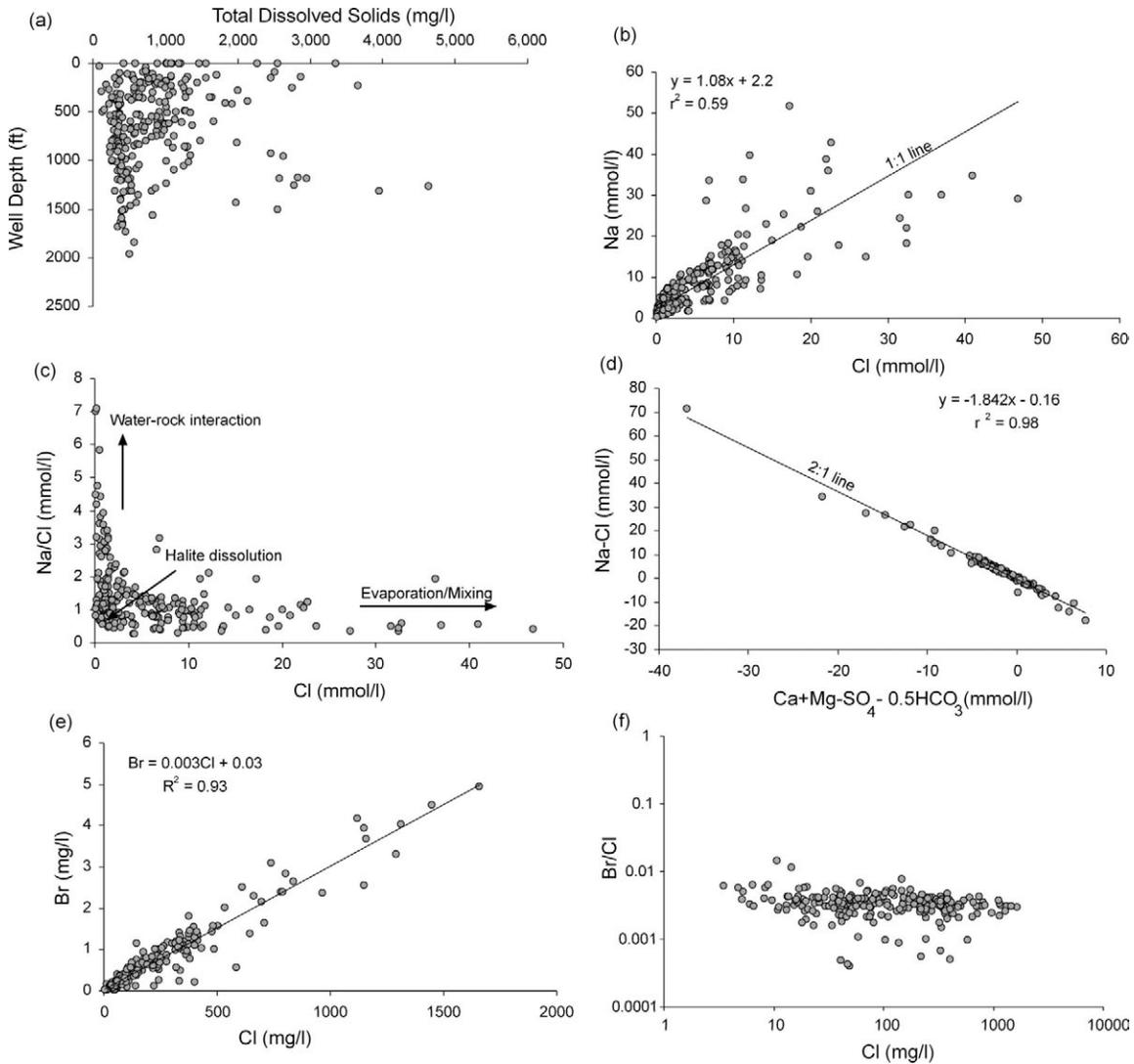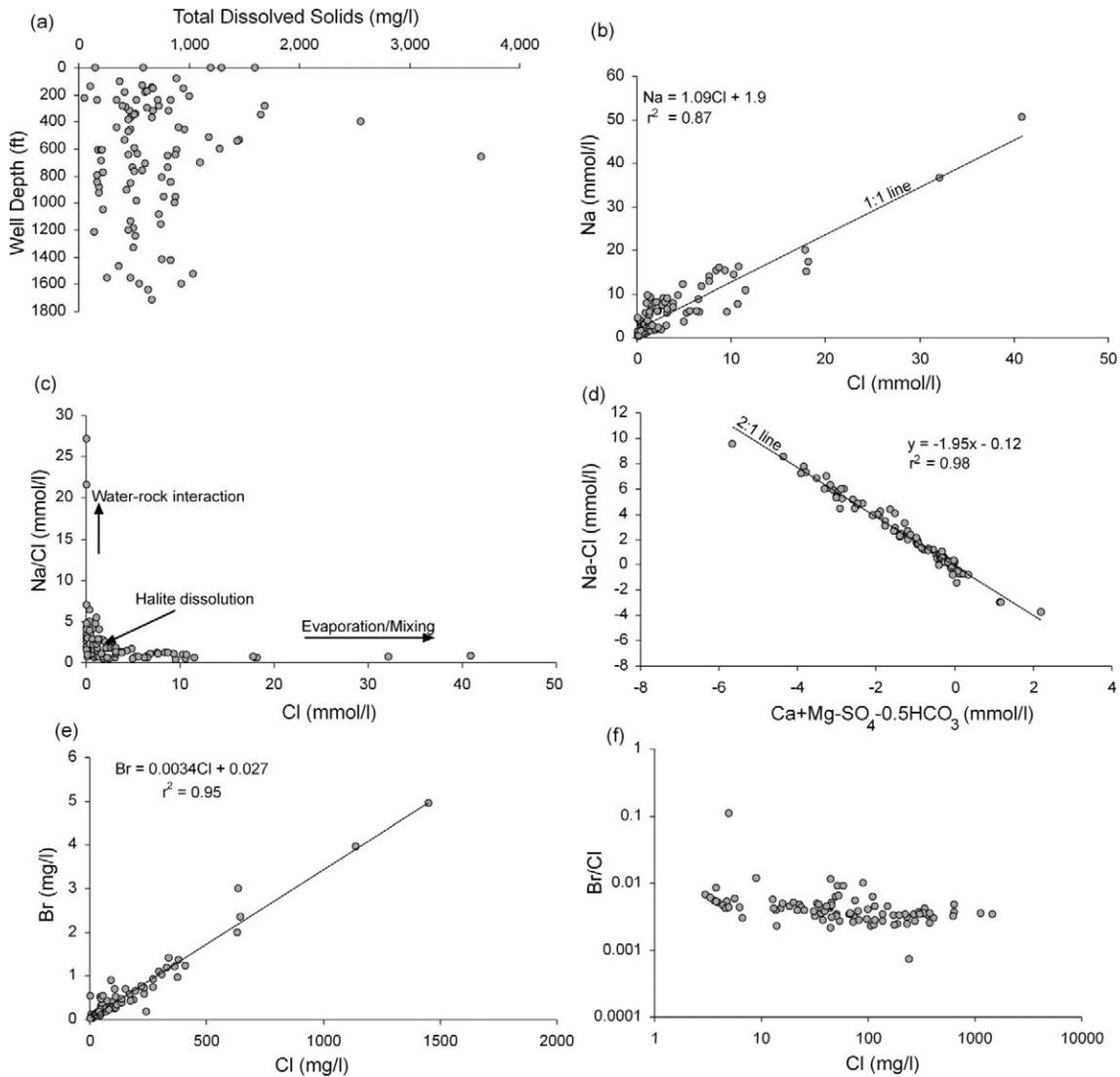
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Figure 5-16. Relationships between (a) total dissolved solids and well depth, (b) Na and Cl, (c) Na/Cl and Cl, (d) Na-Cl and Ca+Mg-SO$_4$-0.5HCO$_3$, (e) Br and Cl, and (f) Br/Cl and Cl for the Jasper aquifer.

investigation on recharge over a small section of the Gulf Coast aquifer in Harris County, observed essentially no tritium at depths greater than 80 feet. Therefore, modern recharge was perhaps not reaching the aquifer beyond that depth in that area. Complex aquifer geometry, heterogeneity of sand bodies, interfingering of clays contained within the sands, and discontinuity of shale beds suggest that younger recharge water may reach to varying depths in the various parts of the Gulf Coast aquifer.

The increased salinity observed in groundwater along regional flow paths in Harris and Galveston counties is partly related to cation-exchange reactions in which sodium attached on clay minerals replaces calcium ions dissolved in groundwater. Modification of groundwater by cation exchange is a well documented process (Kreitler and others, 1977; Appello, 1994). This is supported by an inverse correlation between sodium and calcium (r^2 = -0.66) and a positive

101

correlation between sodium and bicarbonate ($r^2 = 0.81$) in seventeen groundwater samples that we analyzed from Harris and Galveston counties (Figures 5-13a and 5-13b). In an earlier investigation, Foster (1950) had argued that carbon dioxide from organic matter decomposition can cause continuous dissolution of calcite and allow exchange of calcium for sodium. If this was true, cation exchange should have occurred at a one to one ratio, which is not observed in the groundwater from Harris and Galveston counties (Kreitler and others, 1977). In addition, high bicarbonate concentrations observed in the reducing groundwater at depth near the coast (along Matagorda, Brazoria, and Galveston counties) could be derived from sulfate reduction where sulfate is reduced while organic matter is oxidized (Chowdhury and others, in prep.).

When we consider groundwater samples from the rest of the Gulf Coast aquifer, we observe a poor correlation between sodium and calcium and sodium and bicarbonate. For example, correlation coefficients between calcium and sodium are -0.0046 and -0.18, and correlation coefficients between sodium and bicarbonate are 0.19 and 0.0005 for the Chicot and Evangeline aquifers, respectively. Groundwater in the south and central parts of the Gulf Coast aquifer progressively becomes enriched in Na-Cl-SO$_4$ and Na-Cl waters near the coast rather than becoming Na-HCO$_3$ water as observed in the northern part of the Gulf Coast aquifer. This depletion in calcium could partly be caused by cation-exchange reactions which is supported by a near perfect correlation between excess sodium (Na-Cl) and excess calcium and magnesium (Ca+Mg-SO$_4$-0.5HCO$_3$), slopes of about two between them (Figures 5-14d, 5-15d, and 5-16d), and a progressive decrease in the Ca/Na ratio along flow paths across the Gulf Coast aquifer (Chowdhury and others, in prep.).

