Groundwater-Surface Water Interaction in the Brazos River Basin: Evidence from Lake Connection History and Chemical and Isotopic Compositions

by Ali H. Chowdhury, Ph.D., P.G.◆ Tim Osting, P.E.
Jordan Furnans, Ph.D., P.E.◆ Ray Mathews

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GLOSSARY

The following abbreviations were used in this report:

Ca= Calcium, H= Hydrogen, Mg= Magnesium, K= Potassium, Na= Sodium, SO_4= sulfate, Cl= chloride, HCO_3 =bicarbonate, NO_3 = nitrate, B= boron, Sr = strontium, F= fluoride, H_2CO_3 = carbonic acid, NH_4 = ammonium, δ^{18}O = stable isotope of oxygen-18, δ^2H= stable isotope of deuterium, $\delta^{34}S_{SO4}$ = stable isotope of sulfur, SO_2 = sulfur dioxide, $BaSO_4$= barium sulfate

‰ = parts per thousand, CDT= Canyon Diablo Troilite, mg/l= milligrams per liter, µg/l = micrograms per liter, pH=negative logarithm of hydrogen ion concentration, SMOW= standard mean ocean water, TDS = total dissolved solids

Ca–Mg–Na–HCO_3 = calcium–magnesium–sodium–bicarbonate, Na–HCO_3 = sodium-bicarbonate, Ca+Mg-0.5HCO_3-SO_4 = calcium+magnesium–0.5 bicarbonate-sulfate, Na–Cl = sodium-chloride, Ca+Mg/HCO_3 = calcium+magnesium/bicarbonate, HCO_3/Cl = bicarbonate/chloride, Ca–Mg–HCO_3 = calcium–magnesium–bicarbonate, Na–Ca–HCO_3–Cl = sodium–calcium–bicarbonate–chloride, Na/(Na+Ca) = sodium/sodium+calcium

Executive summary

Numerous oxbow lakes occur along the Brazos River, which stretches over 840 miles across Texas. Created by lateral stream erosion and changes in the course of the river, these lakes were formed when the main stream channels were abandoned. When the oxbow lakes and main channel connect during floods, the water from these surface water bodies mixes, resulting in an exchange of aquatic plant and animal species. These exchanges are important avenues for maintaining biodiversity in a river ecosystem.

The main focus of this investigation was to determine the source water of three oxbow lakes near Bryan and Hempstead, Texas. Using site topography and water surface elevation information, we evaluated surface connections of each oxbow lake with the main channel of the river. We estimated recurrence intervals for connections based on historical streamflow and ground survey measurements. Results indicate that Moelhman Slough connects to the Brazos River at least twice per year, Korthauer Bottom connects to the Brazos River more than once per year, and Horseshoe Lake rarely connects to the Brazos River, even during intense flood events.

We sampled the three oxbow lakes, river water near the lakes, adjacent groundwater from the shallow alluvial aquifer, and the Queen City, Sparta, and Evangeline aquifers that lie below the alluvium for isotopic and chemical compositions. Isotopic compositions of the alluvial groundwater, river water, and oxbow lake water show a progressive enrichment in oxygen and deuterium isotopes due to their continued evaporation. Groundwater in the alluvial aquifer shows unenriched isotopic values due to an absence of any significant evaporation during recharge. When groundwater from the alluvium discharges as base flow into the river, it mixes with the river water causing enrichment in isotopic values. In the oxbow lakes, higher evaporation occurs because water is locked into shallow, standing bodies of water, which leads to more enriched values. Groundwater from the Queen City, Sparta, and Evangeline aquifers near the lakes has more depleted isotopes and a sodium-bicarbonate composition that differentiates it from the more enriched isotope and calcium-sodium-bicarbonate composition of groundwater from the Brazos River Alluvium Aquifer.

These differences in chemical and isotopic compositions suggest that there may not be any significant upward discharges from the Queen City, Sparta, and Evangeline aquifers into the Brazos River Alluvium Aquifer and the Brazos River. Water levels and base flow analyses suggest that a substantial portion of the water in the Brazos River is derived from base flow from the shallow alluvial aquifer. Estimated average base flow discharges are significantly higher downstream than upstream. Fresher (less saline) groundwater composition in the lower parts of the alluvial aquifer produces a fresher river water composition downstream.

We estimated recharge into the Brazos River Alluvium Aquifer using base flow and chloride mass balance methods. Using the base flow method, we estimate that average recharge into the aquifer ranges from 0.74 to 0.95 inches per year. Using the chloride mass balance method, we estimate average recharge is about 0.33 inches per year; however, this method may underestimate recharge if chloride is derived from non-precipitation chloride.

Water levels in wells and base flow discharges show no direct responses with precipitation amounts, suggesting that recharge into the aquifer is delayed due to the presence of clay in or above the alluvium, as documented by recent geophysical investigations.

From a combined use of surface water connections, water chemistry, isotopic composition, and base flow amounts in different segments of the Brazos River, we suggest that the source water for Moehlman Slough and Korthauer Bottom differs from Horseshoe Lake. The frequency and duration of surface connections of the oxbow lakes with the river in combination with characteristic chemical and isotopic compositions suggest that the water in Moelhman Slough and Korthauer Bottom originated during flood events. In contrast, base flow from the alluvial aquifer is the dominant source of water for Horseshoe Lake. Water in Horseshoe Lake has experienced extensive evaporation, which is supported by its enriched deuterium and oxygen isotopic compositions and only one surface connection to the Brazos River over the past 20 years. Although chemical composition of the water from Horseshoe Lake should be more saline due to extensive evaporation, it remains surprisingly fresher than all other water. This difference in chemical composition could possibly be attributed to biologically mediated filtering of the ions and/or geochemical reactions.

1 *Introduction*

Oxbow lakes are important for maintaining diverse aquatic flora and fauna populations in river ecosystems. Formed from lateral stream erosion and subsequent changes in the course of a stream, these abandoned stream channels become lakes filled with stagnant water. During flood events, some of these lakes connect temporarily to the main channel. The degree of connectivity of the lakes to the main channel can have a significant bearing on diversity of the aquatic biota (Van Den Brink and others, 1996; Winemiller and others, 2004).

Numerous oxbow lakes occur along the Brazos River in Texas. This study focuses on three—Moelhman Slough, Korthauer Bottom, and Horseshoe Lake—located in the lower Brazos River Basin near Bryan and Hempstead (Figure 1-1).

Originating in New Mexico near the Texas border, the Brazos River flows southeast over various climate conditions and large expanses of sandstone, clay, limestone, and alluvium into the Gulf of Mexico (Figure 1-2). The Brazos River Basin crosses numerous outcrops that contribute to streamflow in the main channel. The river flows over the exposed bedrocks of Permian to Quaternary age sediments that crop out in bands parallel to the coast and dip toward the Gulf of Mexico. The exposed Cretaceous rocks are composed mainly of limestone, marl, and shale and locally form important aquifers. The Permian to Quaternary age rocks composed of sandstone, shale, and clay host the Trinity, Carrizo-Wilcox, Queen City, Sparta, and Gulf Coast aquifers in the lower portion of the Brazos River Basin (Figure 1-3). The Brazos River Alluvium Aquifer locally thickens to about 130 feet (Shah and others, 2007a) and serves as an important water supply source for irrigation purposes. The Brazos River is hydraulically connected to all the adjoining aquifers where it crosses them (Ryder, 1996).

This study formed part of a larger investigation to assess impacts on instream aquatic habitats and salinity migration in the Brazos River estuary from the proposed construction of the Allen's Creek Reservoir (Osting and others, 2004a, b). The proposed reservoir is to be built by impounding one of the tributaries of the Brazos River to help Houston and other coastal basin areas with their long-term water needs (Osting and others, 2004a, b). When completed, the proposed reservoir will supply an additional 92,000 acre-feet of water annually.

The focus of this investigation was to determine sources of the water in the oxbow lakes. To determine those sources and better understand hydraulic interaction between the oxbow lakes, the aquifers, and the river, we established surface connection history between the oxbow lakes and the Brazos River. We also sampled for chemical and isotopic constituents from the three oxbow lakes, surface water from the main channel of the Brazos River adjacent to the oxbow lakes, and groundwater from the alluvial aquifer and the aquifers beneath the alluvium near the oxbow lakes. We evaluated water level information from the alluvial aquifer to establish groundwater flow directions to and from the Brazos River. We examined historical rainfall distribution characteristics in several area weather stations and explored the relationship between rainfall and water levels in wells completed in the Brazos River Alluvium Aquifer. We also estimated recharge rates into the Brazos River Alluvium Aquifer using base flow analyses and the chloride mass balance method.

This report describes the study

methods used, characteristics of the Brazos River and oxbow lakes, and the hydrogeologic setting that hydraulically connects the aquifer, river, and lakes. It also presents the results and conclusions of our analyses.

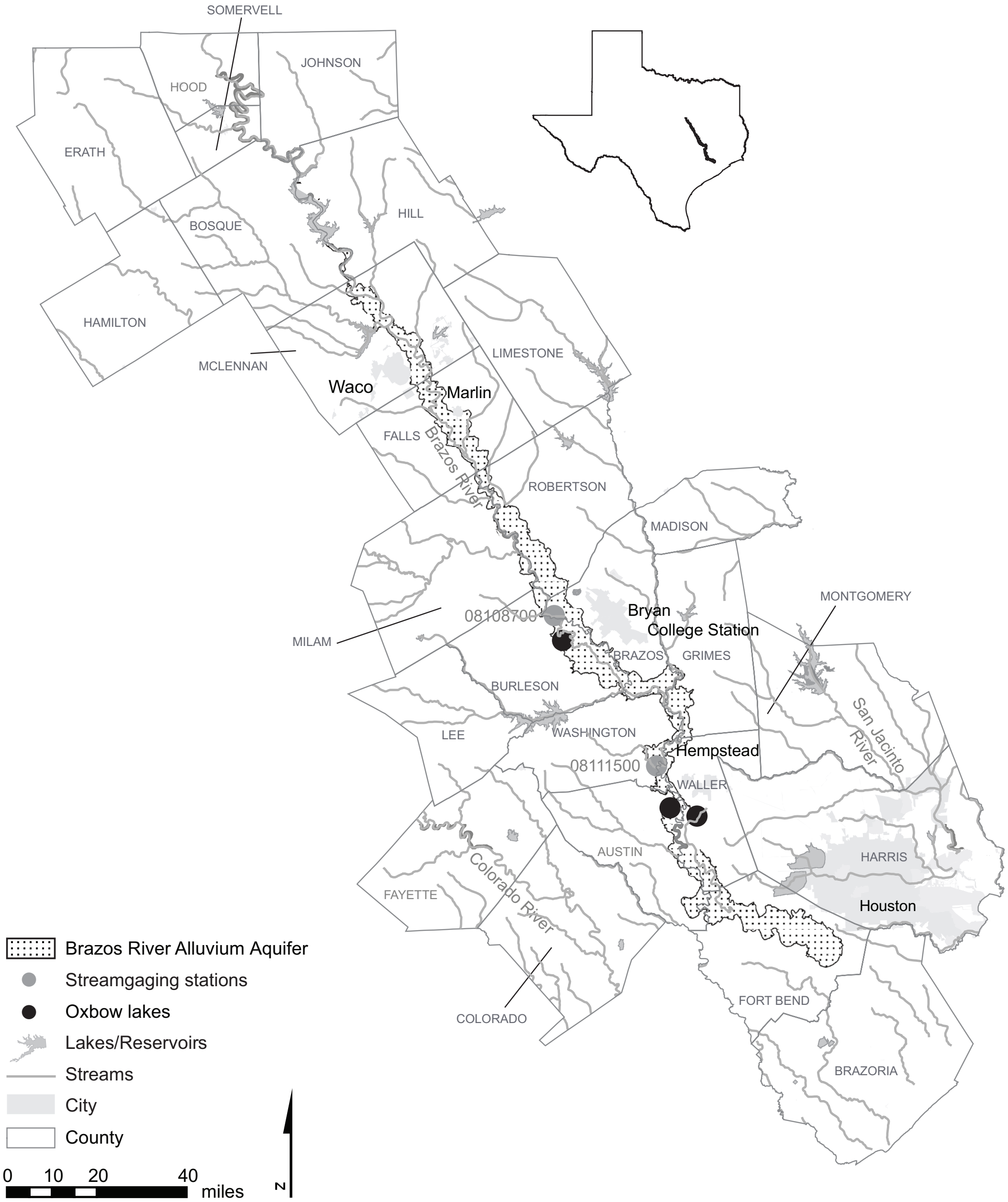

Figure 1-1. Location of the study area relative to major cities, lakes, reservoirs, and streamflow gaging stations near Bryan and Hempstead.

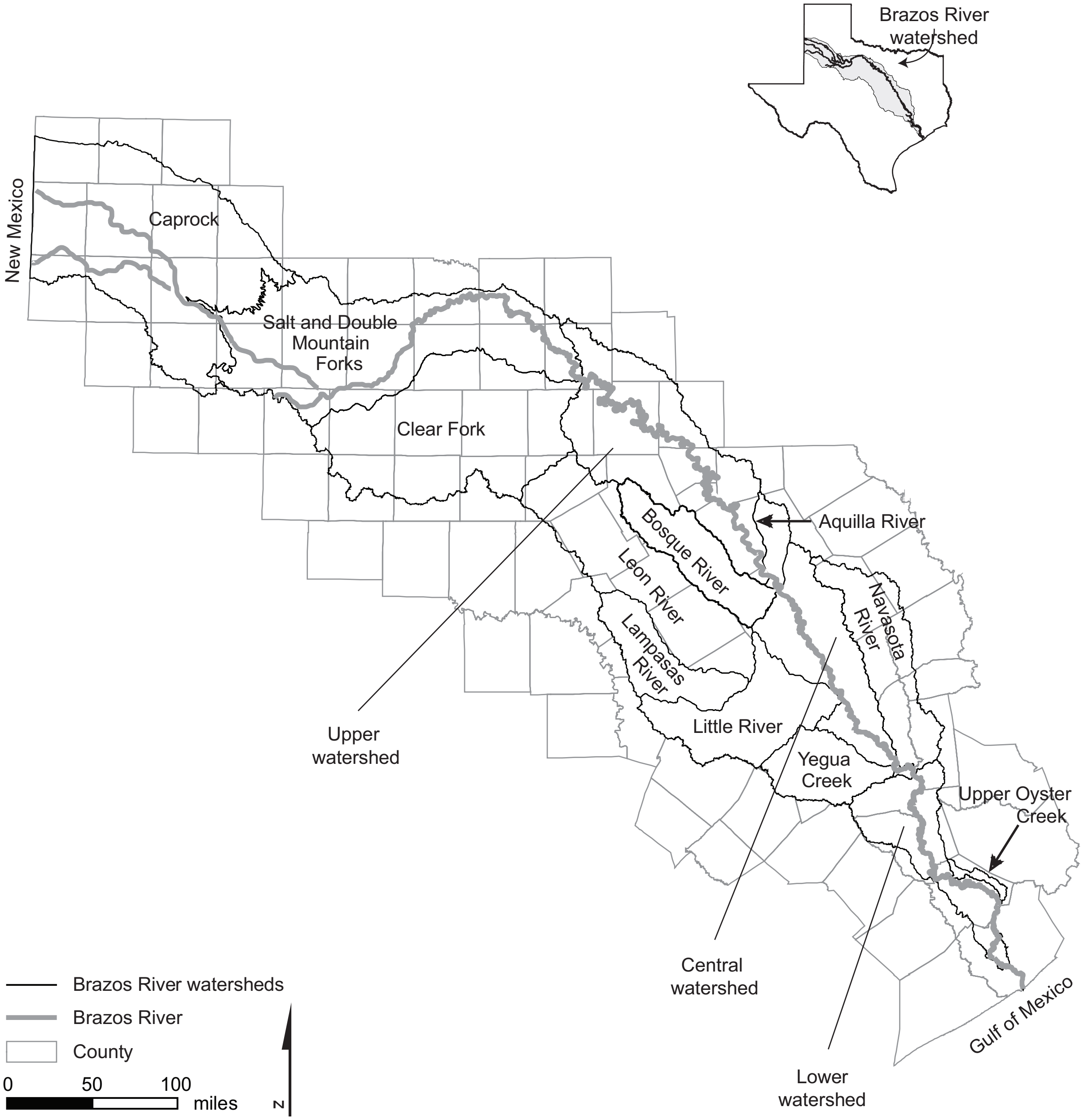

Figure 1-2. Map of the watersheds in the Brazos River Basin in Texas.