Saltwater intrusions have occurred along part of the Gulf Coast due to pumping of the aquifer and a subsequent lowering of the water table. It is noteworthy that potassium occurs in much higher concentrations along the coast in the central part of the Gulf Coast aquifer (along Kleberg, Aransas, Matagorda, and Brazoria counties) suggesting potential salt water intrusion (Chowdhury and others, in prep.). Potassium occurs in much higher concentrations in seawater than fresh water. Potassium in freshwaters is mainly derived from dissolution of potassium feldspars. Much of this potassium in groundwater is rapidly consumed by precipitation of diagenetic potassium feldspars. Saturation indices that indicate potential for mineral precipitation suggest that many of these waters are saturated with respect to potassium feldspars (Chowdhury and others, in prep.). Therefore, the higher potassium in the groundwater along the coast is probably derived from saltwater intrusion. Higher Br concentrations in the groundwater in these areas further support this observation (see later).

Residual connate waters trapped during sedimentation in the clayey portions of the aquifer may contribute to salinity. Numerous clay or shale beds that compartmentalize water-bearing sands may still locally help retain connate waters; this is reflected in their trace to very low percent modern carbon composition at shallow depths, even near outcrop areas, suggesting that some of these fossil waters could well have formed from older recharge (Chowdhury and Mace, 2004). Jorgensen (1977) suggested that freshwater has flushed the original saltwater out of the aquifer to a depth of 2,200 feet in the Houston area, but only to a depth of 150 feet in Galveston. He indicated that flushing may have been more effective in the past, during lower stands of sea level (Frazier, 1974). Bachman (1979) reported that the average depth of the base of the freshwater occurs at depths of about 2,000 feet below land surface. In contrast, artesian conditions of saline

aquifers underlying Duval County make the base of the saline water appear near land surface (Wood and others, 1963).

Trace Elements

Trace elements generally occur in groundwater at concentrations of less than 1 mg/l. Like the major elements, trace elements in groundwater are derived from weathering of minerals and/or human activities. Trace element concentrations in groundwater largely depend on intensity of chemical weathering and their presence in minerals that are subjected to weathering (Drever, 1988). For example, many of the trace elements do not substitute readily in feldspar and other ferromagnesian minerals that are common sources of major elements but may be present in chemically resistant accessory minerals such as zircon, apatite, or zircon or as sulfides. In addition, burning of fossil fuels, smelting of ores, mining activities, and sewage disposal may introduce trace elements in groundwater (Drever, 1988).

Bromide and Iodide

The main source of chloride and bromide in groundwater is derived from atmospherically transported material that falls as wet precipitation and particulate matter (Davis and others, 1998). Near the coast this material is dominated by sea salt entrained in the air from the sea surface (Davis and others, 1998). Dry lake beds can contribute enough dust locally to overwhelm other sources of chloride and bromide (Wood and Sanford, 1995). Dissolution of evaporite and salt deposits, clay compaction, recrystallization of minerals, connate water, and saltwater intrusion may contribute additional bromide. Oil and gas activities, irrigation, and sewage disposal are some of the many human activities that can alter the natural concentrations of chloride (Cl^-) and bromide (Br^-). Ratios of bromide to chloride have been extensively used in the determination of sources of salinity. For example, these ratios have been successfully utilized to (1) make distinction between salinity originating from oil-field brine and salinity related to natural dissolution of halite, (2) identify mixing of brine derived from dissolution of halite and precipitation, (3) determine origin and fate of chloride in regional flow systems, and (4) assess effects of irrigation and sewage disposal on ambient chloride concentrations (Stevens, 1990; Fabryka-Martin and others, 1991; Whittemore, 1993).

Iodide behaves similar to bromide and chloride. These halides, along with their isotopes, are the most conservative constituents of groundwater and therefore may help in determining the origins of the water and subsurface geochemical processes (Fabryka-Martin and others, 1991). The presence of iodide is considered a good indicator of groundwater residence time, since more iodide leaches out of the sediments over time (Lloyd and others, 1982). Ratios of iodide to chloride have been effectively used to differentiate saltwater intrusion from fresh waters (Richter and Kreitler, 1991).

Methods

We collected bromide and chloride concentration data for 2005 from the TWDB's Groundwater Database. We plotted bromide/chloride ratios along with elevations of salt domes on a map to observe any association between them. We cross plotted both bromide and chloride and their

ratios against chloride to observe any trend that might exist between the two parameters, determine any potential mixing between various source waters, and identify sources of these ions.

Only a limited number of samples in the TWDB's groundwater database have iodide values. We observed spatial distribution of iodide and evaluated any relationship that might exist between iodide concentrations and flow systems.

Results

We analyzed bromide (Br⁻) concentrations from the Chicot, Evangeline, and Jasper aquifers (Tables 5-3 and 5-4). Concentrations of Br⁻ range from 0.02 to 5.7 mg/l, 0.02 to 4.94 mg/l, and 0.02 to 4.04 mg/l in the Chicot, Evangeline, and Jasper aquifers, respectively. We observed a higher median value of bromide at shallower depths and a decrease in their concentrations with an increase in well depth (Table 5-3).

Table 5-3. Concentrations of bromide (Br⁻) in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Range of Br concentration (mg/l)	Median Br (mg/l)	Standard deviation	Number of analyses
Chicot aquifer	0.02 - 5.7	0.31	0.87	239
Evangeline aquifer	0.02 - 4.94	0.27	0.83	256
Jasper aquifer	0.02 - 4.04	0.22	0.78	97

Table 5-4. Cl-/Br- ratios in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Br/Cl (weight ratios)				
	Range	Mean	Median	Standard deviation	Number of samples
Chicot	0.0051 - 0.0129	0.003254	0.00304	0.001585	239
Evangeline	0.00004 - 0.01457	0.003413	0.003292	0.001398	256
Jasper	0.00072 - 0.10742	0.00534	0.003853	0.10688	97

Ratios of bromide to chloride have median values of 3.04×10^{-3}, 3.29×10^{-3}, and 3.85×10^{-3} in the Chicot, Evangeline, and Jasper aquifers, respectively (Table 5-4). Both mean and median ratios of bromide to chloride increase from the shallower to the deeper aquifers (Table 5-4). Ratios of bromide to chloride are most variable in the Jasper aquifer as indicated by their large standard deviations (Table 5-4). Plots of bromide versus chloride indicate correlation coefficients of 0.79, 0.93, and 0.95 for the Chicot, Evangeline, and Jasper aquifers, respectively (Figures 5-14e, 5-15e, and 5-16e). Plots of bromide to chloride ratio versus chloride show a general increase with an increase in chloride levels in a few wells (Figures 5-14f, 5-15f, and 5-16f). However, a large majority of the samples in the Chicot, Evangeline, and Jasper aquifers show a near constant bromide to chloride ratio with an increase in chloride concentration (Figures 5-14f, 5-15f, and 5-16f).

When we evaluated iodide concentrations, we observed that iodide exhibits poor correlation with chloride for the Chicot aquifer ($r^2 = 0.05$, n = 17, where n is the number of samples) and a slightly better correlation for the Evangeline aquifer ($r^2 = 0.31$, n = 20). Iodide and bromide similarly show a poor correlation for the Chicot aquifer ($r^2 = 0.07$, n = 17) and a better correlation ($r^2 = 0.28$, n = 20) for the Evangeline aquifer. Iodide is present in relatively small concentrations that range from 0.10 to 0.66 mg/l, with most samples containing less than 0.2 mg/l iodide.

104

Discussion

Concentrations of bromide and chloride in the Chicot, Evangeline, and the Jasper aquifers show good correlation coefficients suggesting a common source to the salinity (Figures 5-17 and 5-18). Salinity in the groundwater must be caused in part by dissolution of halite from salt domes that penetrate the aquifers at different stratigraphic intervals. This is supported by (1) low bromide and low bromide to chloride weight ratios ($\sim 10^{-4}$) in close proximity to salt domes particularly along Brazoria through Harris to Orange counties (Figures 5-17 and 5-18) and (2) molar Na/Cl ratios close to 1 in samples close to the salt domes, which would be expected if dissolution of halite was the source of this salinity. However, the effects of halite dissolution are not observed in groundwater across the aquifers, because the higher density of salt-laden groundwater near the domes causes groundwater to sink (Evans and others, 1991). Effects of
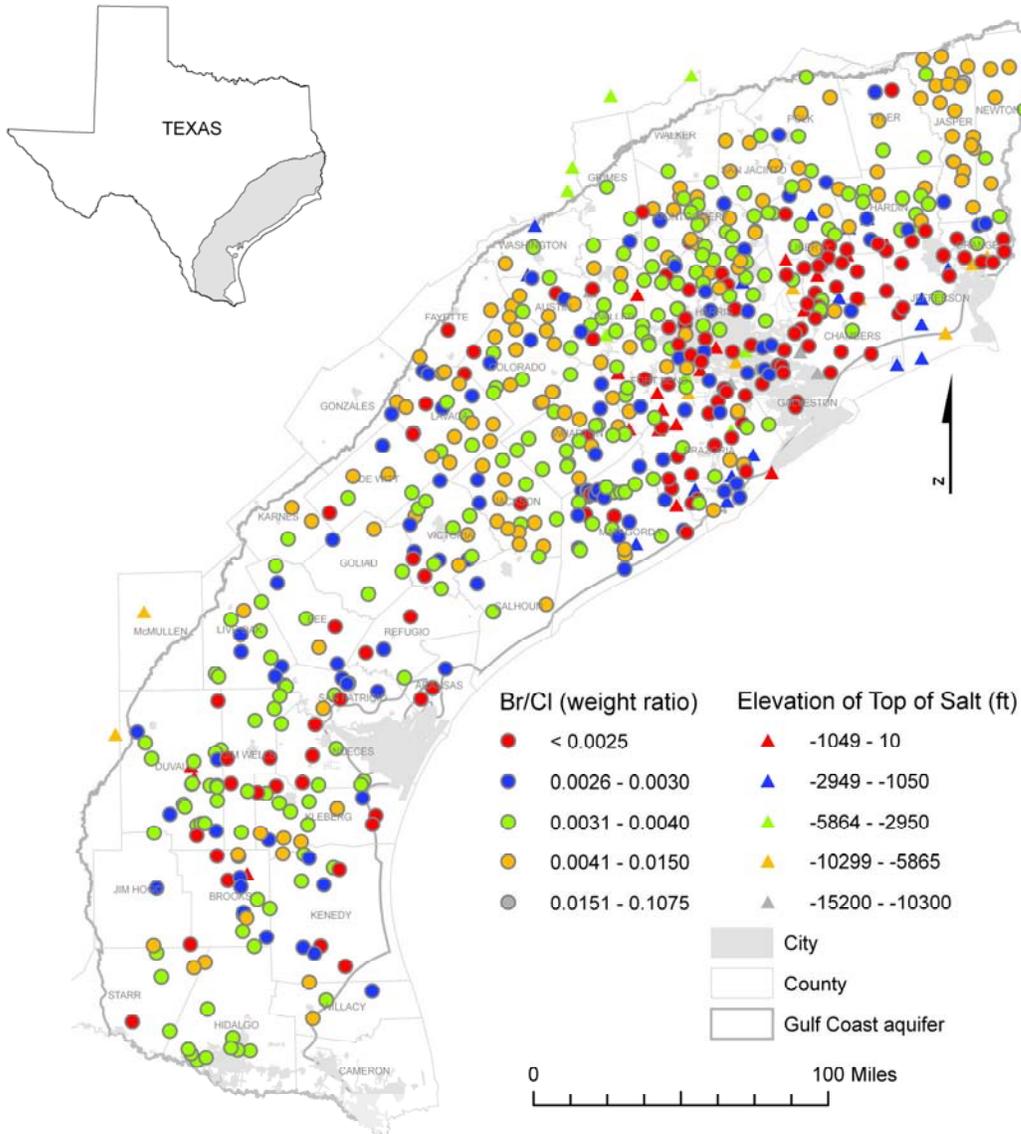
Figure 5-17. Distribution of Br/Cl molar ratios, location of salt domes, and top elevations of salt domes in the Gulf Coast aquifer in Texas (locations and elevations of salt domes after Hamlin, this volume).

105
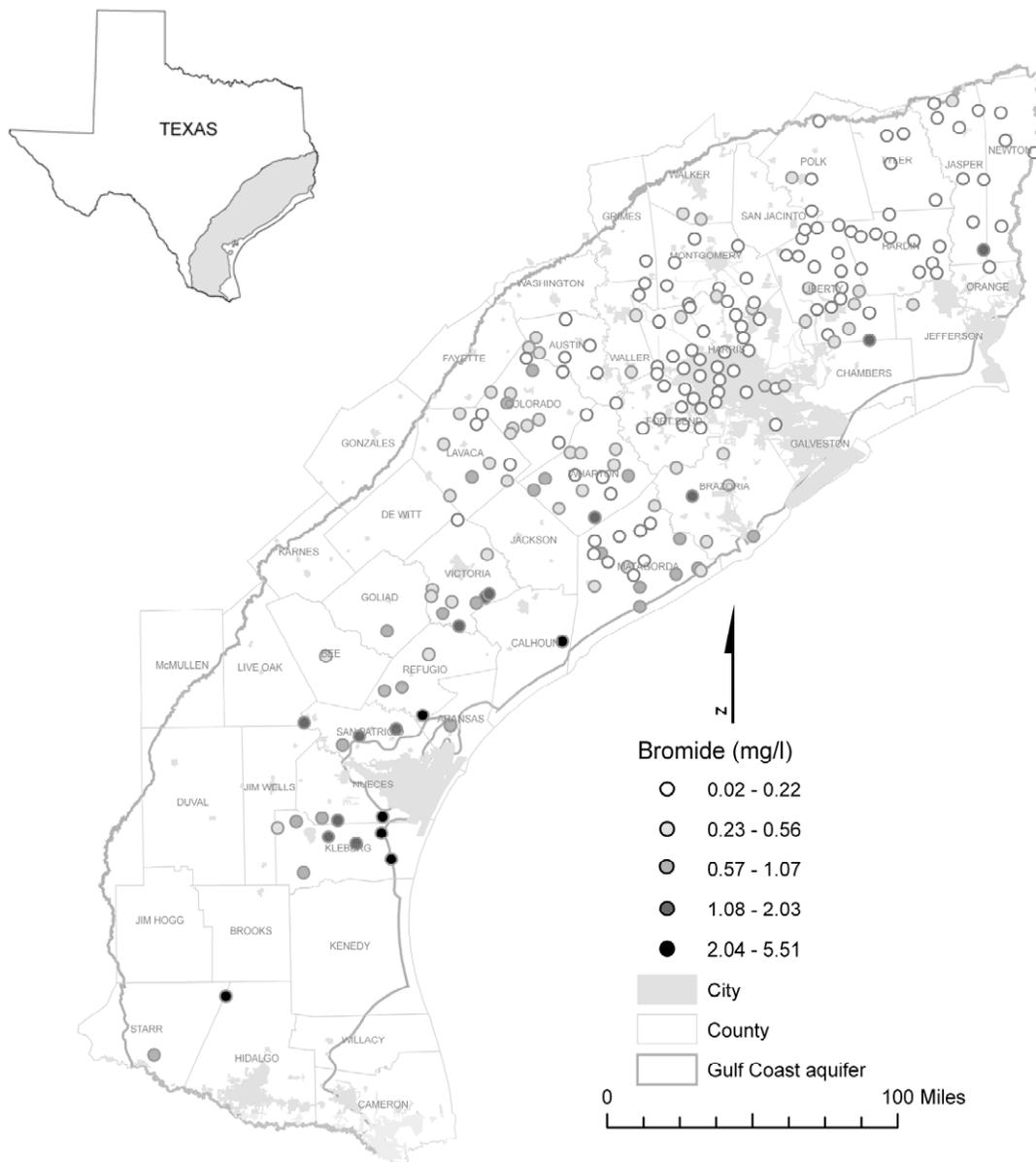
Figure 5-18. Distribution of bromide concentrations in the Gulf Coast aquifer in Texas.

halite dissolution are more commonly observed in groundwater in close proximity to salt domes (Evans and others, 1991). Evans and others (1991) further contend that in salt dome environments groundwater is driven upward by density gradients that are associated with advective transport of dissolved salts and manifested in salinity plumes extending from the top of some salt domes.

When we considered Br/Cl ratios from across the Gulf Coast aquifer, we observed that most of the ratios are an order of magnitude higher than what would be expected if groundwater was mainly affected by halite-dissolution. For example, the median Br/Cl weight ratios are 3.04×10^{-3}, 3.29×10^{-3}, and 3.85×10^{-3} for the Chicot, Evangeline, and Jasper aquifers, respectively (Table 5-

106

4). Ratio of Br/Cl for seawater is about 3.3×10^{-3}, which is close to connate formation water (Richter and Kreitler, 1991, Davis and others, 1998) and not significantly different from fresh waters (3.2×10^{-3} to 3.1×10^{-3}; CB-DP, 2000). Therefore, the Br/Cl ratios suggest that a large number of groundwater samples are dominated by fresh meteoric recharge, with some contributions of residual connate water that escaped flushing during low stands of sea level, particularly in the central and the southern parts of the Gulf Coast aquifer. These groundwater samples have Na/Cl ratios close to 1, which suggests additional mixing of water derived from dissolution of halite and associated evaporites. We recognize that some of these ratios were affected by cation-exchange reactions. The relative importance of the cation-exchange reactions, halite-dissolution, and sea-water intrusion processes are discussed in greater detail elsewhere (Chowdhury and others, in prep.). Several samples along the coast (Kleberg, Nueces, Aransas, Matagorda and Brazoria counties) have higher concentrations of bromide that suggest modern saltwater intrusions have occurred (Figure 5-18).

Numerous groundwater samples across the Gulf Coast aquifer have bromide to chloride ratios that range from 4×10^{-3} to 1×10^{-1} (Figure 5-17). These ratios are typical of formation brines (Kreitler and Richter, 1986). Morton and others (1983) reported that bromide to chloride ratios in Tertiary brines of the underlying formations along the Texas Gulf Coast occur at less than 5×10^{-3} in the northern part, between 5×10^{-3} to 1×10^{-2} in the central and the southern part, and greater than 1×10^{-2} along a narrow band from Kleberg to Jackson counties (Morton and others, 1983). Occurrences of bromide to chloride ratios in groundwater similar to Tertiary brines in different areas of the Texas Gulf Coast aquifer may suggest that upward migration of formation brines may have locally altered their initial bromide to chloride ratios. Upward migration of deeper fluids to shallower depth has been proposed based on similar carbon isotope signatures in methane gas sampled from deep reservoirs and near land surface (Stahl and others, 1981). Others have postulated upward migration of deeper fluids to shallow depths along faults where uranium deposits were formed from mixing of reducing brine and oxidizing meteoric water (Galloway and others, 1982; Goldhaber and others, 1983; Kreitler and Richter, 1986). Therefore, salinity in groundwater in different parts of the Texas Gulf Coast aquifers could be derived from one or more sources, including halite dissolution, residual connate water trapped in the pore spaces during sedimentation, and upward migration of formation brines depending on the geographic area and local hydrogeologic conditions (Chowdhury and others, in prep.).

Slow diffusion of ions from fine-grained clay, silt, and sandstones may partly contribute chloride, bromide, and iodide (Fabryka-Martin and others, 1991). Slow diffusion of bromide and chloride from interstitial water may be facilitated as groundwater movement is hindered through the subsurface by the complex geometry of the aquifer materials and the abundance of fine-grained clays. In the Milk River Formation of Alberta, Fabryka-Martin and others (1991) showed that high concentrations of iodide and bromide in the groundwater down hydraulic gradients are related to organic matter diagenesis. They observed that both bromide and chloride concentrations increase down hydraulic gradients and that chloride, iodide, and bromide show near perfect correlations between them. In the Gulf Coast aquifer, from the limited data on iodide available, we note that iodide is present at less than 0.2 mg/l in most of the analyzed samples. Correlation coefficients between chloride and iodide and iodide and bromide are considerably low ($r^2 = 0.06$ and 0.07, respectively, for the Chicot aquifer and $r^2 = 0.31$ and 0.28, respectively, for the Evangeline aquifer). Moreover, neither iodide nor bromide shows any preferential enrichment along regional flow paths. Therefore, while it is possible that some bromide,

107

chloride, and iodide could be derived from shale contained in the sandstones and shale beds, their contribution, if any, is likely to be small. Additional information on iodide and chloride isotopes may further assist identifying sources of these halogens.