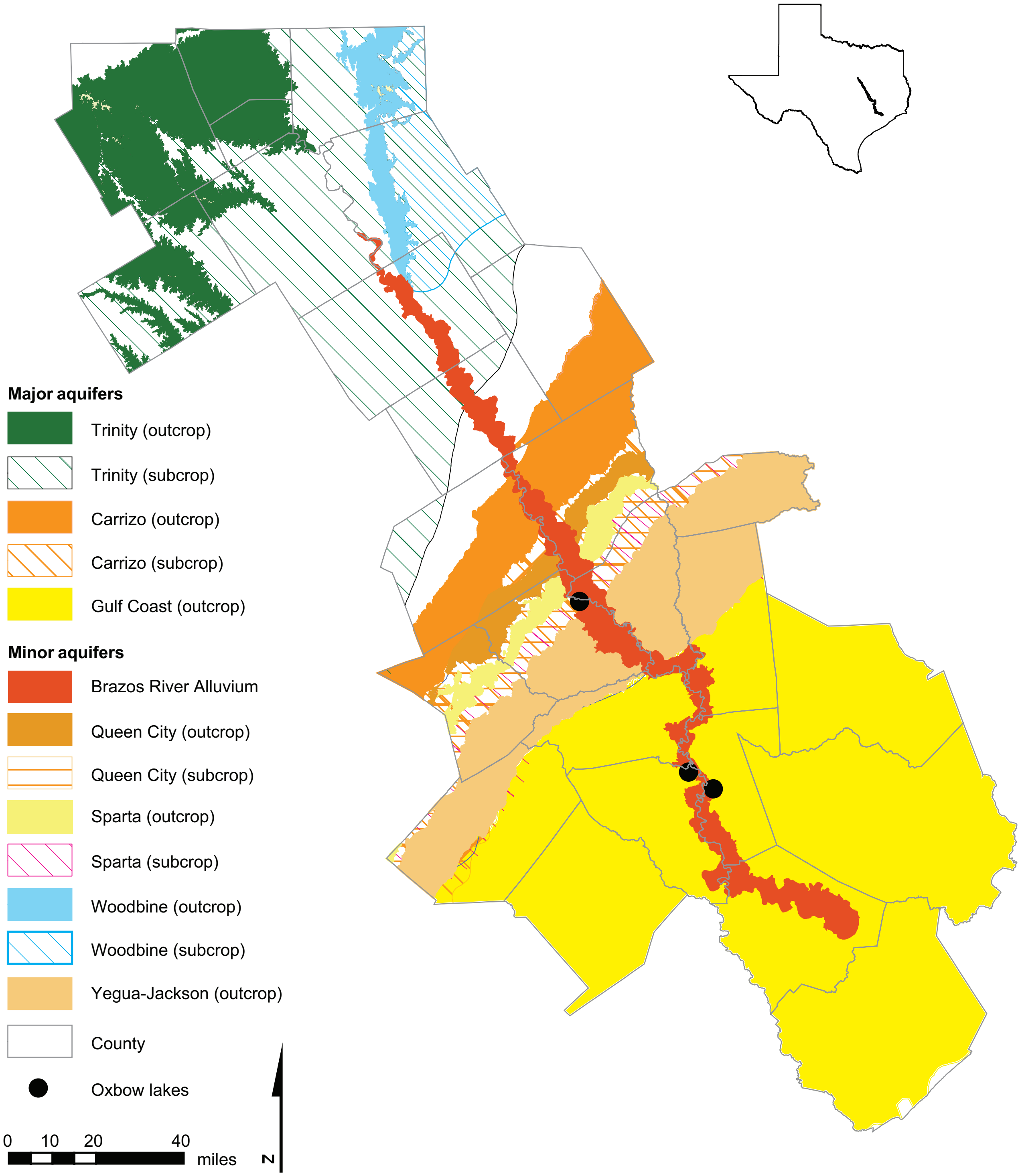

Figure 1-3. Location and extent of the oxbow lakes, Brazos River Alluvium Aquifer, and the major aquifers in the study area.

2 *Analytical methods*

We analyzed historical rainfall data from nine weather stations located across the lower Brazos River Basin (Figures 2-1, 2-2, and 2-3). We also analyzed historical rain water composition data for two National Trends Network sites located in Colorado and Wise counties.

The three oxbow lakes we sampled were (1) Moelhman Slough, (2) Korthauer Bottom, and (3) Horseshoe Lake. We collected three water samples from each lake to examine general chemistry, deuterium, oxygen, and sulfur isotopes. Of the three samples, two were collected near opposite banks of each lake, and the other was collected from the middle, deeper portion of each lake. We also collected three water samples from the main channel of the Brazos River adjacent to the lakes. In addition, we used data provided by the Brazos River Authority to examine historical water compositions from three other sites on the main channel of the Brazos River (Figure 2-4 and Appendix 1).

We also examined chemical compositions of groundwater near the lakes. We collected 12 groundwater samples to analyze general chemistry and deuterium, oxygen, and sulfur isotopes (Figure 2-5). We analyzed additional water composition data for the Brazos River Alluvium Aquifer wells from the Texas Water Development Board's (TWDB) groundwater database (Figures 2-6, 2-7, 2-8, 2-9, 2-10, and 2-11). Because we did not have many wells adjacent to the lakes, we assumed that the groundwater we sampled at some distance from the oxbow lakes was chemically similar to base flow discharged to the Brazos River and the oxbow lakes. We also analyzed water level information for the Brazos River Alluvium Aquifer wells from TWDB's groundwater database.

The Lower Colorado River Authority's Environmental Laboratory analyzed all groundwater and surface water samples by Ion Chromatography-Mass Spectrometry for chemical parameters. The Coastal Sciences Laboratory in Austin, Texas, analyzed oxygen ($\delta^{18}O$), deuterium ($\delta^{2}H$), and sulfur-34 ($\delta^{34}S$). Isotopes for $\delta^{18}O$ were analyzed on a VG Micromass SIRA Series II mass spectrometer using the CO_2 equilibration method (Epstein and Mayeda, 1953). Sulfur-34 ($\delta^{34}S$) was analyzed by extracting SO_2 from the settled $BaSO_4$ using a mass spectrometer VG Model 10, Series II.

To determine surface water connection between the oxbow lakes and the Brazos River, we established the control point elevation of the lakes, which is the water surface elevation that allows water exchanges to occur between the lakes and the Brazos River. The control point elevation is generally the highest elevation of the land surface within the infilled original (now dry) Brazos River channel connecting the current river channel to the lake. A relationship was developed between the control point and the historical stream records, changes in water level elevation between the nearest available river gage, and water surface in the river near the control point (Osting and others, 2004a). The water surface elevation at the oxbow (O_{WSE}) is obtained by

$$O_{WSE} = G_{WSE} + S \times X \,. \qquad (1)$$

In the equation, G_{WSE} is the water surface elevation at the gage, S is the river water surface slope, and X is the distance along the river between the streamflow gaging station and the oxbow lake. A survey-grade global positioning system was used to measure the river slope in the vicinity of each oxbow lake, and the distances downstream from the streamflow gaging stations were measured from digital orthophoto quadrangles (DOQs) using ArcGIS. A pressure transducer was installed to measure the fluctuations in water levels within the largest lake, Moelhman Slough, from October 11, 2003, through September 9, 2004 (Osting and others, 2004a). The measured Moelhman Slough water levels were used to validate usage of Equation 1 for the other Brazos River oxbow lakes in this study.

We also evaluated base flow information from historical streamflow records for two U.S. Geological Survey streamflow gaging stations (08108700 and 08111500) located on the main channel of the lower Brazos River (Figure 1-1). To determine the base flow component, we separated streamflow hydrographs using an automated digital filter (Nathan and MacMahon, 1990; Arnold and others, 1995).

This recursive digital filter technique was originally used in signal analysis and processing (Lyne and Hollick, 1979) and has no true physical basis. It is, however, objective and reproducible for continuous base flow separation (Nathan and McMahon, 1990). In contrast, manual separation of a streamflow hydrograph into surface runoff and groundwater flow is difficult and inexact, with results that are often not reproducible by investigators (White and Sloto, 1990).

Filtering surface runoff (high frequency signals) from base flow is analogous to filtering high frequency signals in signal analysis and processing. The equation of the filter is

$$q_t = \beta\, q_{t-1} + (1+\beta)/2 \times (Q_t - Q_{t-1})\,, \qquad (2)$$

where q_t is filtered surface runoff (quick response) at t time step, β is the original filter parameter, and Q_t is the original streamflow. Base flow, b_t, is calculated with the equation

$$b_t = Q_t - q_t\,. \qquad (3)$$

We compared hydrographs of estimated base flow to rainfall events to determine responses of the aquifer materials to rainfall prior to its discharge to the river. We also compared trends in the historical rainfall record to long-term changes in the water levels in the Brazos River Alluvium Aquifer wells.

To estimate recharge rates, we used the chloride mass balance approach (Allison and Hughes, 1978; Scanlon, 1991, 2000; Scanlon and others, 2002; Philips, 1994). The mass of chloride into the system (precipitation and dry fall out, P) times the chloride in precipitation (C_p) is balanced by the mass out of the system (drainage, D) times the chloride concentration in the drainage water in the unsaturated zone (C_{uz}) (Scanlon and others, 2002). If surface runoff is assumed to be zero, then

$$PC_p = DC_{uz}\,. \qquad (4)$$

Similarly, recharge rates can be determined using chloride in the precipitation, precipitation amount, and groundwater chloride, assuming that most of the chloride in groundwater is essentially derived from precipitation, using the following equation:

$$R = P \times Cl_p / Cl_{gw}\,, \qquad (5)$$

where R = regional historical recharge rate, P = amount of precipitation, Cl_p = chloride concentration in precipitation, and Cl_{gw} = chloride concentration in groundwater.

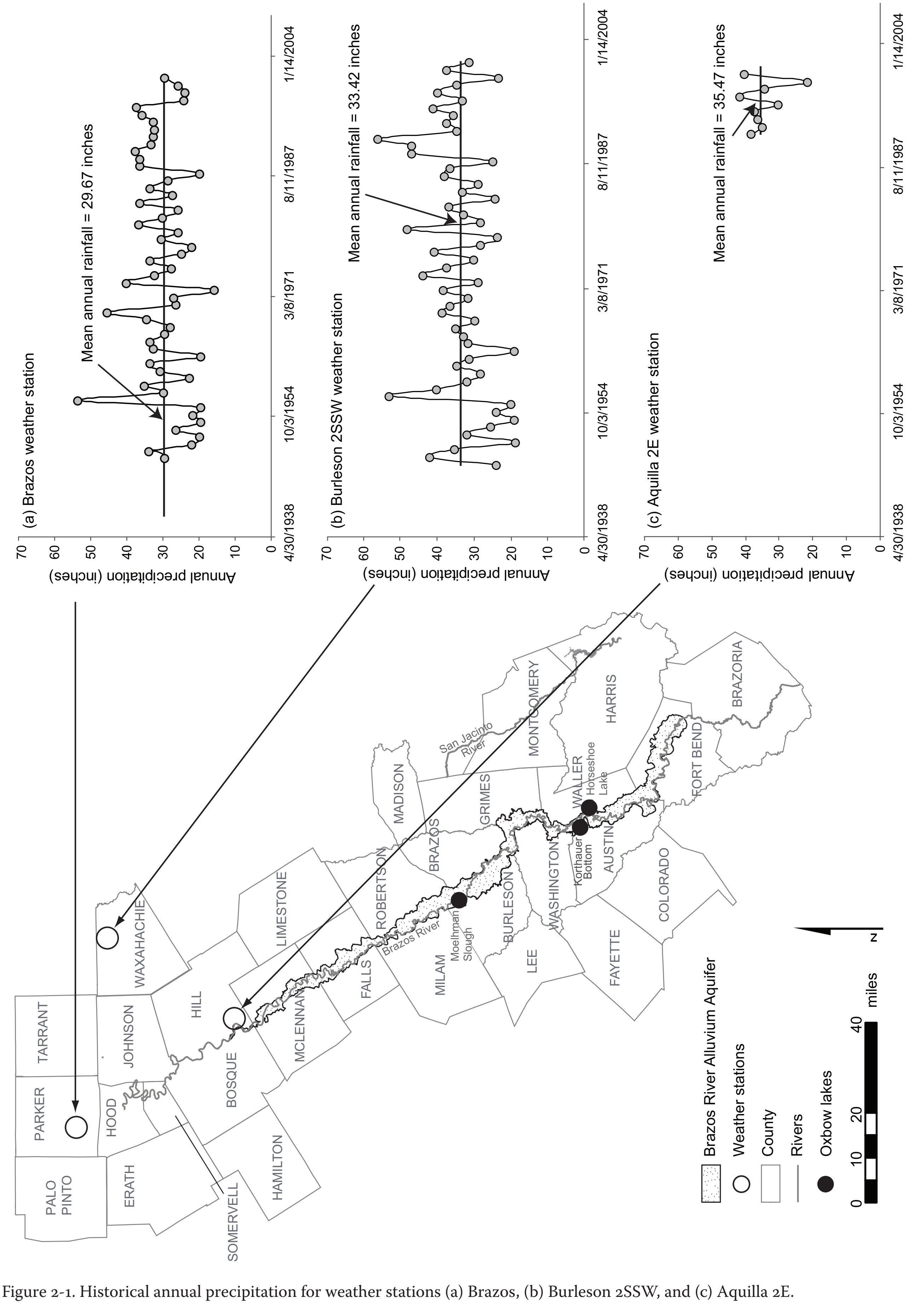

Figure 2-1. Historical annual precipitation for weather stations (a) Brazos, (b) Burleson 2SSW, and (c) Aquilla 2E.

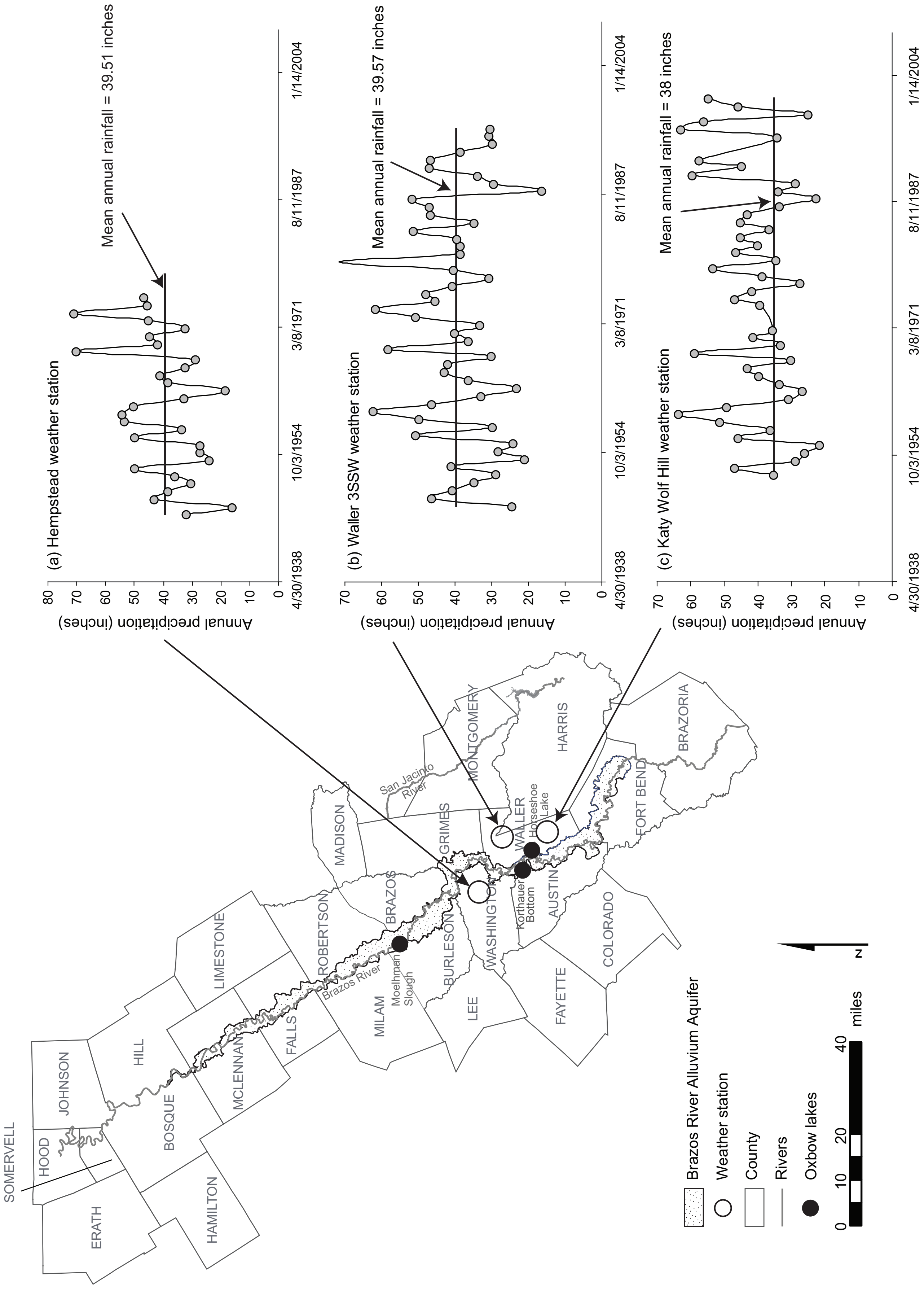

Figure 2-2. Historical annual precipitation for weather stations (a) Hempstead, (b) Waller 3SSW, and (c) Katy Wolf Hill.

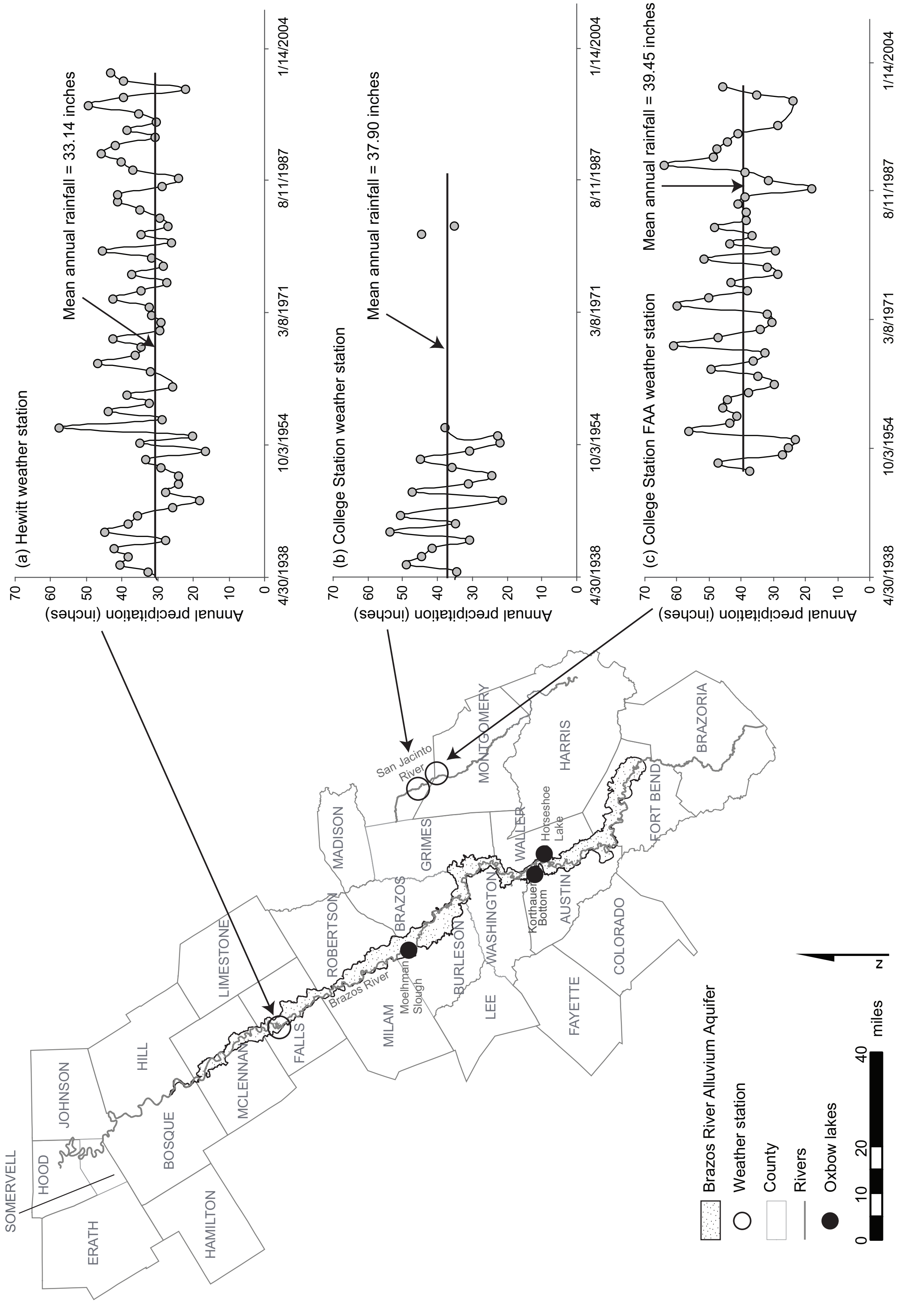

Figure 2-3. Historical annual precipitation for weather stations (a) Hewitt, (b) College Station, and (c) College Station Federal Aviation Administration.

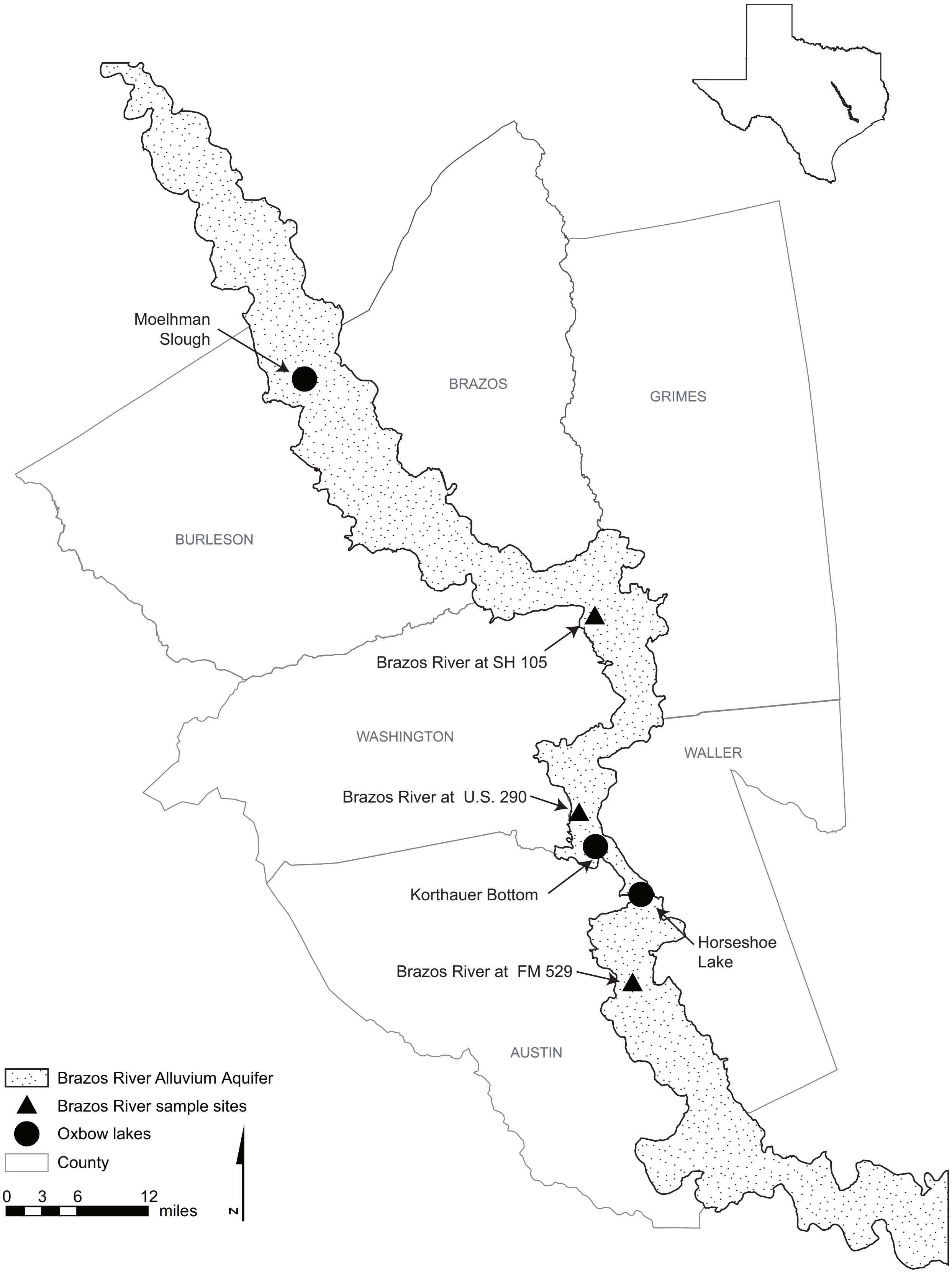

Figure 2-4. Map of the Brazos River sample sites.
SH = State Highway; FM = Farm to Market

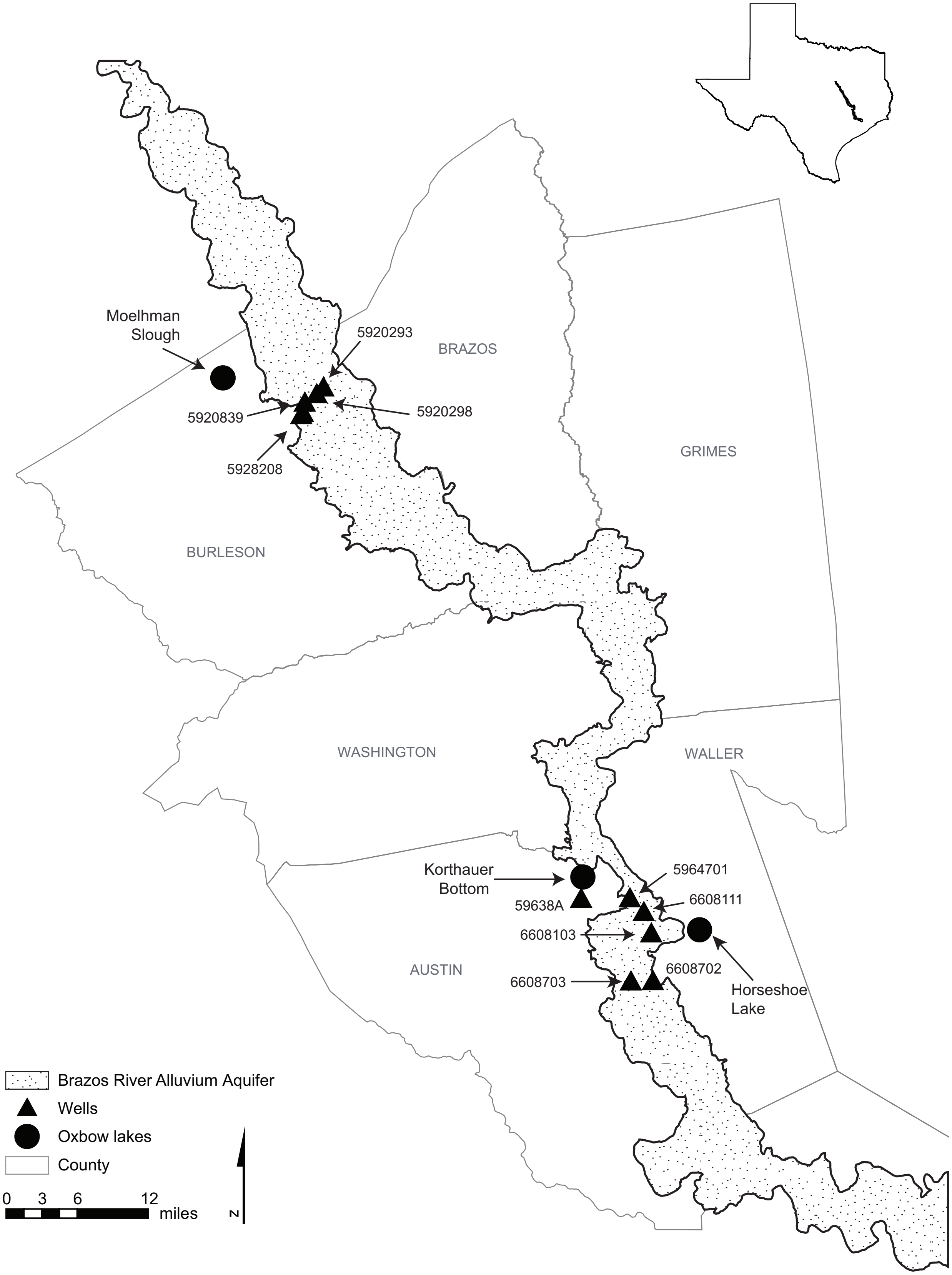

Figure 2-5. Map of well locations selected for isotope analyses.

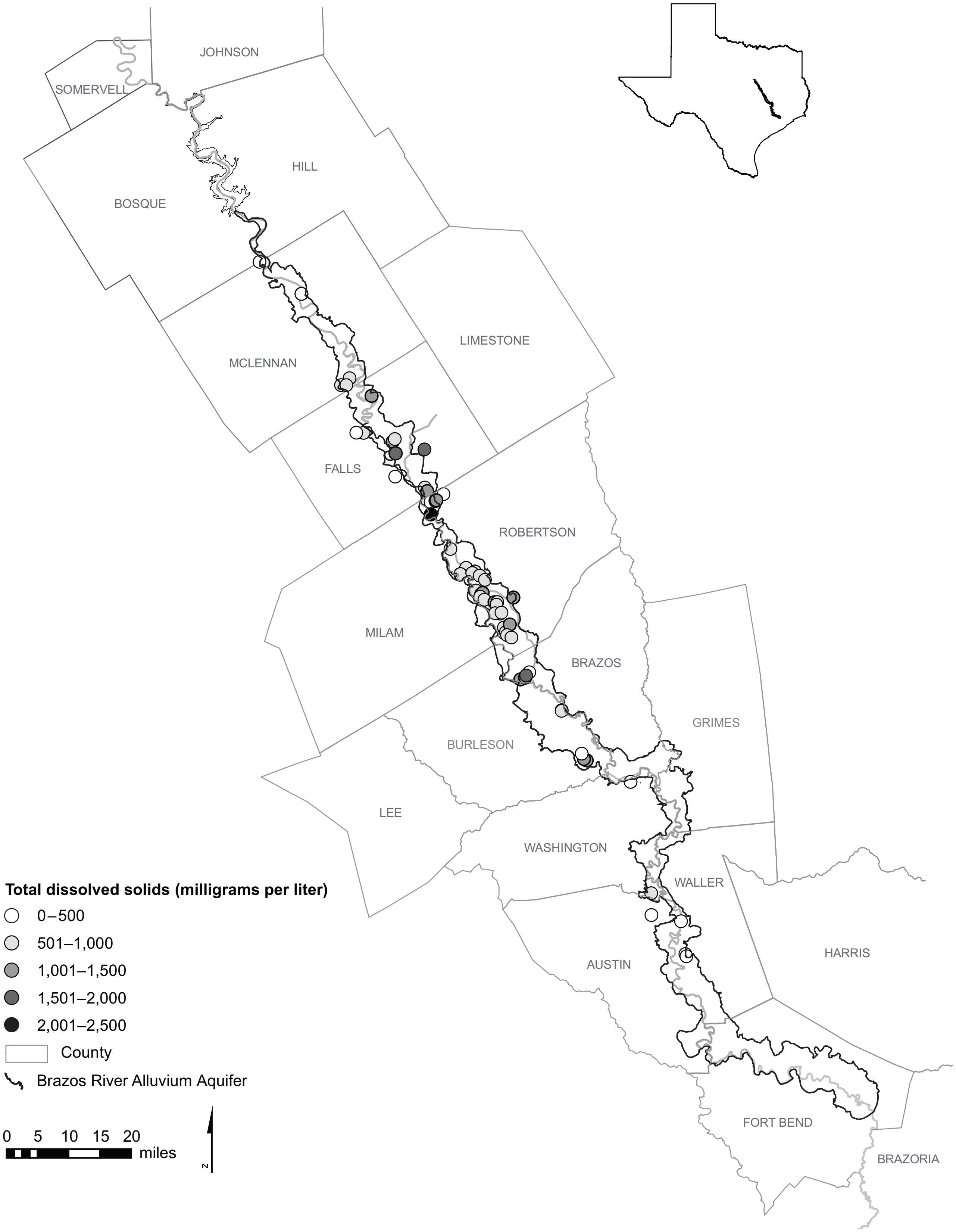

Figure 2-6. Map showing total dissolved solids concentrations in the Brazos River Alluvium Aquifer.

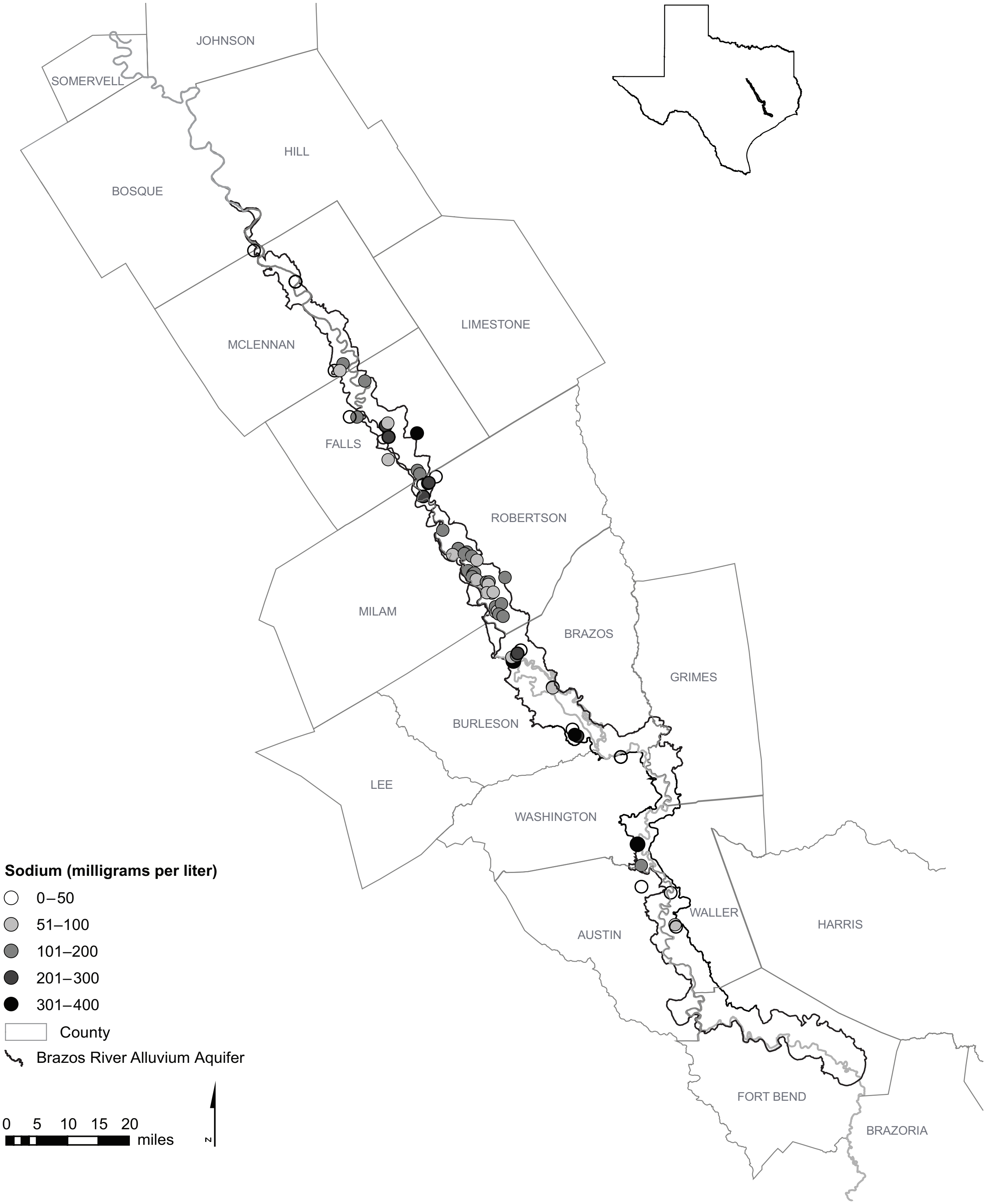

Figure 2-7. Map showing sodium concentrations in the Brazos River Alluvium Aquifer.