Arsenic

Arsenic (As) is introduced in water through dissolution of minerals and ores. Arsenic concentrations in groundwater increase as a result of erosion of local rocks containing iron oxides, iron sulfides, and from geothermal sources (WHO, 2001, Smedley and Kinniburgh, 2002; Scanlon and others, 2005). Anthropogenic sources such as industrial effluents, alloying agents, wood preservatives, defoliants, herbicides, insecticides, and combustion of fossil fuels also contribute arsenic to atmospheric deposition (Stollenwerk, 2003; Scanlon and others, 2005). Inorganic arsenic can occur in several forms, but it commonly occurs as trivalent arsenite (As[III]) or pentavalent arsenate (As[V]) in natural waters. Arsenic is a human health concern because it can contribute to skin, bladder, and other cancers (NRC, 1999).

Methods

We collected all available arsenic data on the Gulf Coast aquifer from TWDB's groundwater database for 1995. However, as only a few samples were collected in 1995 for the Catahoula Formation, we included arsenic data for 1986 to 2005 to provide a better spatial distribution. We analyzed spatial distribution of arsenic in the Gulf Coast aquifer. We plotted several element parameters versus arsenic in order to identify sources of arsenic in the groundwater. We evaluated arsenic concentrations in light of oxidizing-reducing potential of a limited number of groundwater samples from the Evangeline aquifer.

Results

We analyzed arsenic concentrations in the groundwater from the Chicot, Evangeline, and Jasper aquifers (Table 5-5). We observed that arsenic concentrations range from 2 to 26.8 micrograms per liter (µg/l), 2.03 to 75 µg/l, and 2 to 569 µg/l in the Chicot, Evangeline, and the Jasper aquifers, respectively (Table 5-5). About 7.5, 11.5, and 30 percent of groundwater samples from the Chicot, Evangeline, and Jasper aquifers, respectively, have more than 10 µg/l arsenic, the recommended limit for drinking water purposes (U.S. EPA, 2001). The highest concentrations of arsenic occur in the Jasper aquifer. Samples with high concentrations of arsenic commonly occur in the southwestern part of the Evangeline and the Jasper aquifers in the areas of Duval, Webb, Live Oak, Karnes, and Jim Wells counties (Figures 5-19, 5-20 and 5-21). We observed no preferential occurrence of arsenic with depth and no significant relationship at depth with molybdenum or manganese (Figures 5-22a, 5-22c, and 5-22g). On bivariate plots, arsenic and

Table 5-5.   Arsenic concentrations in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Concentrations of arsenic (As) (µg/l)					
	Range of arsenic concentration	Mean	Median	Percent exceedance	Standard deviation	Number of samples
Chicot	2 - 26.8	3.85	2.04	7.5	4.22	319
Evangeline	2.03 - 75	8.03	4.74	11.54	10.17	355
Jasper	2 - 569	18.85	5	30	43.40	295
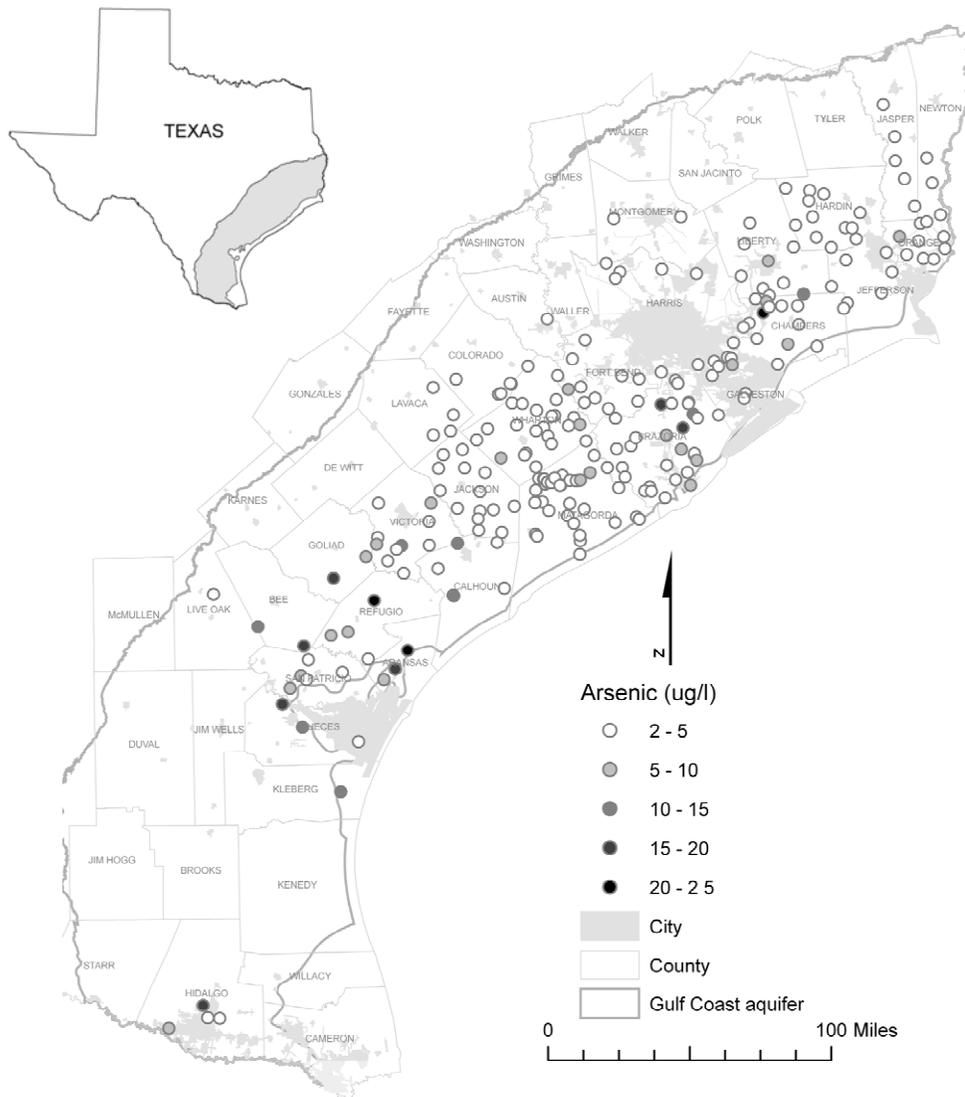
Figure 5-19. Distribution of arsenic concentrations in the Chicot aquifer.

vanadium show strong correlation coefficients ($r^2 = 0.74$; Figure 5-22b), but poor correlations were observed between arsenic and manganese ($r^2 = 0.05$; Figure 5-22c) and arsenic and molybdenum ($r^2 = 0.04$; Figure 5-22g). Arsenic is also poorly correlated with sulfate ($r^2 = 0.03$; Figure 5-22d), chloride ($r^2 = 0.22$; Figure 5-22e), and Br/Cl ratios ($r^2 = 0.02$; Figure 5-22f). Comparison of arsenic concentrations with oxidation-reduction potential of a few samples from the Evangeline aquifer suggest that arsenic concentrations decline slightly under highly reducing (<-300 mV) and oxidizing conditions (>+250 mV; Figure 5-22h). At slightly-oxidizing to slightly-reducing conditions, maximum concentrations of arsenic were observed (Figure 5-22h).

Discussion

Arsenic, molybdenum, selenium, and vanadium in the Gulf Coast aquifer could be derived from weathering of interstratified volcaniclastic debris derived from Sierra Madre Occidental of Mexico and the Trans-Pecos Region of West Texas (Galloway and others, 1982). Smedley and

Figure 5-20. Distribution of arsenic concentrations in the Evangeline aquifer.

Kinniburgh (2002) suggested that the main processes of arsenic enrichment in groundwater are mixing of deeper geothermal waters, desorption and dissolution of iron oxides in reducing environments, desorption of iron oxides in oxidizing environments, and oxidation of pyrite. Bhattacharya and others (2004) indicated that reduced groundwater containing arsenic derived from reductive dissolution of iron oxy-hydrooxides commonly has elevated ammonium and positive correlations between dissolved organic carbon, bicarbonate, total iron and total arsenic. Brandenberger and others (2004) investigated arsenic contamination in Lake Corpus Christi reservoir and nearby groundwater from the Nueces River basin and found strong correlations between chromium, cesium, vanadium, and iron, which made them conclude that arsenic was derived from uranium- and arsenic-rich geological formations rather than any large scale transport of contaminants from upstream uranium mine pits and tailings. Similarly, Scanlon and others (2005) postulated that arsenic in the Texas Gulf Coast aquifer is geologic in origin, related to volcaniclastic deposits and reworked grains that form the aquifer materials. Based on the

110

Figure 5-21. Distribution of arsenic concentrations in the Jasper aquifer. Note color codes refer to higher values than the Chicot and the Evangeline aquifers due to higher concentrations of arsenic in the Jasper aquifer.

results from unsaturated zone studies, Scanlon and others (2005) suggested that cotton production in the southern part of the Gulf Coast aquifer was probably not responsible for arsenic pollution of the groundwater except locally.