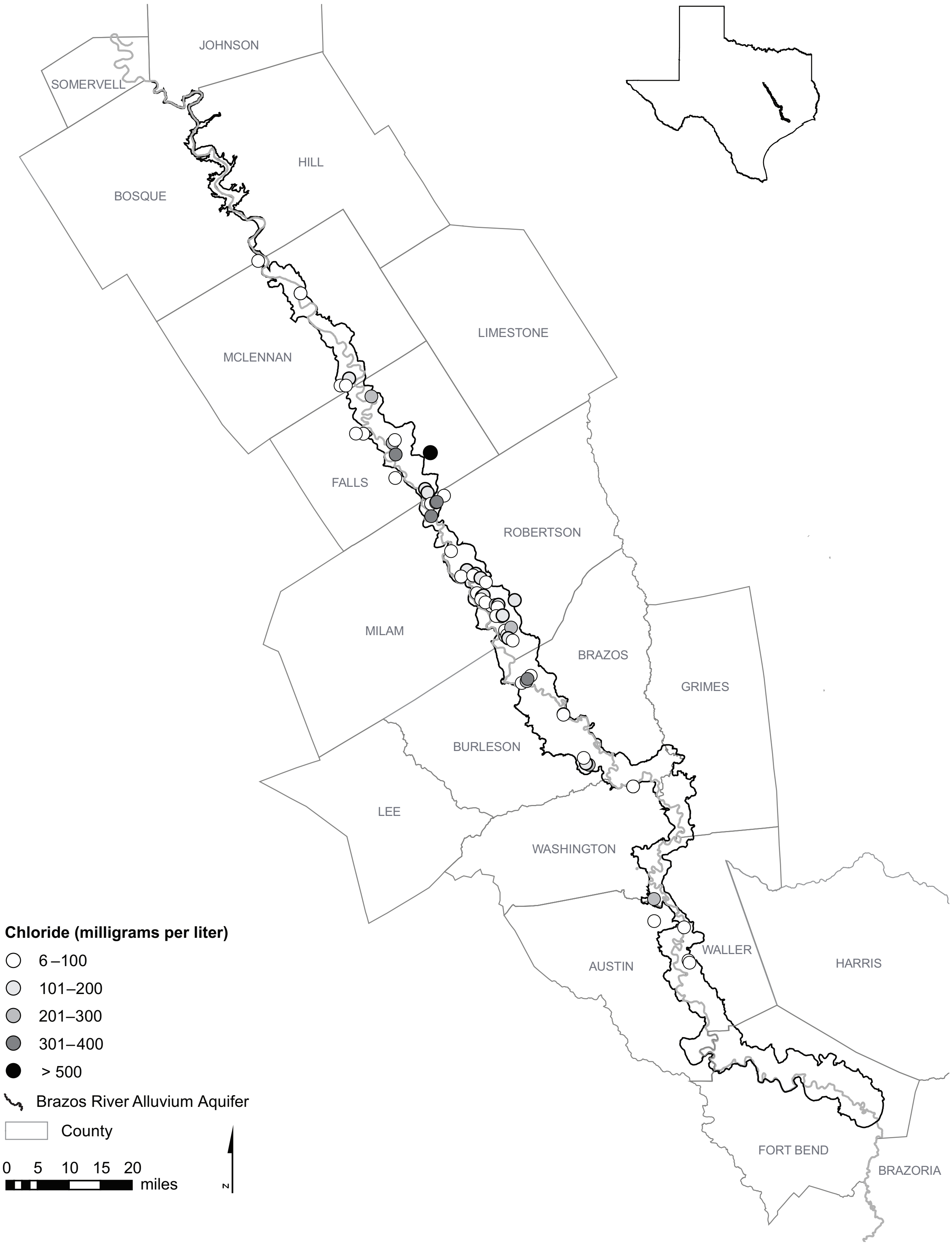

Figure 2-8. Map showing chloride concentrations in the Brazos River Alluvium Aquifer.

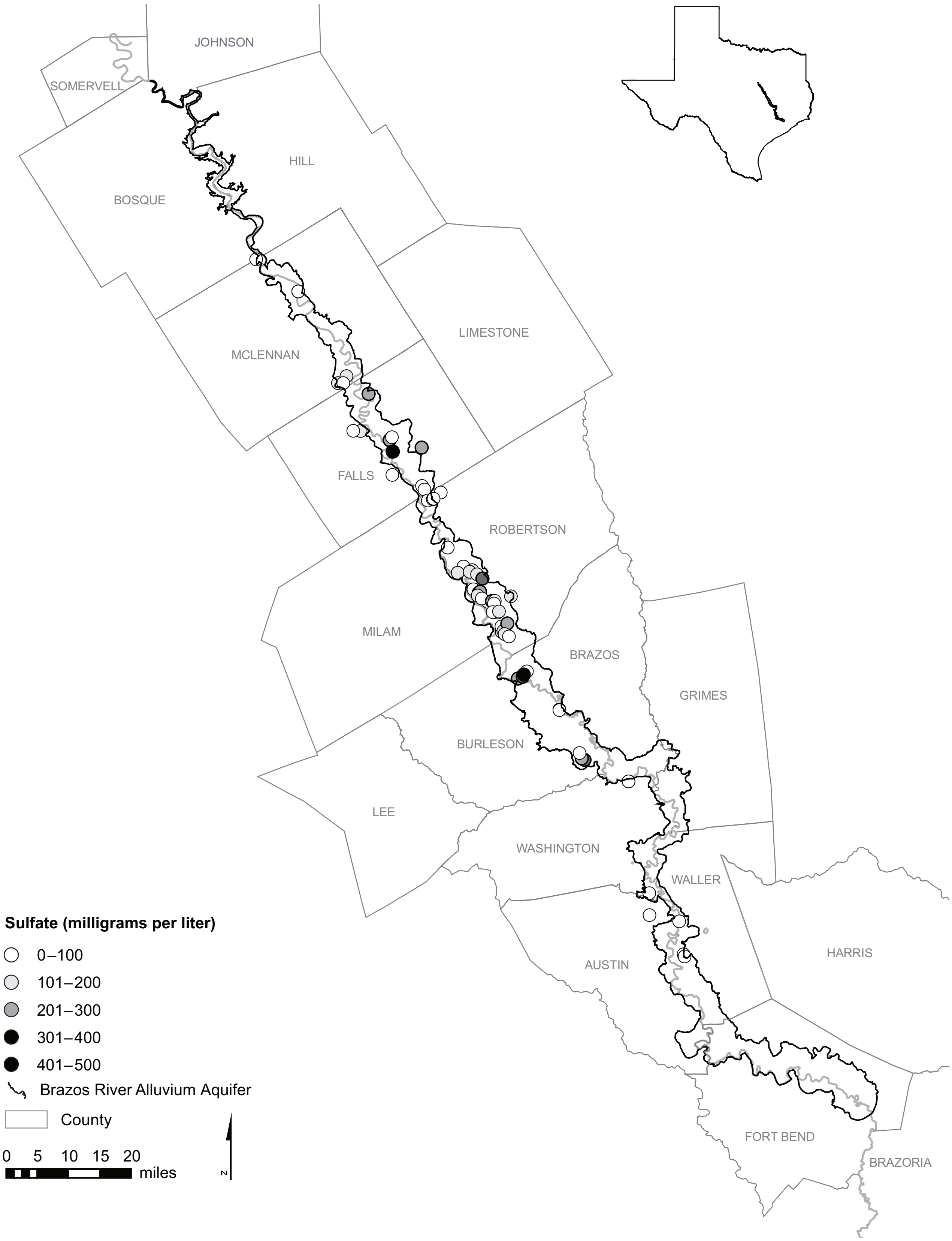

Figure 2-9. Map showing sulfate concentrations in the Brazos River Alluvium Aquifer.

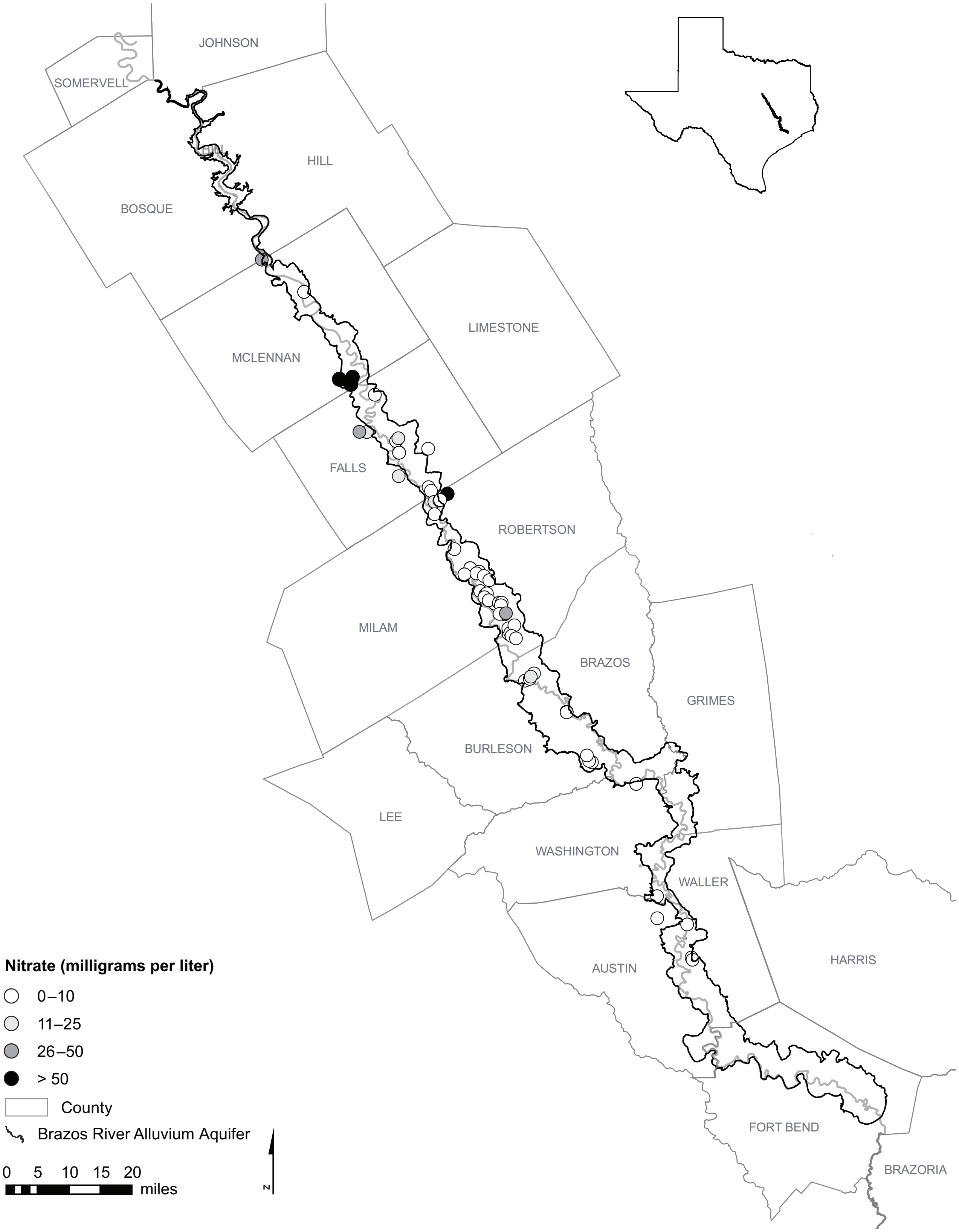

Figure 2-10. Map showing nitrate concentrations in the Brazos River Alluvium Aquifer.

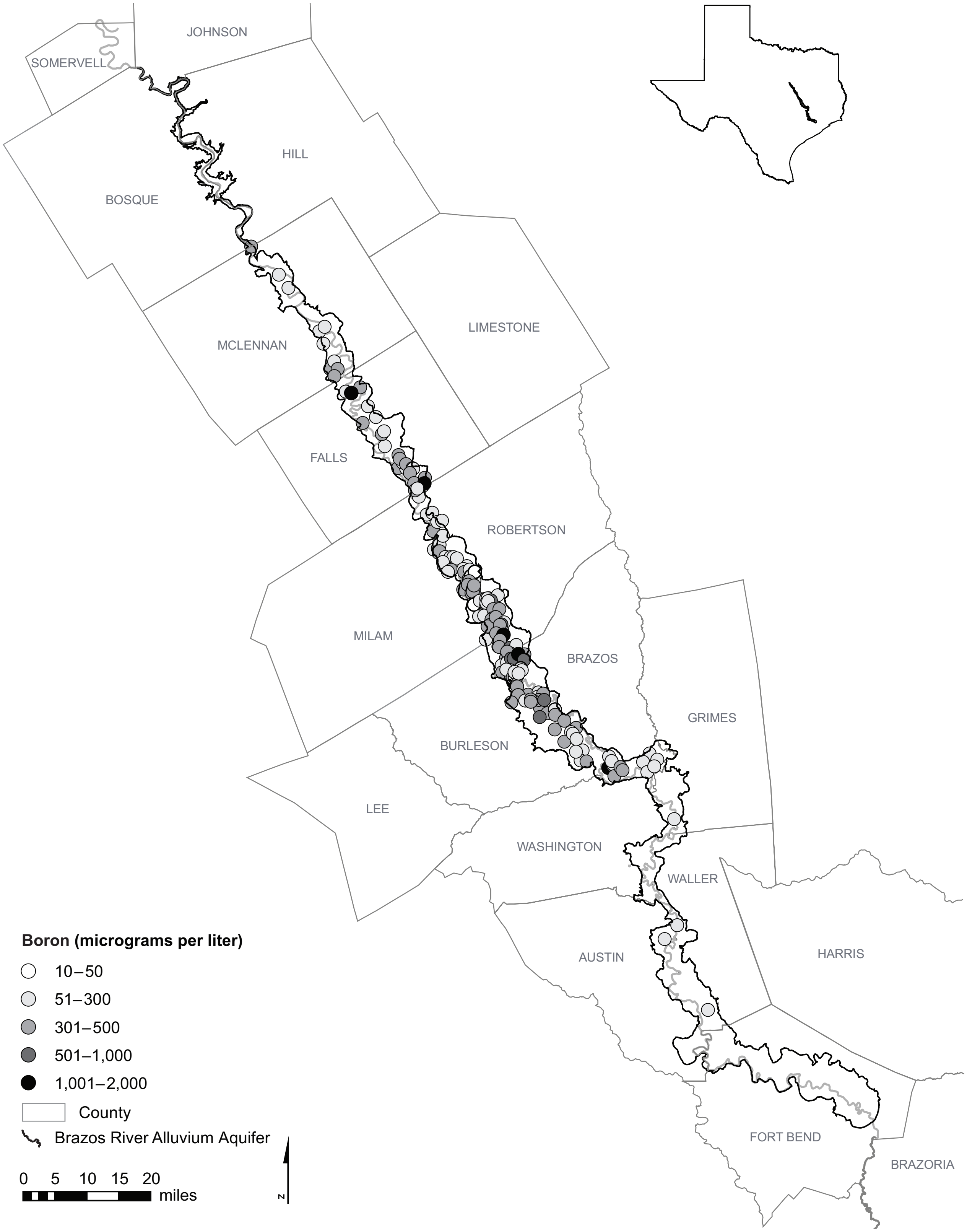

Figure 2-11. Map showing boron concentrations in the Brazos River Alluvium Aquifer.

3 *Description of the Brazos River and oxbow lakes*

The headwaters of the Brazos River are at the foot of the south plains near the Texas-New Mexico border. The river rises at the confluence of its Salt Fork and Double Mountain Fork and runs 840 miles across Texas to its mouth on the Gulf of Mexico, two miles south of Freeport in Brazoria County (Hendrickson, 2001). The two forks emerge from the Caprock 150 miles above the confluence, thus forming a continuous watershed 1,050 miles long, which extends from New Mexico to the Gulf of Mexico and comprises 44,620 square miles, 42,000 of which are in Texas. It is the third longest river in Texas and has the greatest discharge (Hendrickson, 2001). The Brazos River Basin can be divided into 14 major sub-watersheds, including the Caprock, the Double Mountain Fork/Salt Fork of the Brazos, the Clear Fork of the Brazos, the Upper Brazos River, the Bosque River, the Leon River, the Lampasas River, the Aquilla River, the Navasota River, the Central Brazos River, the Little River, the Yegua Creek, the Lower Brazos River, and the Upper Oyster Creek watersheds (Figure 1-2).

The Brazos River flows through a semiarid region near the border with New Mexico. Precipitation in this area is either absorbed by area soils or is contained in the hundreds of playa lakes. Due to low precipitation and chronic low-flow conditions, this region is generally not a contributing source of flow for the remainder of the Brazos River Basin (Brazos River Authority, 2005). The basin spans three climatological zones, with average annual precipitation varying from 15 to 25 inches per year in the northern part and 45 to 50 inches per year in the southern part of the basin. Topography ranges from just over 4,385 feet above sea level in the northern part of the basin to near sea level at the confluence with the Gulf of Mexico (Brazos River Authority, 2005).

Numerous flood control and water supply reservoirs located mainly in the upstream areas of the Brazos River Basin potentially change the natural hydrologic flow system. However, the flow regime in the lower portion of the Brazos River Basin remains similar to the historical flow primarily because the nearest on-channel reservoir, Lake Whitney, is located several hundred miles upstream (Osting and others, 2004b).

The lower Brazos River is characterized as an incised, sand bed channel that meanders through the Holocene and Pleistocene deposits of the Gulf Coastal Plain. Like any typical meandering alluvial channel, river flow erodes cohesive materials on the concave side (outer bend) of the river and deposits sandy and silty materials on the convex side (inner bend) of each bend (Osting and others, 2004b) (Figure 3-1). The slope of the river in the lower basin is about 0.7 feet per mile (Dunn and Raines, 2001).

Moelhman Slough is located about 1.4 miles downstream from the U.S. Geological Survey streamflow gaging station 08108700 near Bryan. The slough formed in the 1920s when it was 8 feet deep. Presently, it is 4 feet deep when not connected to the Brazos River. During flood events, significant quantities of water may not reach the slough until the water in the Brazos River has begun flowing through the main channel. Moelhman Slough is located in the outcrop areas of the Carrizo-Wilcox Aquifer.

Korthauer Bottom is located about 10.5 miles downstream of the U.S. Geological Survey streamflow gaging station 08111500 on the Brazos River near Hempstead. The lake is located in the outcrop areas of the Gulf Coast Aquifer. The majority of connections to the Brazos River occur during the spring.

Horseshoe Lake is located about 15.8 river miles downstream of the U.S.

Geological Survey streamflow gaging station 08111500 on the Brazos River near Hempstead. The lake is located in the outcrop areas of the Gulf Coast Aquifer on a plateau and rarely connects to the Brazos River (Osting and others, 2004a).

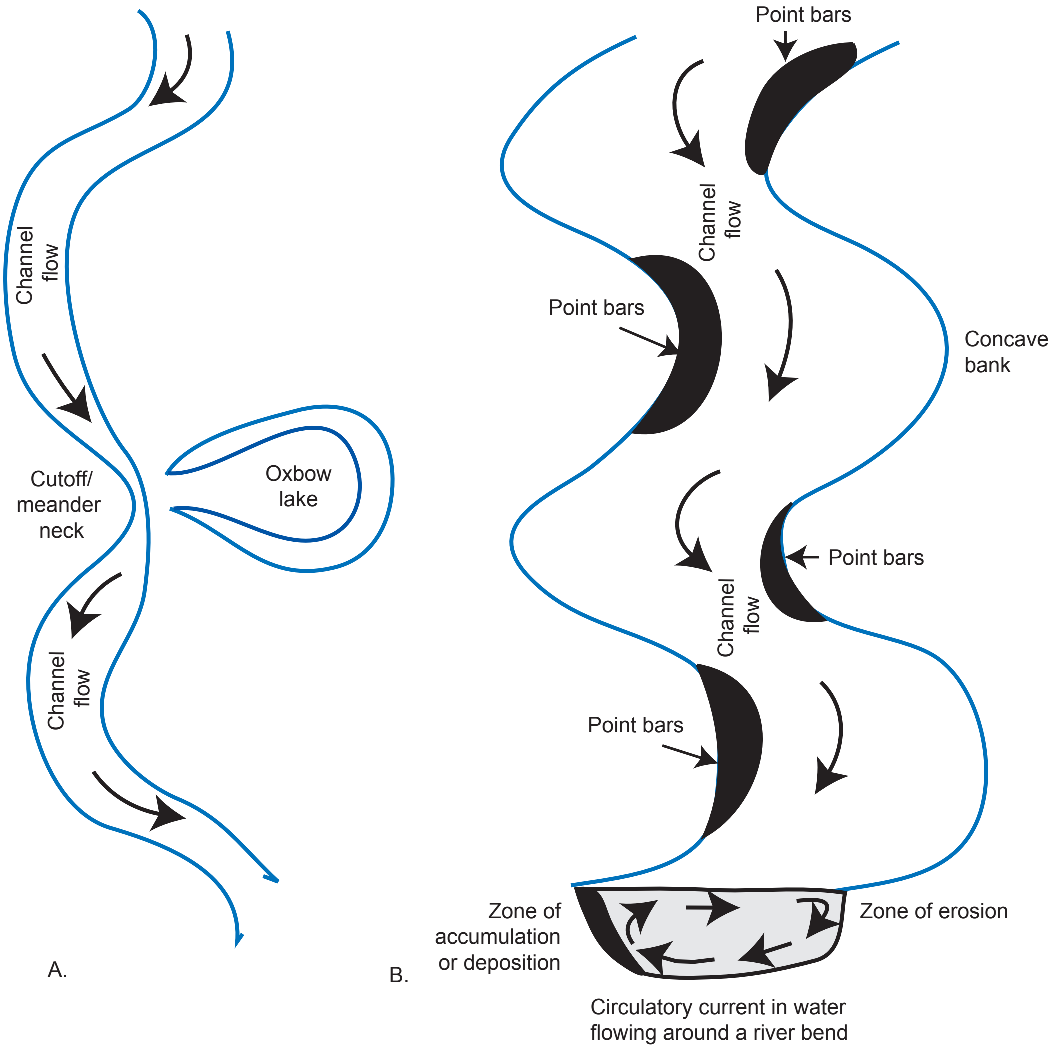

Figure 3-1. Sketch of a meandering channel (A) that shows formation of an oxbow lake as erosion eats through a meander neck forcing a cutoff from the main channel and areas of erosion and deposition along the banks of the main channel (B).

4 *Hydrogeologic setting*

We describe geology, hydraulic properties of the aquifer materials, groundwater recharge characteristics, water quality, and regional groundwater flow direction in the following section.

4.1
GEOLOGY, HYDRAULIC PROPERTIES, RECHARGE, AND WATER QUALITY

The Brazos River Alluvium Aquifer hosts large quantities of groundwater along the river between northern McLennan and central Fort Bend counties in Texas. The floodplain alluvium consists predominantly of gravel and fine to coarse sand, with lesser amounts of clay and silt. Generally, fine-grained sediments occur at the top, and coarser-grained sediments occur at the base of the unit. Maximum thickness of the alluvium is about 100 feet, with an average thickness of about 45 feet (Ryder, 1996). The thickness of the alluvium increases downstream (Ryder, 1996). It is thin in McLennan and Falls counties and thicker along the east than the west side of the river (Shah and others, 2007a). Locally, the alluvium may be as much as 130 feet thick in Fort Bend County, but in several areas along the Brazos River the alluvium is as thin as 20 feet (Shah and others, 2007a). The width of the alluvium across the river valley varies from about 1 mile in the upstream region to about 8 miles in the downstream areas. Groundwater from the alluvial aquifer is primarily used for irrigation.

The alluvial deposits are of Quaternary age and overlie rocks that range in age from Permian to Quaternary. The underlying rocks dip toward the Gulf of Mexico and contain several major aquifers that crop out parallel to the coast: the Queen City, Sparta, Carrizo-Wilcox, and Gulf Coast aquifers.

Hydraulic properties of the aquifer materials in the alluvium are highly variable, with permeability values determined in the laboratory, ranging from 0.0001 to 2,406 feet per day. The lower values represent clay, and the higher values represent gravel (Cronin and Wilson, 1967). Transmissivity measurements range from about 1,000 to 28,000 square feet per day (average 5,600 feet squared per day) based on 351 specific capacity measurements. Specific yield measurements range from 4 to 35 percent, with an average of 24 percent (Cronin and Wilson, 1967). To simulate water levels in the central Carrizo-Wilcox groundwater availability model, Dutton and others (2003) used a hydraulic conductivity of 20 feet per day for the alluvium. More recently, Shah and others (2007a) compiled hydraulic conductivity and specific capacity information for the Brazos River Alluvium Aquifer. They observed that hydraulic conductivity ranges from about 180 to 447 feet per day based on 7 measurements. Specific capacity values range from less than 1 to 1,460 gallons per day per foot based on 358 measurements. Transmissivity of the aquifer ranges from 289 to about 24,000 square feet per day (Shah and others, 2007a).

Recharge to the alluvial aquifer is mainly derived from precipitation that falls on the floodplain and alluvial terraces. Estimates of recharge range from 2 to 5 inches per year (Cronin and Wilson, 1967). Cronin and Wilson (1967) estimated recharge by determining differences in groundwater flow between upstream and downstream sections of the saturated alluvium between two successive flow lines, which they assumed equal to the infiltration from precipitation. However, groundwater flow modeling studies report much lower recharge rates of 0.3 to 0.4 inches per year (Dutton and others, 2003). Rainfall in the area ranges from 32 to 43 inches per year, and the alluvium in some areas is readily recharged under normal conditions. The average annual rate of recharge is estimated at about 155,000 acre-feet per year for a five-year period (1957 to 1961) (Cronin and Wilson, 1967).

Water in the Brazos River Alluvium Aquifer is generally fresh, with most of the water containing total dissolved solids of less than 1,000 milligrams per liter (Figure 2-6). Higher salinity groundwater containing dissolved solids in excess of 1,500 milligrams per liter occurs from Marlin to Bryan (Figure 2-7). High chloride and sulfate also occur locally throughout the alluvium (Figures 2-8 and 2-9). Most of the groundwater has less than 10 milligrams per liter in nitrate concentrations (Figure 2-10). However, nitrate as high as 300 milligrams per liter occurs in the aquifer along the McLennan and Falls County line. Boron concentrations range from 10 to 2,000 micrograms per liter in the aquifer, with the highest concentrations occurring near Bryan (Figure 2-11).

4.2

WATER LEVELS AND GROUNDWATER FLOW

Using data sets from TWDB's groundwater database, we compiled water level measurements and constructed water level maps for the Brazos River Alluvium Aquifer. We included water level measurements from 1960 through 2000. If multiple measurements were available, we included the measurement closest to winter to offset pumping effects on water levels.

Water levels in the area generally follow the topography, with higher water levels occurring at higher ground elevations and lower water levels at lower ground elevations. Although the Brazos River Alluvium Aquifer is mainly unconfined, artesian conditions are present where there are extensive clay lenses. The depth to the water table in the aquifer ranges from near land surface to 60 feet below the land surface (Figure 4-1). Near the oxbow lakes, the water table in the aquifer lies at depths of 30 to 45 feet.

Water level elevations in the Brazos River Alluvium Aquifer range from 230 feet in Burleson County to 110 feet in Waller County. The aquifer's water levels generally lie above the river stage, and water from the aquifer discharges into the river as base flow under normal hydrologic conditions. However, during high-water stages in the river, the gradient is temporarily reversed locally over small areas adjacent to the stream, and water from the river infiltrates into the aquifer. Locally, lowering of the artesian pressure in the Carrizo-Wilcox, Queen City, and Sparta aquifers has caused a downward flow of the groundwater from the alluvium (Cronin and Wilson, 1967).

Water levels in the alluvium slope toward the river with a hydraulic gradient of 3×10^{-4} to 9×10^{-4} (Figure 4-2). Hydrographs from several wells show no long-term changes in the water levels (Figures 4-3 and 4-4). Although a few wells show responses in water levels that mimic precipitation events, others only show changes in water levels due to pumping. Significant changes in water levels (30 to 40 feet) over short periods of time were observed in a few wells, presumably caused by pumping, as irrigation wells are extensively used in the summer in Falls, Robertson, Brazos, and Burleson counties.

Water levels in the Gulf Coast, Queen City, and Sparta aquifers that lie beneath the Brazos River Alluvium follow the topographic gradient and discharge near the Brazos River. In many areas, the Brazos River Alluvium is very thin (Cronin and Wilson, 1967; Shah and others, 2007a), which would allow direct upward discharges from the aquifers to the ground surface. For example, groundwater moves from the upland areas in the outcrop areas of the Carrizo-Wilcox Aquifer toward the river bottomlands (Dutton and others, 2003).

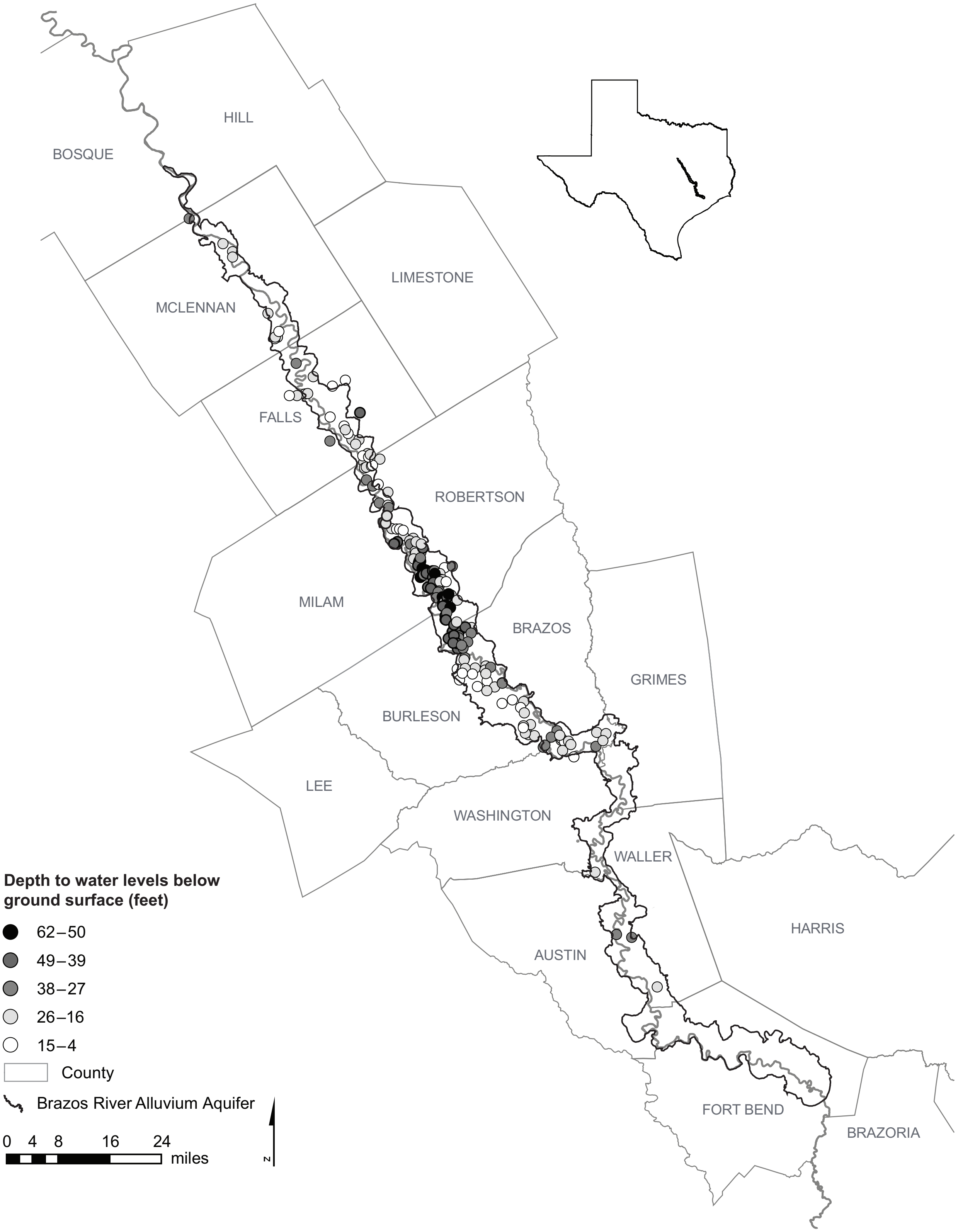

Figure 4-1. Map of water levels expressed as depth below ground surface (includes water level measurements from 1960 to 2000).