We observed that arsenic concentrations become enriched at depth, progressing from the Chicot to the Evangeline and to the Jasper aquifers (Table 5-5).There is a large degree of variability in arsenic concentrations within each aquifer, as evident from their significant standard deviations (Table 5-5). For example, in the Goliad Sand and the Catahoula Formation, arsenic occurs at random with depth and shows a wide scatter in concentrations. This irregularity in arsenic occurrence may partly be attributed to the depositional facies with finer-grained materials containing more arsenic. Brandenberger and others (2004) suggested that arsenic enrichment in
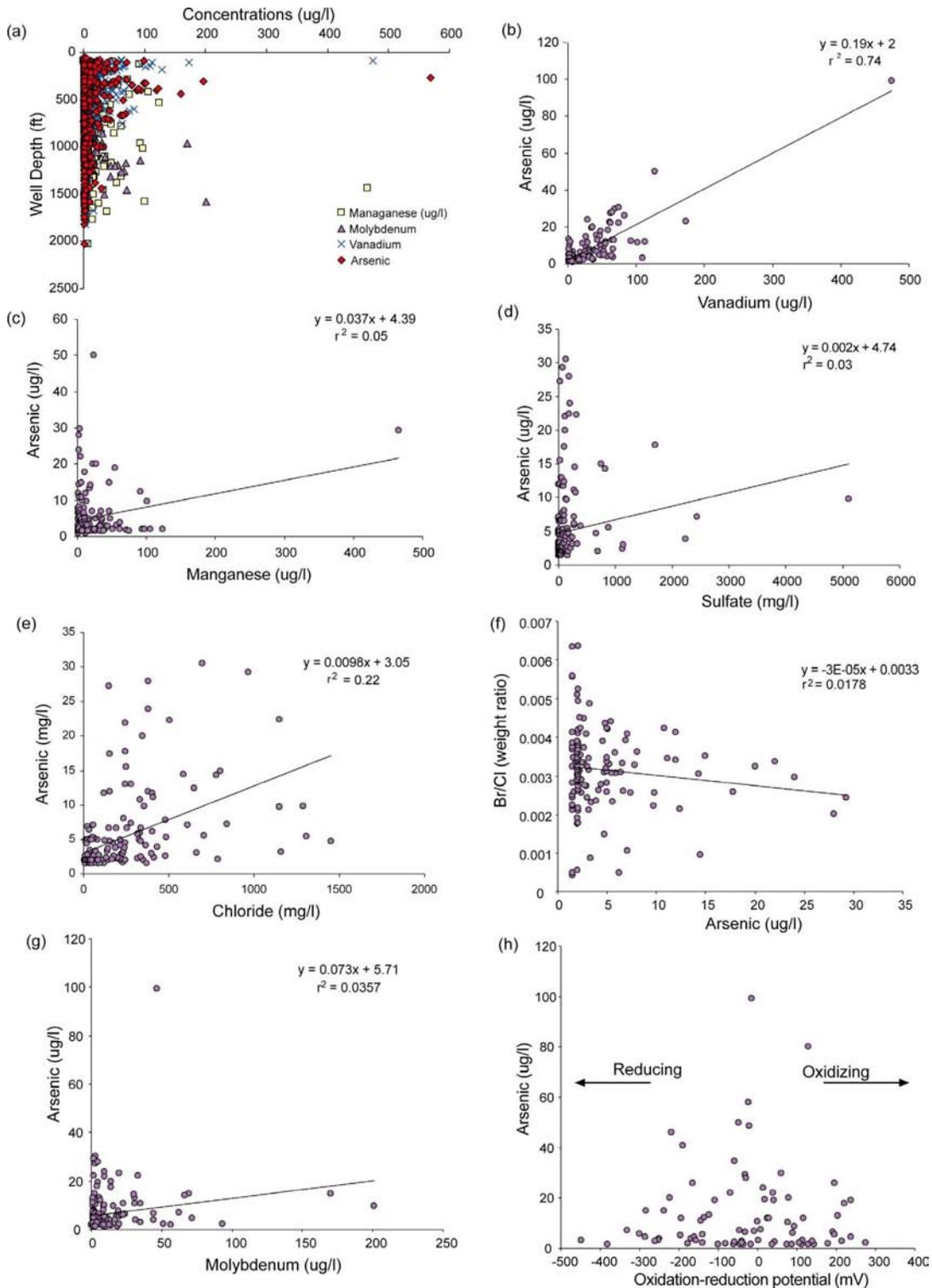
Figure 5-22. Relationships in the Evangeline aquifer between: (a) arsenic concentration and well depth, (b) concentrations of arsenic and vanadium, (c) concentrations of arsenic and manganese, (d) concentrations of arsenic and sulfate, (e) concentrations of arsenic and chloride, (f) Br/Cl weight ratios and arsenic concentrations, (g) concentrations of arsenic and molybdenum, and (h) arsenic concentrations and oxidation-reduction potential.

112

the groundwater and the surface water in the Nueces River Basin is caused by iron-rich detrital clay minerals and not reactive iron oxy-hydroxides.We observed a spatial bias to the occurrence of higher concentrations of arsenic in south Texas (in Duval, Webb, Live Oak, Karnes, and Jim Wells counties) following the outcrop of the Jasper aquifer (Oakville and Catahoula formations) that host most of the uranium deposits (Figures 5-20 and 5-21). Therefore, in addition to the reworked volcanoclastic materials, arsenic may source from dissolution of arsenic-rich sulfides and/or desorption of iron oxides present in uranium deposits. These sulfide-rich waters may flow upward to move dissolved arsenic farther from the source in the Catahoula Formation to the Evangeline and the Chicot aquifers. Reductive dissolution of iron hydroxides may cause development of arsenic in the reducing parts of the aquifer.

Low concentrations of dissolved iron and manganese in the groundwater suggest that most of these waters are probably under slightly reducing to slightly oxidizing conditions. For example, dissolved median values of iron concentrations in the Chicot and the Evangeline aquifers are about 0.1 mg/l (n = 1,700). Similarly, dissolved median values of manganese concentrations in the Chicot and the Evangeline aquifers are about 0.01 mg/l (n = 442) and 0.02 mg/l (n = 622), respectively. Henry and others (1982) used Eh measurements to illustrate that groundwater is under oxidizing conditions near the outcrop and progressively becomes more reducing down flow paths in the Oakville sand. We observed a poor correlation between arsenic and molybdenum ($r^2 = 0.04$) and arsenic and manganese ($r^2 = 0.05$) and a strong correlation between arsenic and vanadium ($r^2 = 0.74$) (Figures 5-22b, 5-22c, and 5-22g). A strong association between arsenic and vanadium indicate their derivation from similar mineral sources, probably from desorption under high pH conditions (Lee and Herbert, 2002; Smedley and Kinniburgh, 2002). Poor correlations between arsenic and sulfate ($r^2 = 0.03$) (Figure 5-22d), arsenic and chloride ($r^2 = 0.22$) (Figure 5-22e), and arsenic and Br/Cl ratios ($r^2 = 0.02$) (Figure 5-22f) suggest that arsenic was less likely to have directly derived from the upwelling of deeper formation brines. Additional data on redox and nutrient conditions in the groundwater is required to further constrain processes responsible for mobilization of arsenic (Chowdhury and others, in prep.).

Comparison of oxidation-reduction potential to arsenic concentrations in several groundwater samples from the Evangeline aquifer indicate that arsenic concentration is higher in slightly-reducing to slightly-oxidizing (-100 to +100 mV) conditions, perhaps due to preferential dissolution of iron sulfides and iron oxides in this environment (Figure 5-22h). A decrease in arsenic concentrations under highly oxidizing and highly reducing conditions could probably be attributed to arsenic co-precipitation and adsorption by interaction with Fe- and Mn-oxides, as well as precipitation of sulfidic minerals containing co-precipitated arsenic in these environments (Smedley and Kinniburgh, 2002).

Radioactivity

High levels of radioactivity in drinking water are a potential carcinogen to humans (Cech and others, 1987b; Hudak, 2005). An association between radioactivity in groundwater and cancer has been documented in numerous epidemiological studies (Lyman and others, 1985). Radium-226 and radon-222, products of the uranium-238 decay series, are the precursors to radioactivity observed in groundwater samples. Radium-226 has a half-life of 1,602 years and radium-228 has a half-life of 5.7 years (Cech and others, 1987a). Radon-222 has a half-life of 3.82 days.

Sediments formed under reducing conditions generally contain high levels of trace metals, including uranium and thorium (Langmuir, 1997). The U.S. Environmental Protection Agency recommends maximum contaminant levels (MCL) of 15 picocuries per liter (pCi/l) for alpha activity or 50 pCi/l for beta activity (U.S. EPA, 1976).

Methods

We collected all available radioactivity data on the Gulf Coast aquifer from TWDB's Groundwater Database. We analyzed spatial distributions of radioactivity in the Gulf Coast aquifer. We plotted alpha versus beta activities to observe whether any genetic relationship exists between them. We also evaluated radium-225 and radon concentrations on a few samples.

Results

We analyzed radioactivity levels in samples from the Chicot, Evangeline, and Jasper aquifers (Figures 5-20, 5-21, and 5-22). Groundwater from the Evangeline aquifer in Harris County and groundwater from the Evangeline aquifer in areas south of Bee County have high concentrations of alpha activity relative to the rest of the aquifer system. Radioactivity generally increases from the northern part to the southern part of the Gulf Coast aquifer (Figures 5-23, 5-24, and 5-25). Radioactivity occurs irregularly with depth and shows no trend in composition (Figures 5-26a, 5-26c, and 5-26e). Radioactivity in the TWDB's Groundwater Database is mainly expressed as gross-alpha and gross-beta. A small portion of the samples that we examined exceed in alpha activity (Table 5-6). Only about one percent of samples from the Chicot aquifer, six percent of samples from the Evangeline aquifer, and three percent of samples from the Jasper aquifer have more than the MCL for alpha activity (Table 5-6). Nearly all samples that we analyzed are below the MCL for beta activity (Table 5-7). We observed low positive correlations between alpha and beta activities ($r^2 = 0.47$, $r^2 = 0.05$, and $r^2 = 0.55$ for the Chicot, Evangeline, and Jasper aquifers, respectively; Figures 5-26d, 5-26e, and 5-26f). About a dozen samples have radium-226 and radon-222 concentrations and corresponding alpha activity in the TWDB's Groundwater Database for the Gulf Coast aquifer. We found that radium-226 concentrations range from 0.6 to 2.1 pCi/l. Radon-222 concentrations range from 101 to 203 pCi/l with 2 to 21 µg/l of uranium-238. We observed only a low positive correlation between radon-222 and alpha activity (Figure 5-26g).

Discussion

Several authors have sought to determine the origin of high concentrations of radium-226 in groundwater from the Gulf Coast aquifer of Texas (Kraemer and Reid, 1984; Cech and others, 1987b; Hudak, 2005). They reported that high concentrations of radium in groundwater from the Gulf Coast aquifer could probably be related to uranium occurrences in the aquifer materials (Cech and others, 1987b). In deeper formation brines of the Texas Gulf Coast, the presence of higher concentrations of radium-226 was attributed to formation water and mineral matrix reactions and preferential retention of radium-226 ions in solution; at higher salinity, the abundant positive ions compete with radium ions for adsorption sites (Tanner, 1964; Kraemer and Reid, 1984).