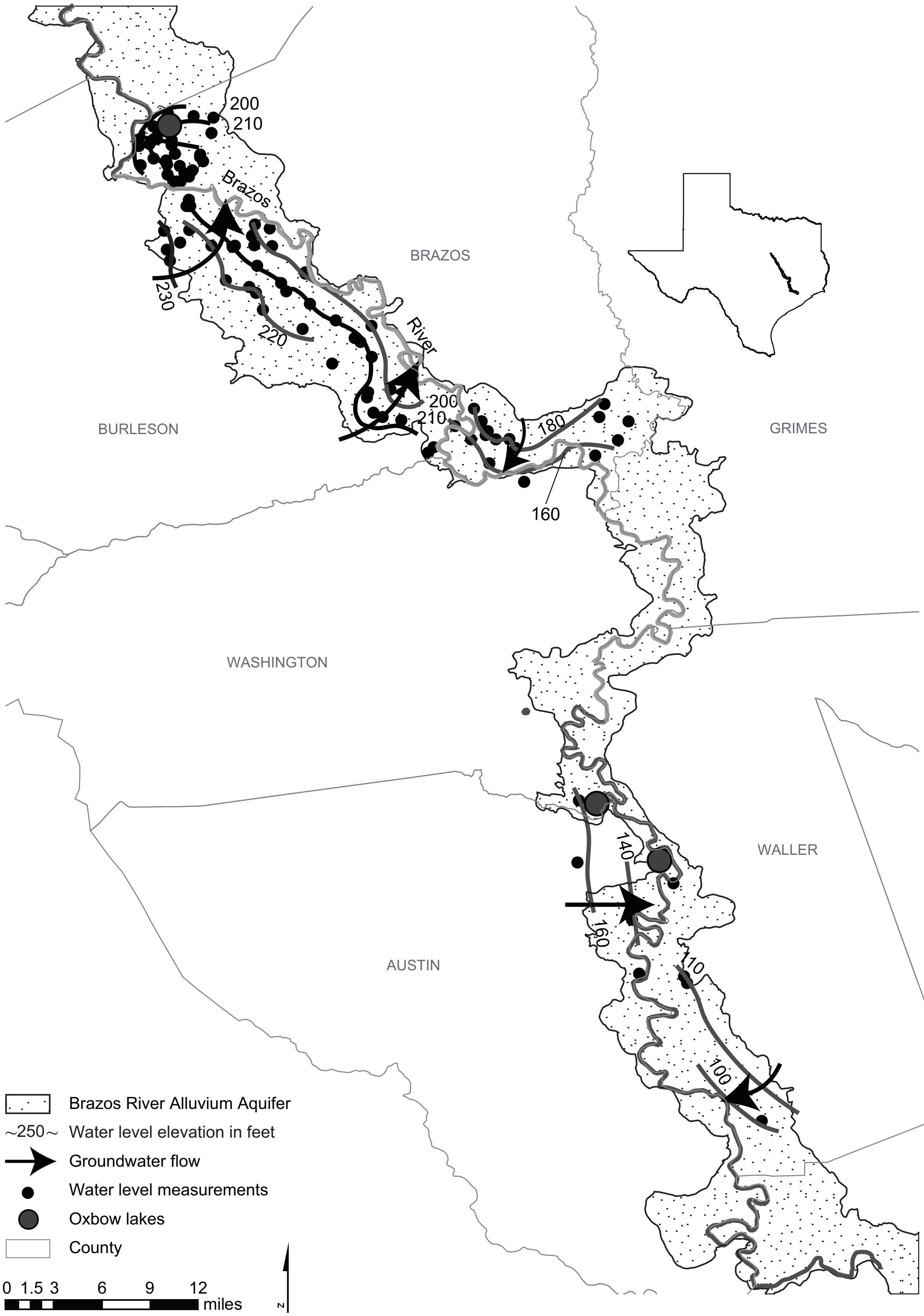

Figure 4-2. Water level elevation map of the Brazos River Alluvium Aquifer (includes water level measurements from 1960 to 2000).

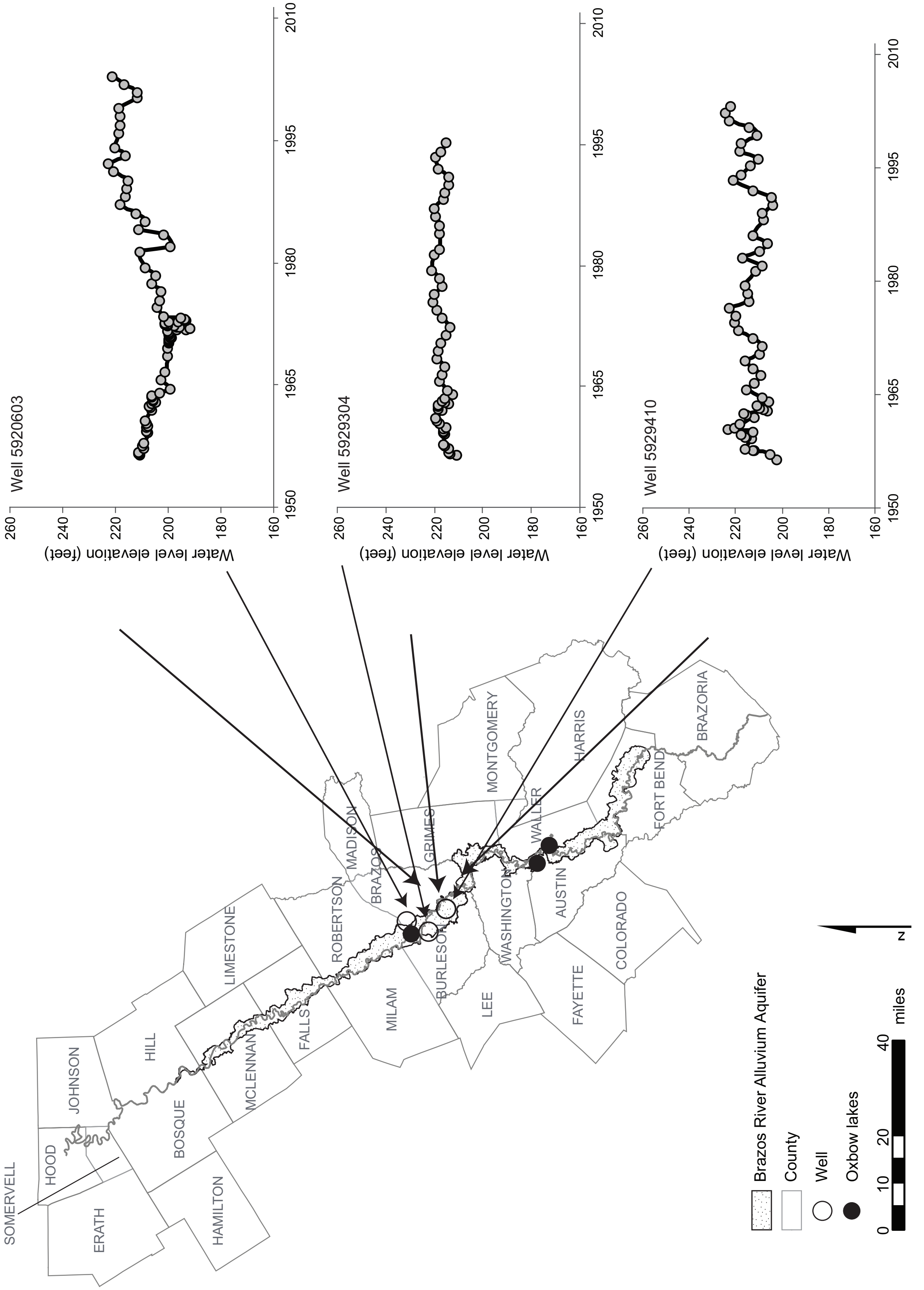

Figure 4-3. Hydrographs of water levels from the Brazos River Alluvium Aquifer wells.

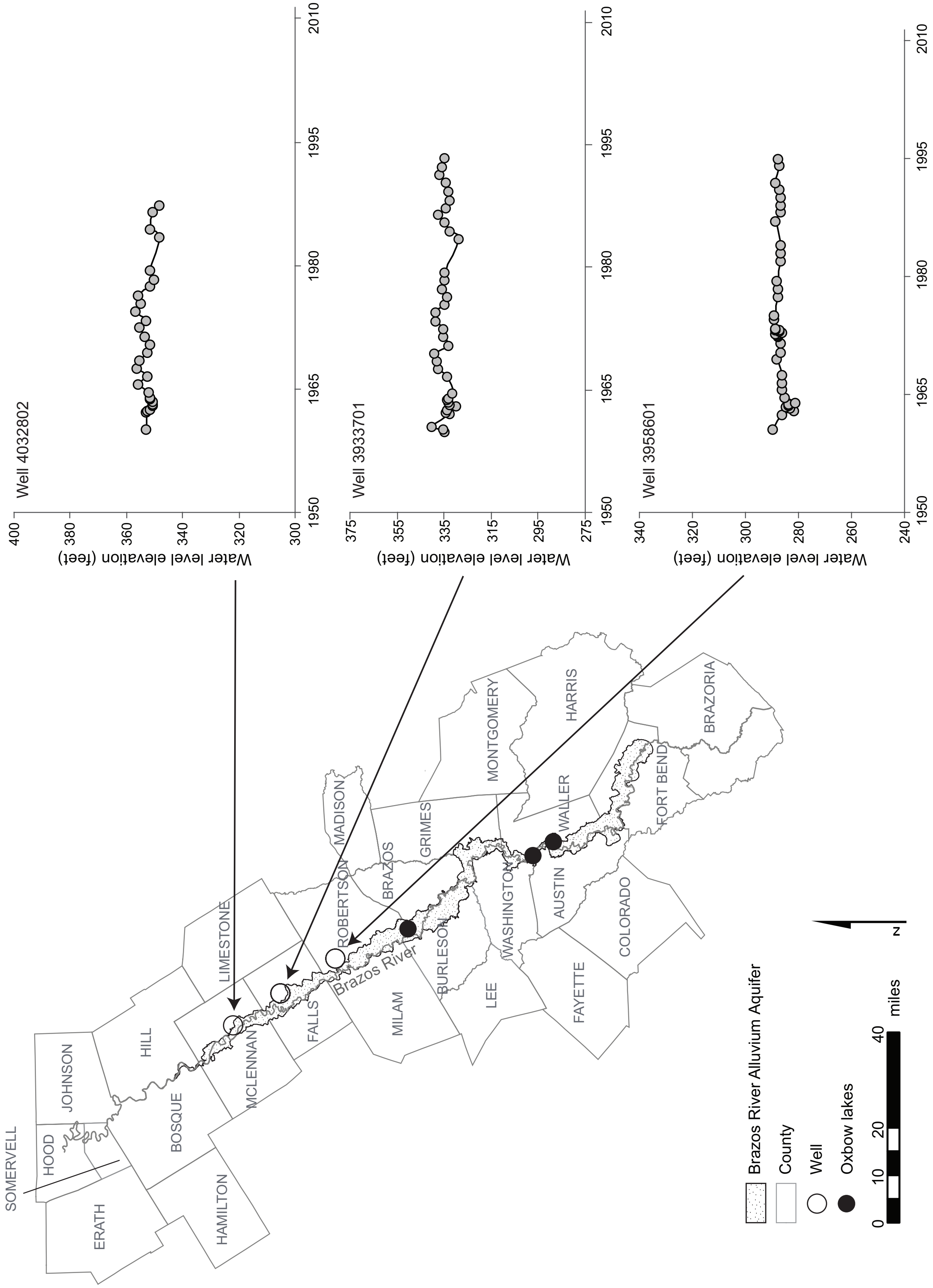

Figure 4-4. Hydrographs of water levels from the Brazos River Alluvium Aquifer wells.

5 *Results*

In this section, we report (1) historical measurements of surface water connections between the oxbow lakes and the Brazos River, (2) estimates of groundwater recharge using base flow analyses and chloride mass balance method, and (3) water chemistry data used to establish possible hydraulic connections between the oxbow lakes, Brazos River, and the adjacent aquifers.

5.1
SURFACE WATER CONNECTIVITY

Measurements from pressure transducers suggest that Moelhman Slough was connected to the Brazos River on three occasions from December 2003 through September 2004 (Figures 5-1 and 5-2). Analyses of streamflow records from 1934 to 2004 suggest that Moelhman Slough would have been frequently connected to the Brazos River, particularly over the last 20 years, with each connection lasting an average of four days (Osting and others, 2004a). This analysis assumes no historical change to the control point elevation (the water level at which river water spills into the oxbow lake) over the period of this analysis. The natural progression of sedimentation processes are toward complete infill of each oxbow, which causes the connection elevation to rise over time. As a result, the actual number and duration of historical connections are uncertain. The validity of this assumption was not addressed in this project.

Analyses of historical streamflow records from 1938 to 2004 indicate Korthauer Bottom would have been connected to the Brazos River much more frequently than was Moelhman Slough, with each connection lasting an average of eight days (Figure 5-3), given unchanging connection levels (Osting and others, 2004a). Most connections would have occurred from March through May.

Horseshoe Lake would have had the fewest connections with the Brazos River for the historical record of 1938 to 2004 (Figure 5-4). Over the entire period, only five connections would have occurred, with most probably occurring before 1970.

5.2
ESTIMATED BASE FLOW, RECHARGE, AND GROUNDWATER FLOW VELOCITY

Base flow is the amount of water that discharges from the shallow parts of an aquifer into a stream. Determining the amount of base flow in a stream is useful in estimating recharge, basin evapotranspiration, and aquifer storage parameters, such as storage coefficient, diffusivity, and transmissivity (Arnold and others, 1995). We separated base flow values from streamflow for two gages on the Brazos River using an automatic digital filter (Arnold and others, 1995).

Base flow values derived from using the digital filter range from 125 to 12,107 cubic feet per second for streamflow gaging station 08108700, with an average of 1,601 cubic feet per second (Table 5-1 and Figure 5-5). For gaging station 08111500, base flow ranges from 62 to 24,535 cubic feet per second, with an average of 2,397 cubic feet per second (Table 5-1 and Figure 5-6). Only the low-flow values estimated from this analysis show a better match with the base flow values reported by Cronin and Wilson (1967). Using manual hydrograph separation techniques, Cronin and Wilson (1967) reported a base flow value of 46 cubic feet per second, or about 0.38 cubic feet per second per mile, between Waco and Bryan and 46 cubic feet per second, or 0.55 cubic feet per second per mile, between Marlin and Bryan.

We estimated recharge for each drainage area using results from base flow analyses. The drainage area for gages 8108700 and 8111500 is estimated at 29,843 and 34,314 square miles, respectively. By assigning the base flow amount to the drainage areas, we estimate that the recharge amount for the drainage areas ranges from 0.02 to 9.7 inches per year (Table 5-1). We assumed that recharge equals base flow, which is not necessarily true, because pumpage, evapotranspiration, and groundwater flow to the deeper parts of the aquifers may affect base flow determination (Scanlon and others, 2002). Recharge values from our study, however, are similar to previously published values for the Brazos River Alluvium Aquifer (Cronin and Wilson, 1967; Dutton and others, 2003). For example, Cronin and Wilson (1967) estimated recharge that ranges from 1.8 to 5.3 inches per year, with an average of 3 inches per year for Falls, Robertson, and Burleson counties. They contended that recharge values may have been overestimated because irrigation return flow was included in the recharge calculation. Dutton and others (2003) estimated a much lower recharge value of 0.3 to 0.4 inches per year for the Brazos River Alluvium, using estimates of annual precipitation and soil permeability for modeling the central part of the Carrizo-Wilcox Aquifer.

When we compare mean monthly base flow data from 1938 to 2006 to the rainfall amount recorded at a nearby weather station, we observe no distinct relationship between them (Figure 5-7).