Cech and others (1987a) observed up to 22.5 pCi/l of radium-226 in groundwater in Harris County. They found high concentrations of radium-226 near salt domes, especially in wells located at depths between 180 to 350 meters. Due to limited data (n = 7), we were unable to
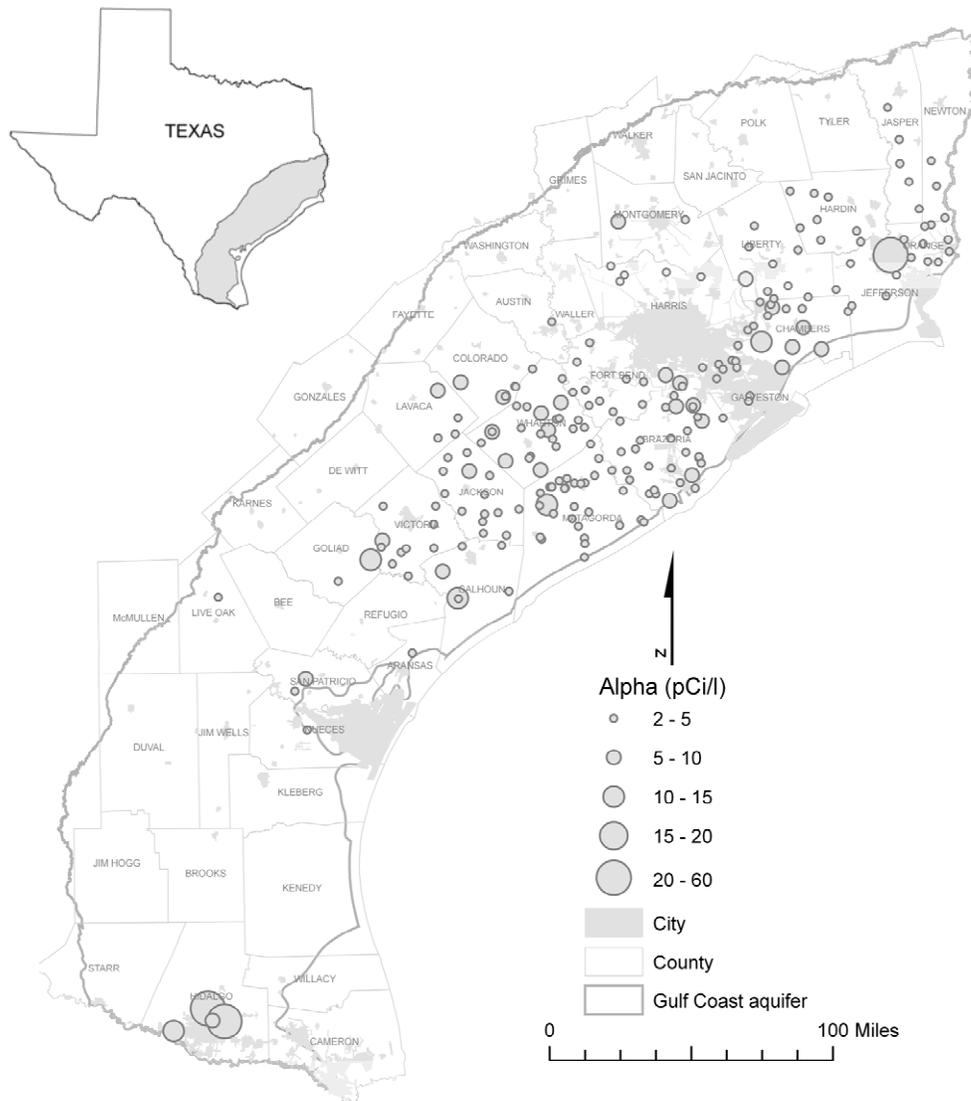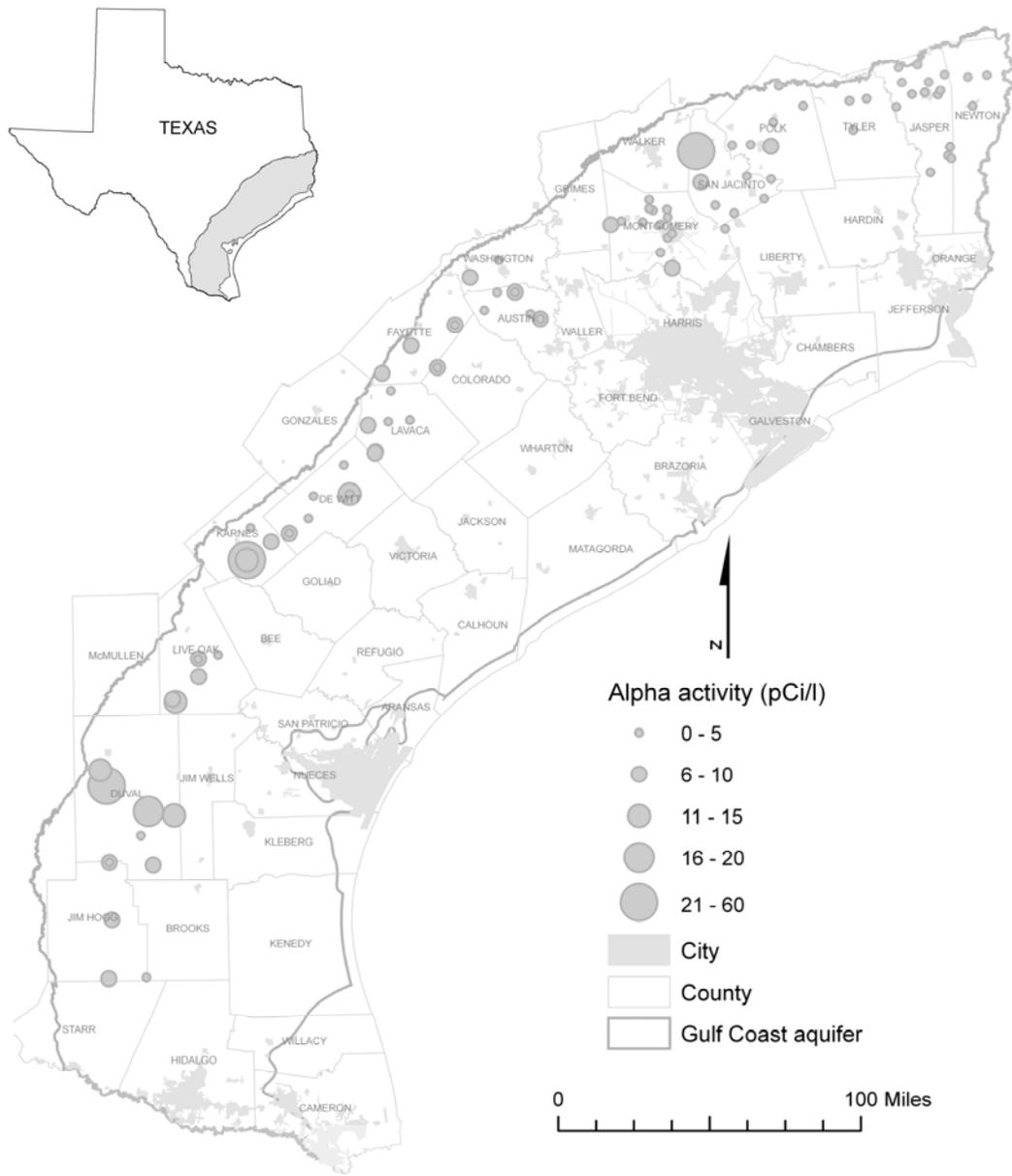
Figure 5-23. Distribution of alpha activity in the Chicot aquifer.

evaluate any relationship that might exist between radium-226 and alpha activity. Radium-226 concentrations in the analyzed groundwater are small and range from 0.1 to 0.6 pCi/l. Radon-222 and alpha activity show moderate correlation ($r^2 = 0.42$; Figure 5-26g). A small portion of the samples that we examined exceed the MCL of alpha activity (Table 5-6). Only about one percent of samples from the Chicot aquifer, six percent of samples from the Evangeline aquifer, and three percent of samples from the Jasper aquifer have alpha activity that exceeds the MCL (Table 5-6). No preferential enrichment in alpha activity with depth was noted in the Chicot, Evangeline, or Jasper aquifers. However, there appears to be a spatial bias, with higher alpha activity in the southern and central parts than in the northern part of the Gulf Coast aquifer. This enrichment in higher alpha activity may likely be related to higher concentrations of uranium deposits, relative abundance of volcaniclastics in the aquifer materials, and wider influx of formation brines in the area.
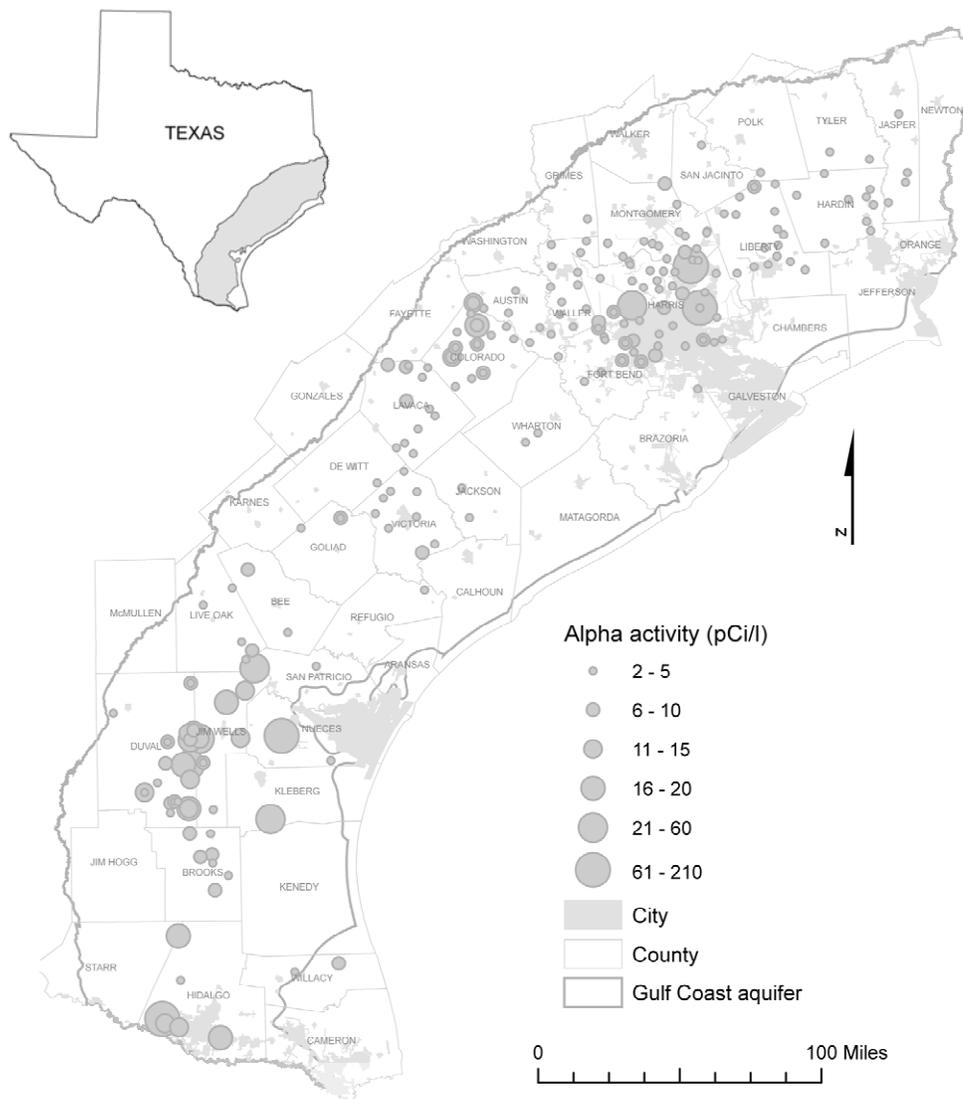
Figure 5-24. Distribution of alpha activity in the Evangeline aquifer.