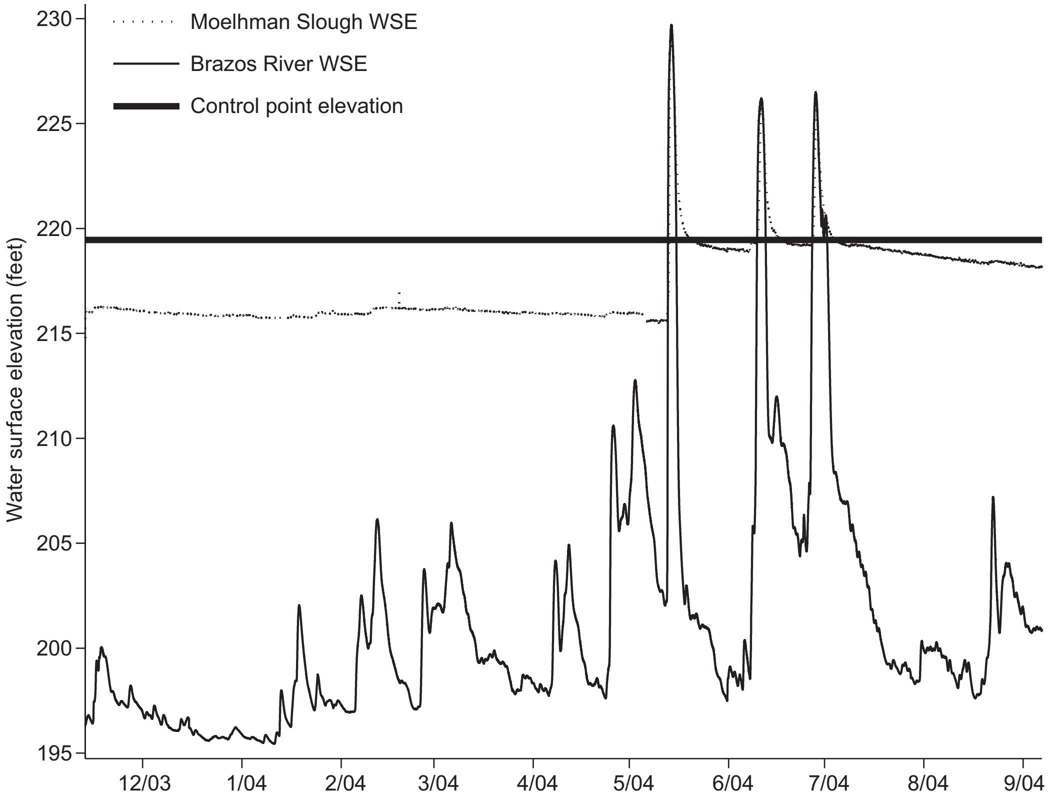

Figure 5-1. Water surface elevations of the Brazos River and Moelhman Slough as measured by U.S. Geological Survey streamflow gaging station 08108700 and temporary pressure transducers installed near the slough (December 2003 through September 2004).
WSE=water surface elevation

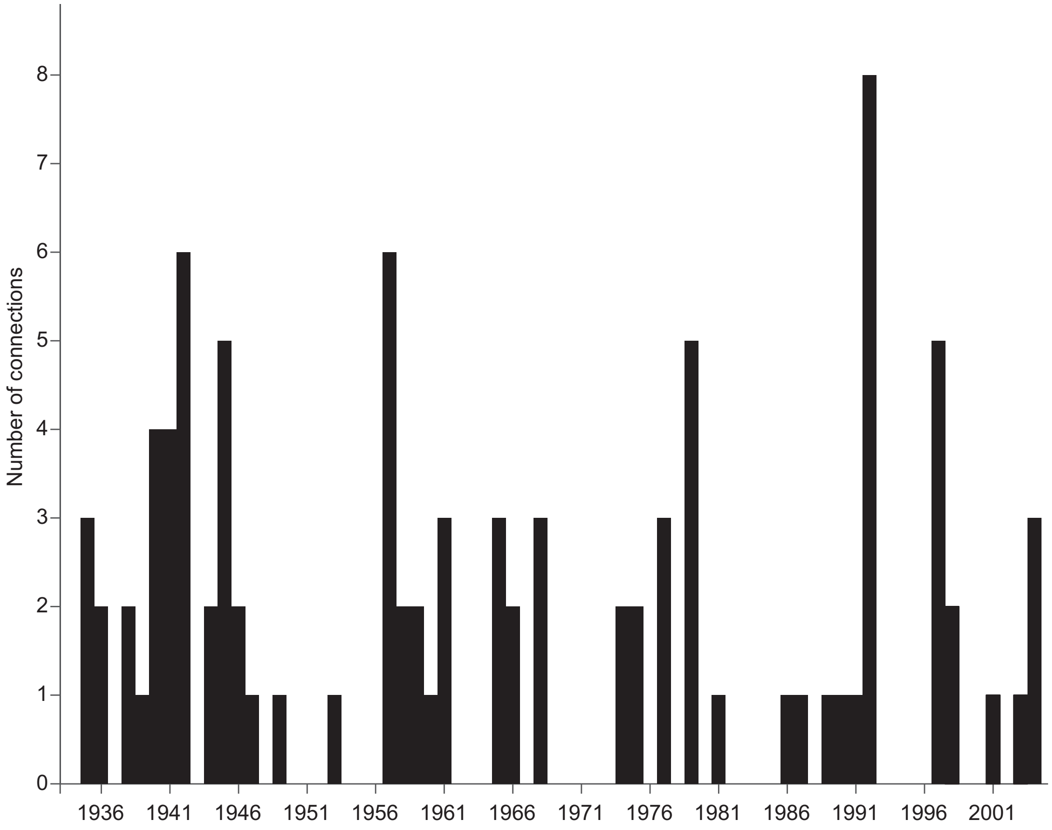

Figure 5-2. Histogram showing annual connections between the Brazos River and Moelhman Slough based on streamflow data from 1934 to 2004. Data before 1993 is approximate.

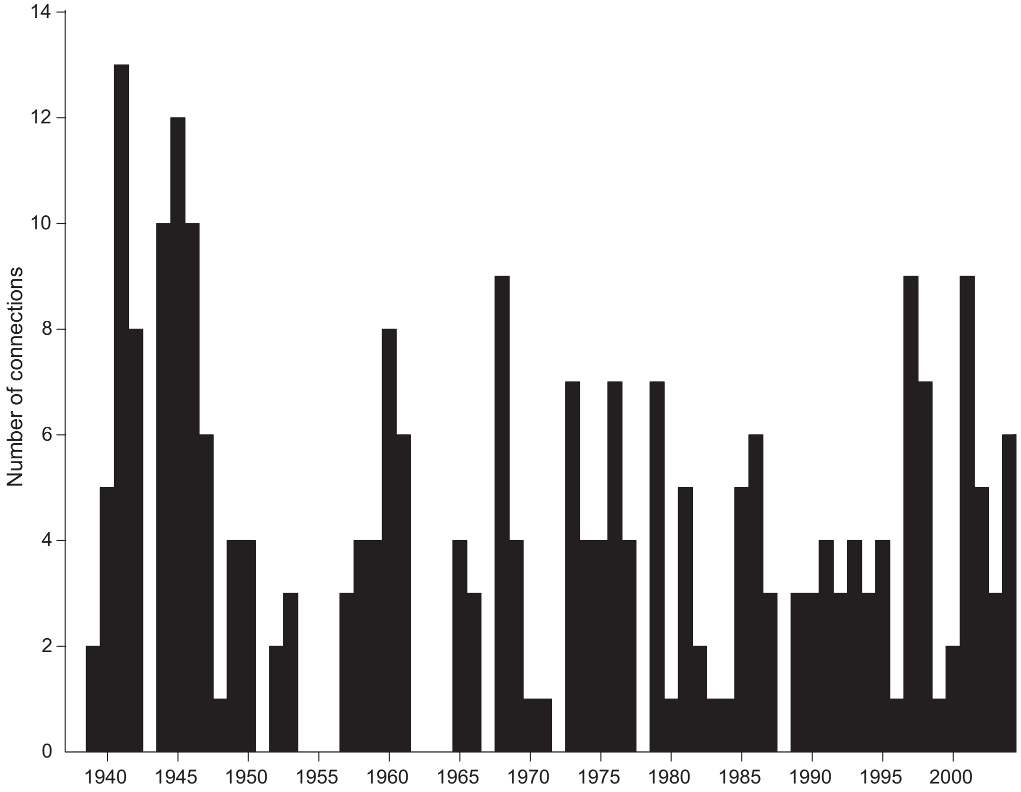

Figure 5-3. Histogram showing annual connections between the Brazos River and Korthauer Bottom based on streamflow data from 1938 to 2004. Data before 1995 is approximate.

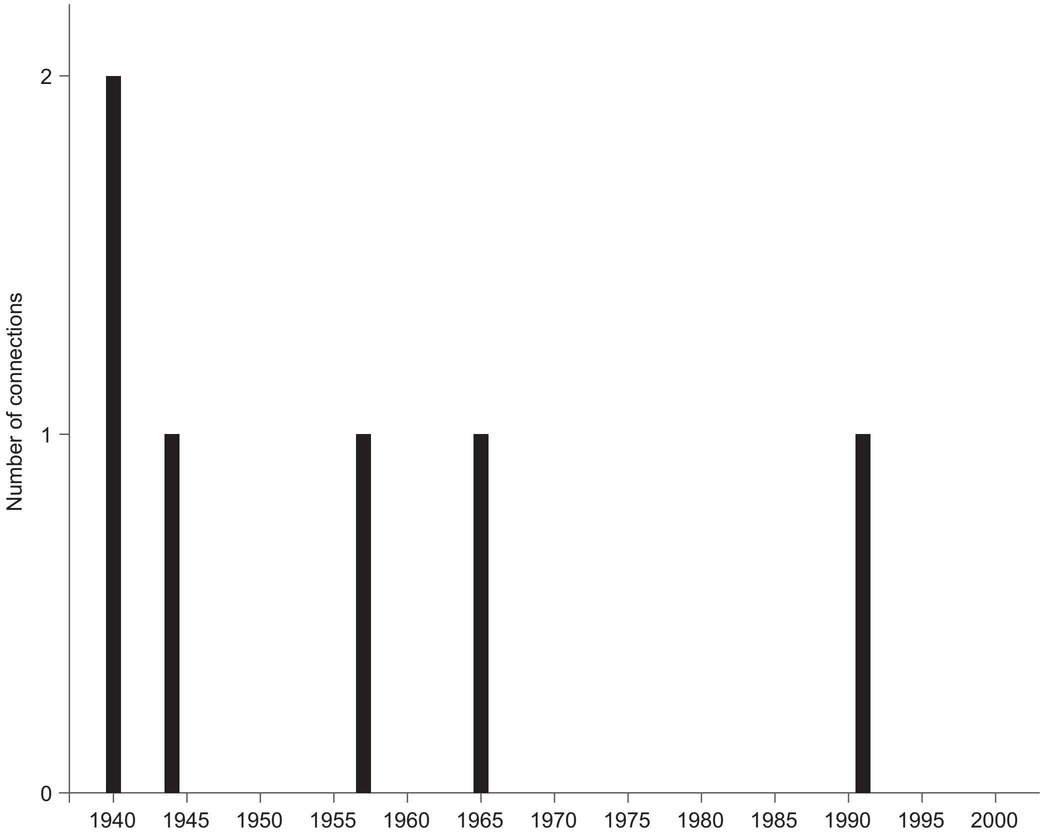

Figure 5-4. Histogram showing annual connections between the Brazos River and Horseshoe Lake based on streamflow data from 1940 to 2000. Data before 1995 is approximate.

Table 5-1. Estimated recharge from selected streamflow gaging stations and previous studies.

	Base flow (cfs)			Recharge (in/yr)				
Year	Min.	Max.	Avg.	Min.	Max.	Avg.	Method	Source
1994–2004[a]	125	12,107	1,601	0.06	5.57	0.74	Digital base flow separation	This study
1934–1998[b]	62	24,535	2,397	0.02	9.70	0.95	Digital base flow separation	This study
				0.11	3.39	0.33	Chloride mass balance	This study
1957–1961				1.80	5.30	3.50	Flow between lines	Cronin and Wilson (1967)
				0.30	0.40	0.35	Groundwater model	Dutton and others (2003)

[a] Base flow estimates for streamgage 8108700 near Bryan

[b] Base flow estimates for streamgage 8111500 near Hempstead

cfs = cubic feet per second; in/yr = inches per year; Min. = minimum; Max. = maximum; Avg. = average

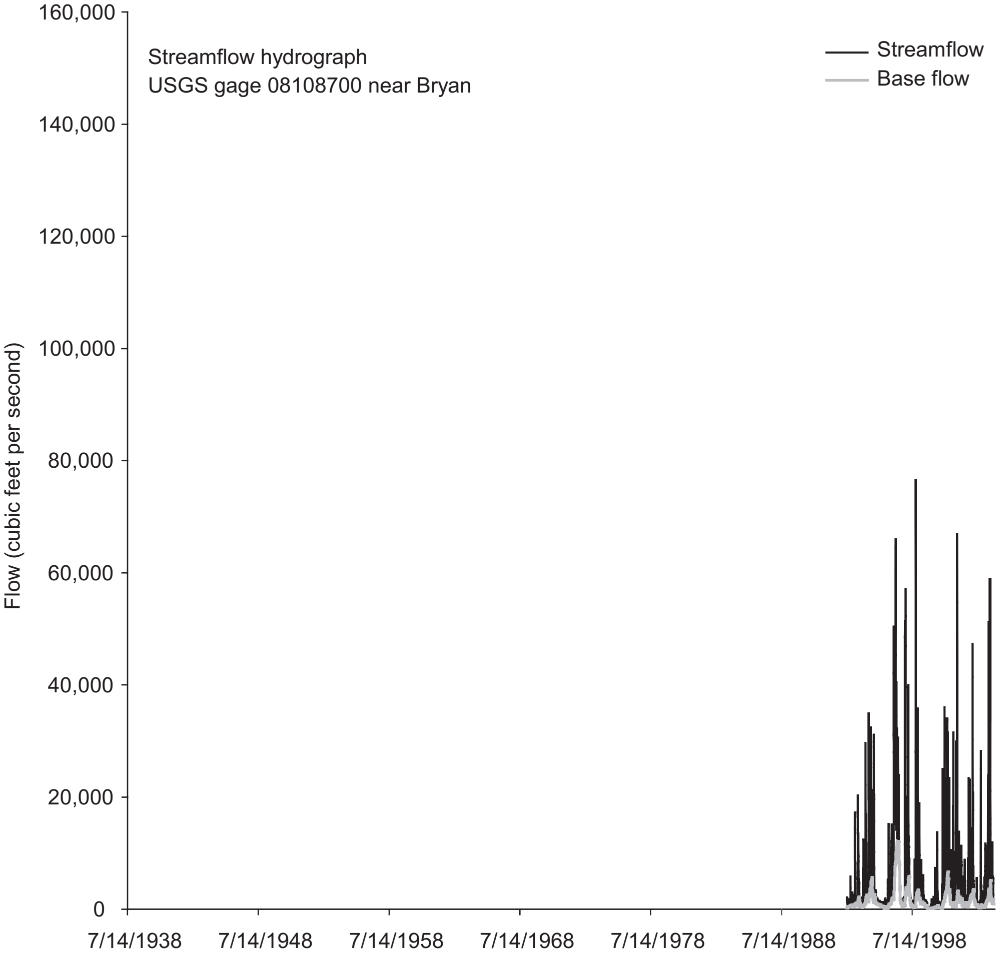

Figure 5-5. Measured streamflow and estimated base flow hydrograph for streamflow gaging station 08108700 near Bryan.
USGS=U.S. Geological Survey

For example, in part of the historical record (1) peaks in maximum base flow either show a substantial offset with the peaks of the maximum rainfall or (2) base flow appears subdued when the rainfall record shows considerable precipitation. Therefore, base flow discharges may be affected by areas of clay lenses that retard rapid recharge. The development of base flow and/or bank storage may release substantial discharge when there is no record for adequate precipitation.

In an unconsolidated, transmissive aquifer in hydraulic connection with the land surface, rain water readily infiltrates into and moves across the aquifer. In such aquifers, rainfall and water levels show a direct correlation, provided pumpage is insignificant. To evaluate any relationship that might exist between rainfall and aquifer water levels, we compared rainfall records with aquifer water levels from selected wells. Long-term trends in water level changes show responses to local precipitation in some wells, but no immediate responses are produced in water levels from short-term changes in precipitation. In other words, long-term records for years with high rainfall record show high water levels, and years with low rainfall records show low water levels (Figure 5-8). This suggests that there is a large time lag between rainfall events and arrival of the recharge water in the aquifer. Although pumping of the aquifer can also alter the baseline

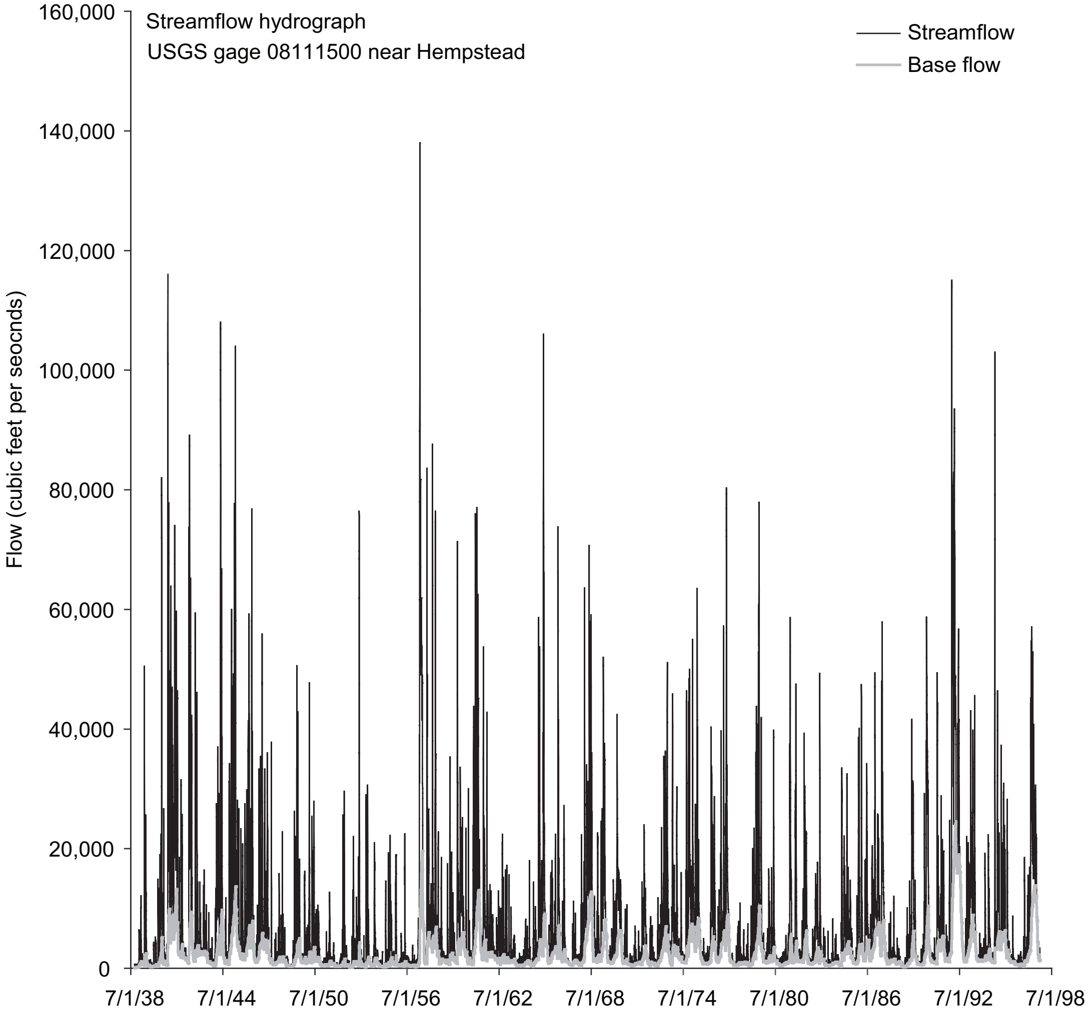

Figure 5-6. Measured streamflow and estimated base flow hydrograph for streamflow gaging station 08111500 near Hempstead.