Most of the groundwater analyzed from the Chicot, Evangeline, and Jasper aquifers has low beta activity (Table 5-7). Beta activity is moderately to poorly correlated to alpha activity in the Chicot ($r^2 = 0.47$), Evangeline ($r^2 = 0.05$), and Jasper aquifers ($r^2 = 0.55$; Figures 5-23b, 5-23d, and 5-23e). Primary sources of beta activity in groundwater include radiation from ^{40}K and ^{228}Ra (Welch and others, 1995). Ingrowth of beta-emitting radionuclide can contribute to gross-beta activity during sample holding times, particularly in groundwater exceeding gross-beta activities of 10 pCi/L (Welch and others, 1995). It is believed that both alpha and beta activities are sourced from parent uranium activity in groundwater (Hudak, 2005). Therefore, both these parameters should be well correlated. However, we observe that some samples containing the highest concentrations of alpha activity have the lowest concentrations of beta activity (Table 5-7; Figures 5-26d, 5-26e, and 5-26f). Additional information is needed to better constrain the sources of alpha and beta activity. The radioactivity in the groundwater is discussed in more detail in Chowdhury and others (in prep.).

116

Figure 5-25. Distribution of alpha activity in the Jasper aquifer.
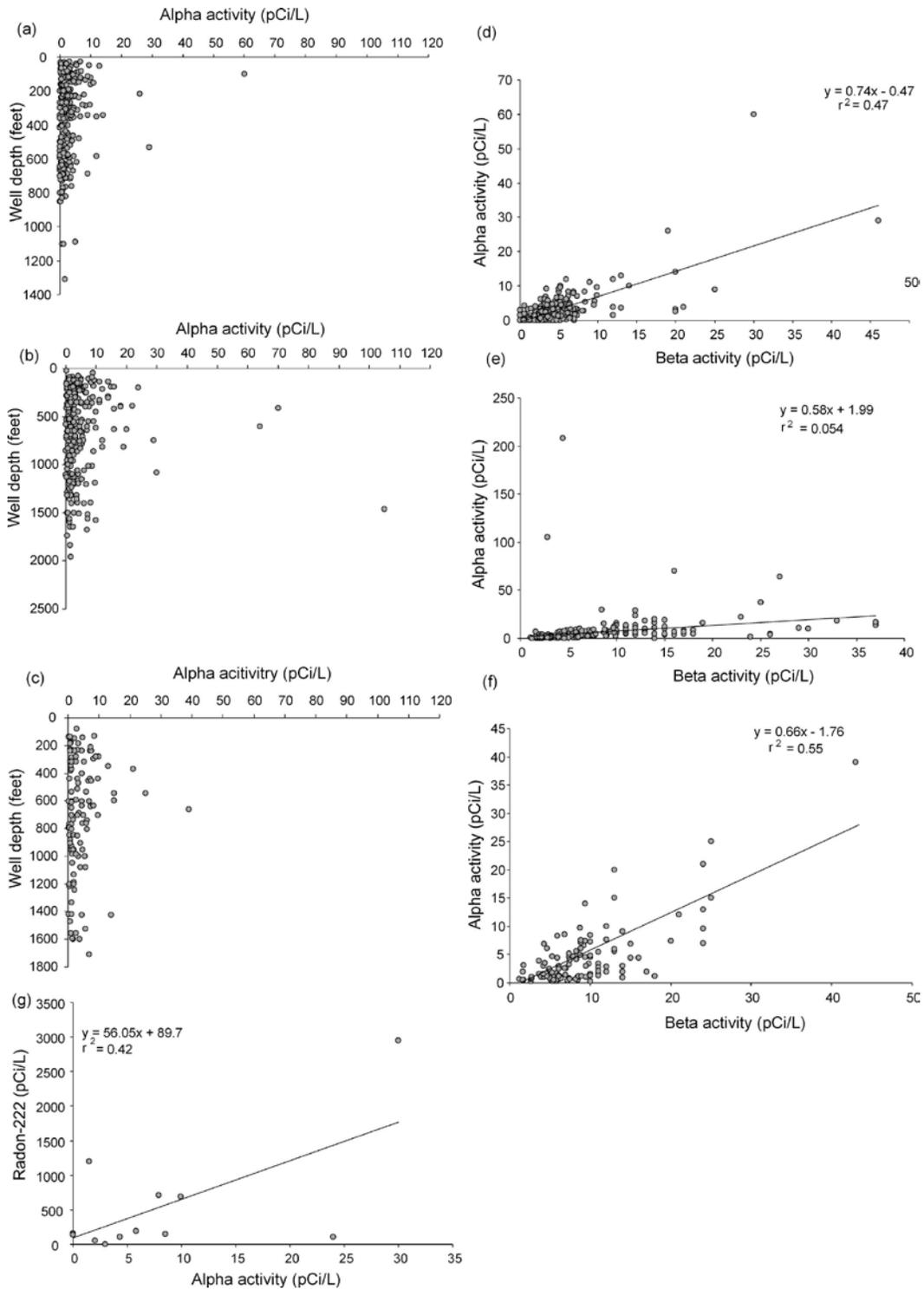
117

Figure 5-26. Relationships between alpha activity and well depth in the (a) Chicot aquifer, (b) Evangeline aquifer, and (c) Jasper aquifer; relationships between alpha versus beta activities in the (d) Chicot aquifer, (e) Evangeline aquifer, and (f) Jasper aquifer; and (g) relationship between alpha and radon-222 activities in the Evangeline aquifer.

Table 5-6. Alpha activity in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Alpha activity (pCi/l)					
	Minimum	Maximum	Mean	Median	Percent exceedance	Number of samples
Chicot aquifer	0	60	2.90	1.90	1.03	289
Evangeline aquifer	0	208	6.05	2.60	6.27	272
Jasper aquifer	0.20	39	4.45	2.65	3.41	117

Table 5-7. Beta activity in the Chicot, Evangeline, and Jasper aquifers.

Aquifer	Beta activity (pCi/l)					
	Minimum	Maximum	Mean	Median	Percent exceedance	Number of samples
Chicot aquifer	0.00	80.00	4.96	3.60	0.34	289
Evangeline aquifer	0.60	33.00	6.72	4.65	0.00	272
Jasper aquifer	1.20	43.00	9.39	7.70	0.00	117

Relationships between Water-level Decline and Groundwater Composition

Groundwater composition in interbedded sand and shale aquifers are commonly affected by decline in water levels in wells. Initial pumping removes water from the sandier portions of the aquifer that are readily removed due to higher hydraulic conductivity of the aquifer materials. Continued pumping removes water from the more finer-grained clay beds that commonly host more saline water. Under natural conditions, recharge to and discharge from an aquifer are in equilibrium (Theis, 1940). In order to maintain a dynamic equilibrium in an aquifer, recharge must equal to discharge. With continued groundwater pumping, natural discharge areas may decrease, recharge areas may increase, and/or aquifer storage may decline.

Water levels in the Gulf Coast aquifer have declined by several hundred feet due to groundwater pumping (Chowdhury and others, 2004; Kasmarek and Robinson, 2004). Water-level decline causes expulsion of water from interbedded clays due to compaction and rearrangement of the clays (Kasmarek and Robinson, 2004). Continued water-level decline may result in subsidence of the land surface.

Methods

We developed hydrographs for selected wells using historical information from various parts of the Gulf Coast aquifer in areas with large drawdown and/or land-surface subsidence (Harris and Wharton counties) to document effects of water-level decline on groundwater composition. To investigate the possible relationship between groundwater compositions and water-level decline, we plotted TDS, Na, Cl, HCO_3, and specific conductance values with water-level decline. Relationships between groundwater composition and water-level decline as observed in three wells are presented below.

Results

We selected a few wells from areas where water levels have declined historically and caused land-surface subsidence (Figures 5-27a, 5-27b, and 5-27c). We compared changes in
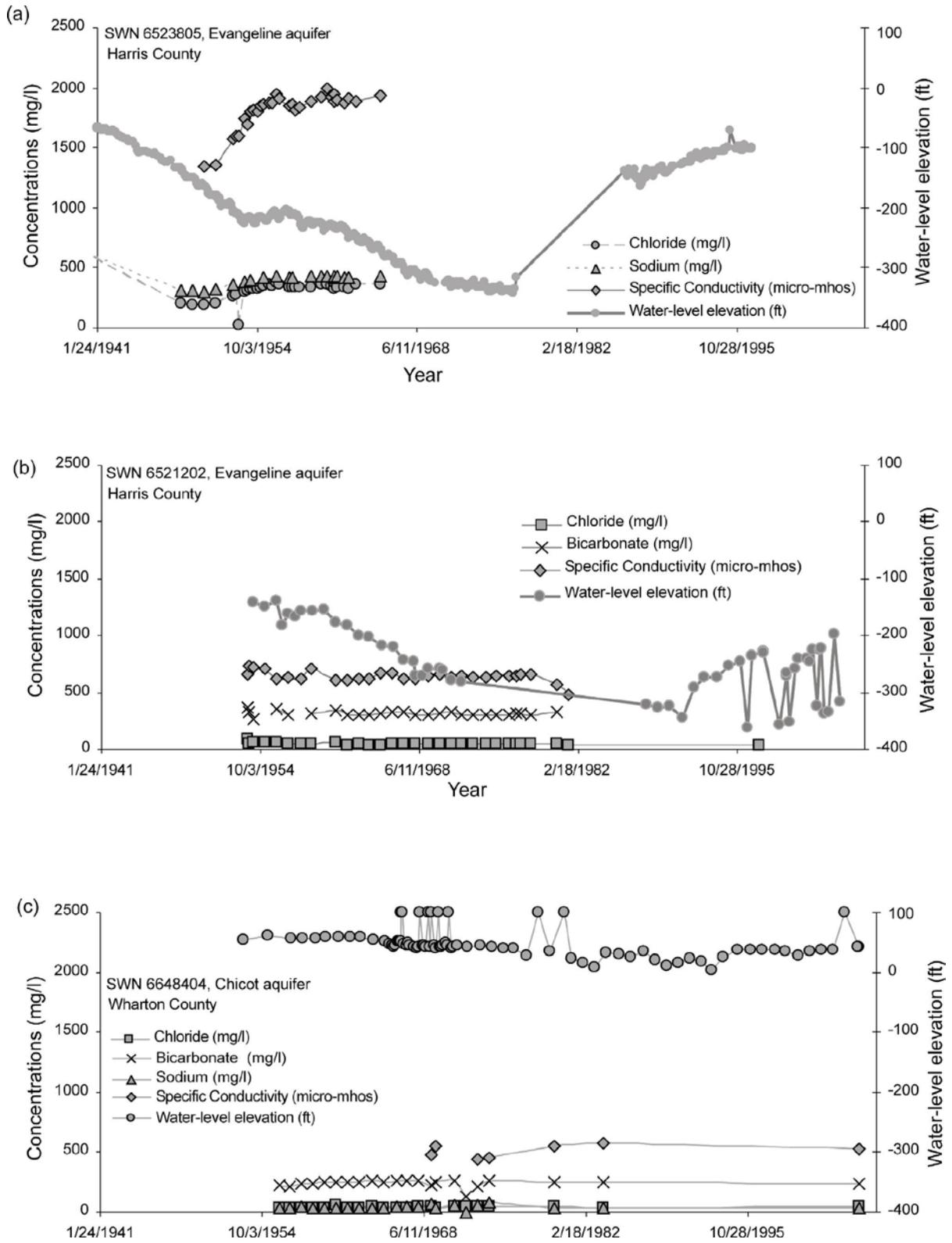
Figure 5-27. Changes in groundwater composition with water-level declines during the historical record from selected wells in Harris and Wharton counties.

120

groundwater composition in some of these wells with water-level declines through time. We observed that groundwater composition does not appear to significantly change with water-level declines (Figures 5-24b and 5-24c). In some cases, a slight but gradual increase in salinity was observed (Figure 5-24a). However, in a few shallow wells, water-level decline is associated with a freshening of the aquifer probably due to changes in the hydraulic regime that captures fresher water from the outcrop.

Discussion

Groundwater quality commonly deteriorates with residence time in the aquifer. Therefore, in the presence of unstable minerals in the aquifer, progressive water-rock interaction makes groundwater more saline. Clays and shale beds contained within the aquifer are inefficient to flush out connate water due to their low effective porosities. In the northern part of the Gulf Coast aquifer in Texas, excessive groundwater pumping leads to clay compaction that causes expulsion of water contained within the pore spaces of the clays (Kasmarek and Robinson, 2004). More than 25 percent of the groundwater in the northern part of the Gulf Coast aquifer is believed to have been derived from clay compaction (Jorgensen, 1975; Kasmarek and Robinson, 2004). We attempted to evaluate to what extent groundwater becomes saline due to water-level decline in wells.

In several wells, we observed that there are no significant changes in groundwater composition, even though water levels declined by hundreds of feet (Figure 5-27b). Composition may not change because water that is expelled due to clay compaction occurs through slow diffusive processes, as compaction and subsidence is small over time. For example, Gabrysch (1984) noted that land-surface subsidence was 0.5 feet from 1964 to 1973. Therefore, a small volume of water that is expelled from the clays mixes and become diluted in the larger freshwater reservoir in the aquifer. However, in some wells this deterioration in groundwater composition is more pronounced where the groundwater becomes more saline with progressive water-level decline (Figure 5-27a). This increase in salinity could occur if there is no significant mixing of the water expelled from the clays or if the clays had relatively fresher connate water. Jorgensen (1977) analyzed groundwater composition from clays at depths of 2 to 24 feet from Harris County. He found that groundwater composition is highly variable, generally increases in salinity with depth, and has specific conductance values that range from 586 to 2,120 micro-mhos (μmhos). In some wells that we analyzed, we note a freshening of the groundwater with water-level decline, possibly because pumping alters the natural hydraulic gradient and captures more fresh water from the outcrop. Relationships between water-level decline and changes in groundwater composition are discussed in more detail elsewhere (Chowdhury and others in prep.).

Conclusions

Fresh meteoric water containing less than 300 mg/l total dissolved solids occurs in numerous wells throughout the Gulf Coast aquifer in Texas from near land surface to depths of about 2,000 feet. Sandstone compositions in the northern part of the Gulf Coast are more commonly quartz arenite while to the south, sandstone compositions are more likely arkosic and greywackes containing abundant feldspar and rock fragments. A dominant quartz composition of the aquifer materials may have inhibited mineral reactions, thus retaining low dissolved solids content of the

recharge water. Groundwater in the central and southern parts of the Gulf Coast aquifer contains significantly more chloride, sulfate, and sodium than in the northern part of the Gulf Coast aquifer. These differences in composition from north to south are related to varying lithologies, rainfall levels, evaporation rates, and mineral reactions across the Gulf Coast aquifer. Cation exchange that removes dissolved calcium from the water and replaces it with sodium ions adsorbed on clay surfaces is a dominant process. This is supported from a gradual decrease in Ca/Na ratio along flow paths from the outcrop towards the coast.

Local enrichment in groundwater salinity around salt domes was probably caused by dissolution of halite that penetrates the aquifers at different stratigraphic intervals. This is supported by (1) low bromide and low bromide to chloride weight ratios ($\sim 10^{-4}$) in close proximity to salt domes, particularly in Brazoria, Harris, and Orange counties and (2) molar Na/Cl ratios close to 1 in samples close to the salt domes, as would be expected if dissolution of halite was the source of this salinity. When we considered Br/Cl ratios from across the Gulf Coast aquifer in Texas, we observed that most of the ratios are an order of magnitude higher than what would otherwise be expected if groundwater was mainly affected by halite dissolution. These ratios are more typical of seawater or connate formation water. Therefore, these Br/Cl ratios may suggest that some of this groundwater is a mixture of fresh meteoric water and connate formation water that escaped flushing during low sea-level stands, particularly in the central and the southern parts of the Gulf Coast aquifer. Some of this water has very low modern carbon activity indicating their origin from older recharge events. Local saltwater intrusion has occurred along the coast in Kleberg, Aransas, Matagorda, and Brazoria counties as indicated by higher bromide and potassium concentrations in these areas.

We observed that arsenic concentrations become enriched in progressing from the Chicot to the Evangeline to the Jasper aquifers. More arsenic occurs in proximity to the uranium deposits contained in the Catahoula Formation. Therefore, arsenic occurrence appears to be related to possible dissolution of sulfides and/or desorption of iron oxides from uranium deposits and their transport upwards into the Evangeline and the Chicot aquifers. However, arsenic is spatially distributed at random suggesting a possible role of iron oxides and sulfides available locally in the aquifer materials. Poor correlations between arsenic and Br/Cl ratios, chloride, and sulfate suggest that arsenic was less likely to have been directly derived from upwelling of deeper saline fluids. Comparison of oxidation-reduction potential with arsenic concentrations in several groundwater samples from the Evangeline aquifer indicate that arsenic mobilization is highest under slightly-reducing to slightly-oxidizing conditions, perhaps due to preferential dissolution of iron sulfides and iron oxides in this environment.

A small portion of the samples that we examined exceed maximum contaminant levels in alpha activity. Only about one percent of samples from the Chicot aquifer, six percent of samples from the Evangeline aquifer, and three percent of samples from the Jasper aquifer exceed maximum contaminant levels for alpha activity. We did not note preferential enrichment in alpha activity with depth in the Chicot, Evangeline, or Jasper aquifers. However, there appears to be a spatial bias with higher alpha activity in the southern and central parts than in the northern part of the Gulf Coast aquifer. Higher alpha activity may be associated with higher concentrations of uranium, relative abundance of volcaniclastics in the aquifer materials, and wider influx of deeper formation brines in the area. Most of the groundwater analyzed from the Chicot, Evangeline, and Jasper aquifers has low beta activity.

Groundwater composition may or may not change with water-level decline, depending on local hydrogeologic conditions. In several wells, we observed no significant changes in groundwater composition, even though water levels declined by hundreds of feet. This may be due to expulsion of connate water from the clays through diffusion and subsequent mixing and dilution with the larger freshwater reservoir in the aquifer. In a few wells, groundwater becomes more saline with water-level decline. This increase in salinity could occur due to an absence of mixing of the connate water with the fresher water in the aquifer. Other wells show a freshening of the aquifer with water-level decline, possibly because pumping alters the natural flow system, capturing more fresh water from the outcrop.

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