USGS=U.S. Geological Survey

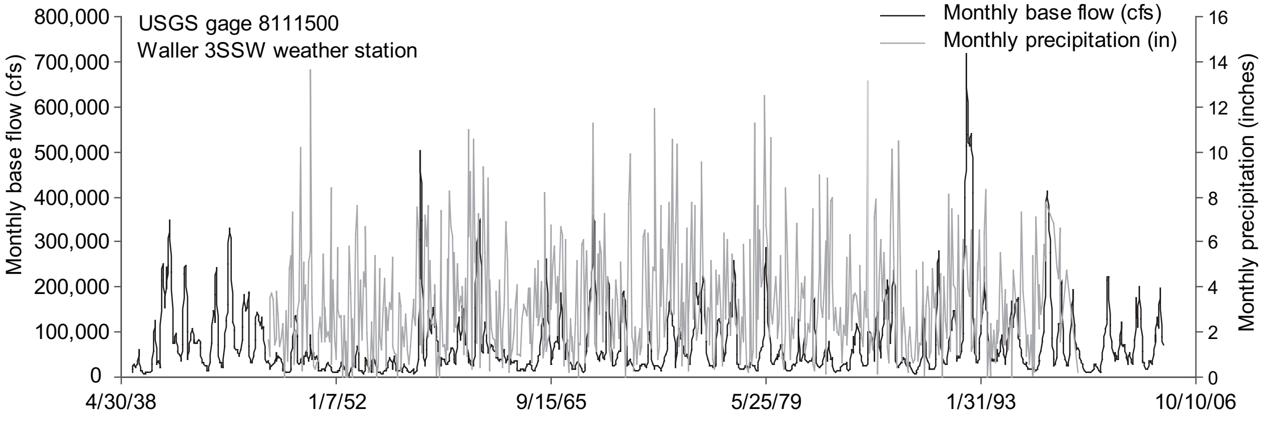

Figure 5-7. Relationship between mean monthly base flow and rainfall.

cfs=cubic feet per second; in=inches; USGS=U.S. Geological Survey

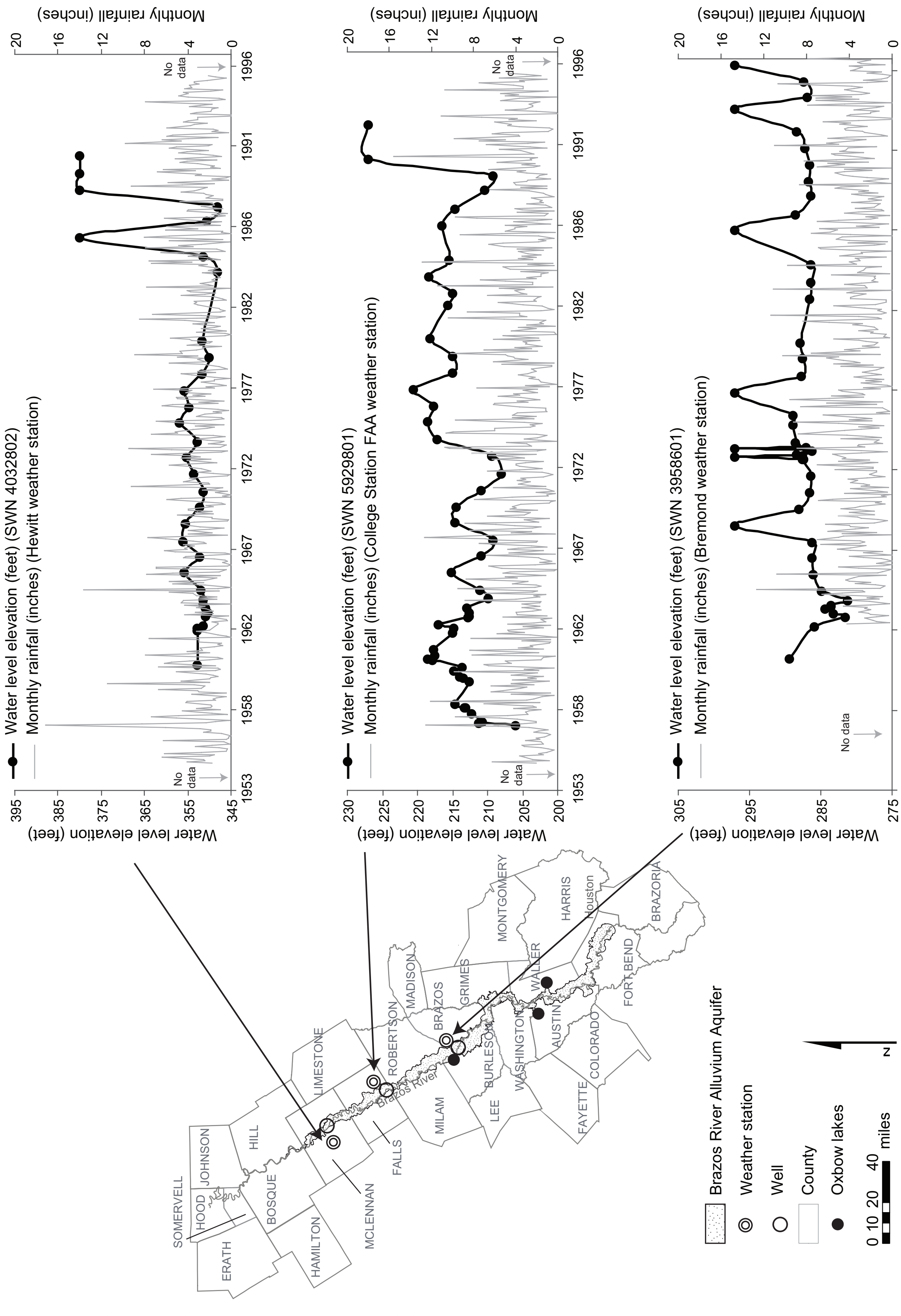

Figure 5-8. Relationship between monthly mean rainfall and water level elevations.
SWN=state well number; FAA=Federal Aviation Administration

water levels developed by precipitation recharge, this is unlikely given low pumpage along with the low recharge potential and hydraulic conductivity of the fine-grained alluvium.

In addition, we estimated recharge into the Brazos River Alluvium Aquifer using the chloride mass balance method (Scanlon and others, 2002), which includes precipitation amount, chloride in precipitation, and chloride in the groundwater (Table 5-2). However, if chloride in the groundwater is not directly derived from precipitation or is changed by soil processes or chemical reactions in the aquifer materials, then estimated recharge results may also be equally affected.

We estimate that recharge into the Brazos River Alluvium Aquifer ranges from 0.11 to 3.39 inches per year, with an average recharge of about 0.33 inches per year. These values are in general agreement with the recharge estimated from base flow and modeling studies.

We estimated average groundwater flow velocity in the alluvium using reported hydraulic conductivity and porosity and Darcy's Law with the following equation:

$$V = Ki/n, \tag{6}$$

where K is hydraulic conductivity (feet per day), i is hydraulic gradient, n is porosity, and V is groundwater flow velocity. Using an average hydraulic conductivity of 20 feet per day, hydraulic gradients of 3×10^{-4} to 9×10^{-4}, and an average porosity of 0.24, we estimate that groundwater flow velocity ranges from about 9 to 27 feet per year. However, Cronin and Wilson (1967) observed a higher flow velocity, ranging from 70 to 75 feet per year in the Brazos River Alluvium Aquifer, using the following equation:

$$v = \frac{PI}{7.48\,p}, \tag{7}$$

where v = velocity in feet per day, P = permeability in gallons per day per square feet, I = slope of the water table expressed in feet, and p = porosity in percent. They suggested that the flow velocity is likely to be variable throughout the Brazos River Alluvium Aquifer, as permeability of the aquifer materials and the slope of the water table varies spatially. Shah and others (2007a) also observed a sharp variability in the spatial distribution of hydraulic conductivity in the aquifer. They reported that the highest and lowest hydraulic conductivity values could be found at closely spaced wells in Burleson County.

Therefore, given the width of the alluvium (1 to 8 miles), the variability of aquifer transmissivity, and the slope of the water table, some of the recharge water from the alluvial aquifer may take a long time to discharge into the river as base flow. This observation is further supported from an absence of a direct relationship between rainfall, base flow, and water level changes in the aquifer.

Table 5-2. Estimated recharge in the Brazos River Alluvium Aquifer using the chloride mass balance method.

Amount	**Precipitation amount**[a]	**Chloride in precipitation (mg/l)**	**Chloride in groundwater**[b] **(mg/l)**	**Estimated recharge (in/yr)**
Minimum	34.85	0.66	6	0.11
Maximum	48.72	1.29	375	3.39
Average	40.70	1.15	139	0.33

[a] Precipitation amounts estimated from average precipitation record of 1970 to 2000 (Narasimhan and others, 2005). Chloride in precipitation was downloaded from the National Atmospheric Water Deposition Web site.

[b] Chloride data from wells completed in the Brazos River Alluvium Aquifer.

in/yr = inches per year; mg/l = milligrams per liter

5.3
WATER CHEMISTRY

Groundwater composition in an aquifer is controlled by residence time of the flow system, aquifer mineralogy, and the degree of chemical reactions between the groundwater and the aquifer minerals. In a highly transmissive sand and gravel aquifer, recharge infiltrates rapidly and moves quickly through the flow system, retaining the composition of the rain water. However, recharge infiltrates slowly in an aquifer with poor transmissivity, leading to slow groundwater movement, a longer residence time of groundwater, and increased groundwater salinity resulting from chemical reactions. In addition, when the water table is at or near the surface, groundwater salinity increases as evapotranspiration removes water. Agricultural activities may also affect groundwater salinity by the infiltration of irrigation return flow, which is commonly enriched with dissolved solids and nutrients.

Groundwater in the Brazos River Alluvium Aquifer appears more saline from Marlin to Bryan than in the southern parts of the aquifer where salinity progressively decreases. Higher salinity in the groundwater in these areas could be caused in part by agricultural activities in Falls, Robertson, Brazos, and Burleson counties. For example, Cronin and Wilson (1967) reported that as much as 73,000 acres over the Brazos River Alluvium Aquifer were irrigated between Whitney Dam and Richmond. However, irrigated acreages in most of these counties have declined over the last several years (TWDB, 2001) (Figure 5-9). Therefore, it is unlikely that agricultural activities are contributing to the groundwater salinity currently observed in the Brazos River Alluvium Aquifer.

Low nitrate levels (Figure 2-10) and low boron concentrations (Figure 2-11) in the groundwater further support that no substantial amount of irrigation return flow is reaching the aquifer. This is perhaps caused by the presence of clay

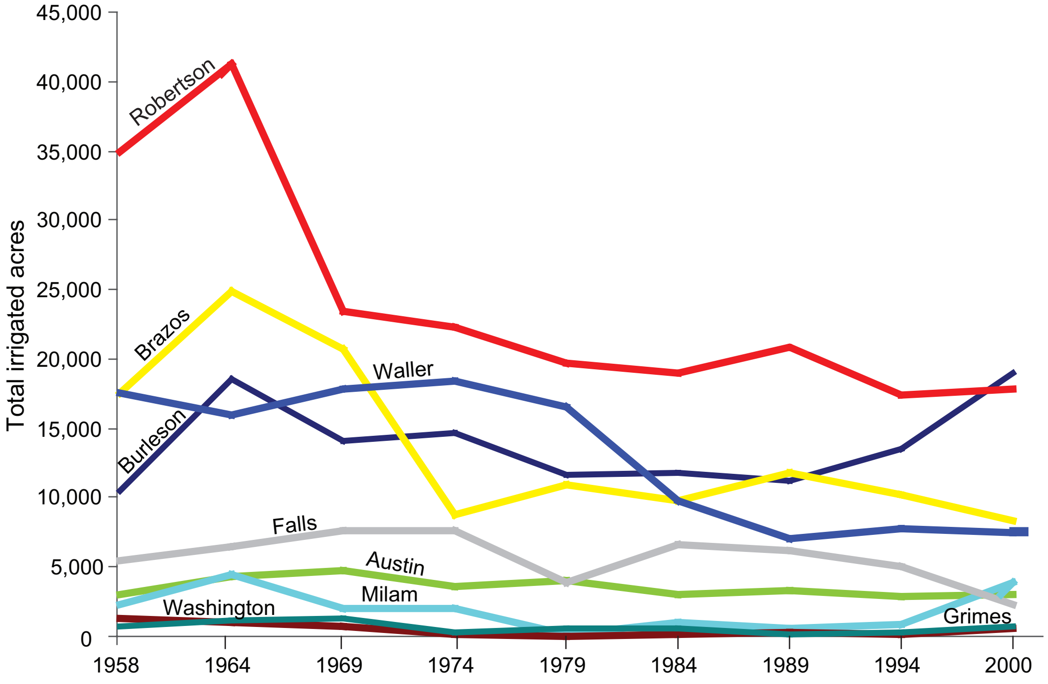

Figure 5-9. Total irrigated acres in the counties along the Brazos River Alluvium Aquifer (data from TWDB, 2001).

overlying the alluvium, preventing direct infiltration of irrigation return flow. The occurrence of the clay above the alluvium has been recently documented through a geophysical study (Shah and others, 2007b). However, the extent of this clay is not known.

Boron is one of the most important elements in irrigation water, as small concentrations of it are essential for plant growth. However, at high concentrations, boron may be toxic to some plants (Cronin and Wilson, 1967). Only a few samples had boron in excess of 2,000 micrograms per liter, which may make it unsuitable for irrigation.

The observed groundwater salinity is most likely attributed to evapotranspiration caused by a relatively shallow water table in the alluvium and chemical reactions with the aquifer materials. We also conclude that surface water could not be the source of groundwater salinity because the Brazos River is largely a gaining stream. This means that surface water from the river does not flow into the aquifer unless hydraulic gradient changes when the river stage sufficiently rises during floods. However, during these temporal rises in the river stage, surface water most likely does not reach the aquifer for the same reason irrigation return flow does not: the large expanses of clay (Shah and others, 2007b) that overlie the Brazos River Alluvium Aquifer.

A plot of groundwater compositions in Piper diagrams suggests that groundwater in the alluvium is mainly Ca-Mg-Na-HCO_3 type, and groundwater in the Queen City, Sparta, and Evangeline aquifers that underlie the alluvium is mainly Na-HCO_3 type (Figure 5-10 and Table 5-3). A plot of Na versus Cl shows an excess of Na with respect to Cl ions in the groundwater from the Queen City, Sparta, and Evangeline aquifers in contrast to the Brazos River Alluvium Aquifer, the river, and the oxbow lake water (Figure 5-11). This Na enrichment is probably caused by cation exchanges because excess Na (Na-Cl) from sources other than halite and excess Ca and Mg ($Ca+Mg-0.5HCO_3-SO_4$) from sources other than carbonate and gypsum dissolution plot along a line at a 2:1 ratio as would be expected in the case of cation exchange (Figure 5-12). Increased cation exchanges between dissolved Ca and Na attached on clay surfaces in the sediments hosting the Queen City, Sparta, and Evangeline aquifers are more likely to occur due to longer travel time required for groundwater to move through the thicker sediment sections before their discharge to the Brazos River. On the other hand, a much thinner, alluvial aquifer holds groundwater in short transit and shows no excess Na, suggesting a lack of cation exchange. Surface waters from the river and the oxbow lakes also have no excess Na and plot on the 1:1 line in the Na versus Cl plot, which suggests a mainly halite source for Na and Cl.

A plot of $(Ca+Mg)/HCO_3$ versus Cl shows a slight increase in the ratio at higher Cl, presumably due to precipitation of carbonate minerals because cations initially occur at a higher ratio than HCO_3 (Herczeg and Edmunds, 2000) (Figure 5-13). A plot of HCO_3/Cl versus Cl shows a progressive decrease in the ratio at higher Cl (Figure 5-14), suggesting that carbonates were generated early in the evolution and later removed during evapotranspiration. A plot of Ca and SO_4 indicates a slight increase in Ca, with an increase in SO_4 (Figure 5-15) probably due to weathering of calcic-plagioclases and/or evaporative concentration. Gypsum is not known to occur in these aquifer sediments, so the sulfate is probably not derived from gypsum dissolution.

Surface water from the oxbow lakes is mainly Ca-Mg-HCO_3 type, but the Brazos River water is Na-Ca-HCO_3-Cl type (Figure 5-16 and Table 5-4, Appendix 1). Salinity decreases downstream in the Brazos River, with higher salinity observed in the river near Moelhman Lake and lower salinity observed near Horseshoe Lake (Figures 2-6 and 2-7).

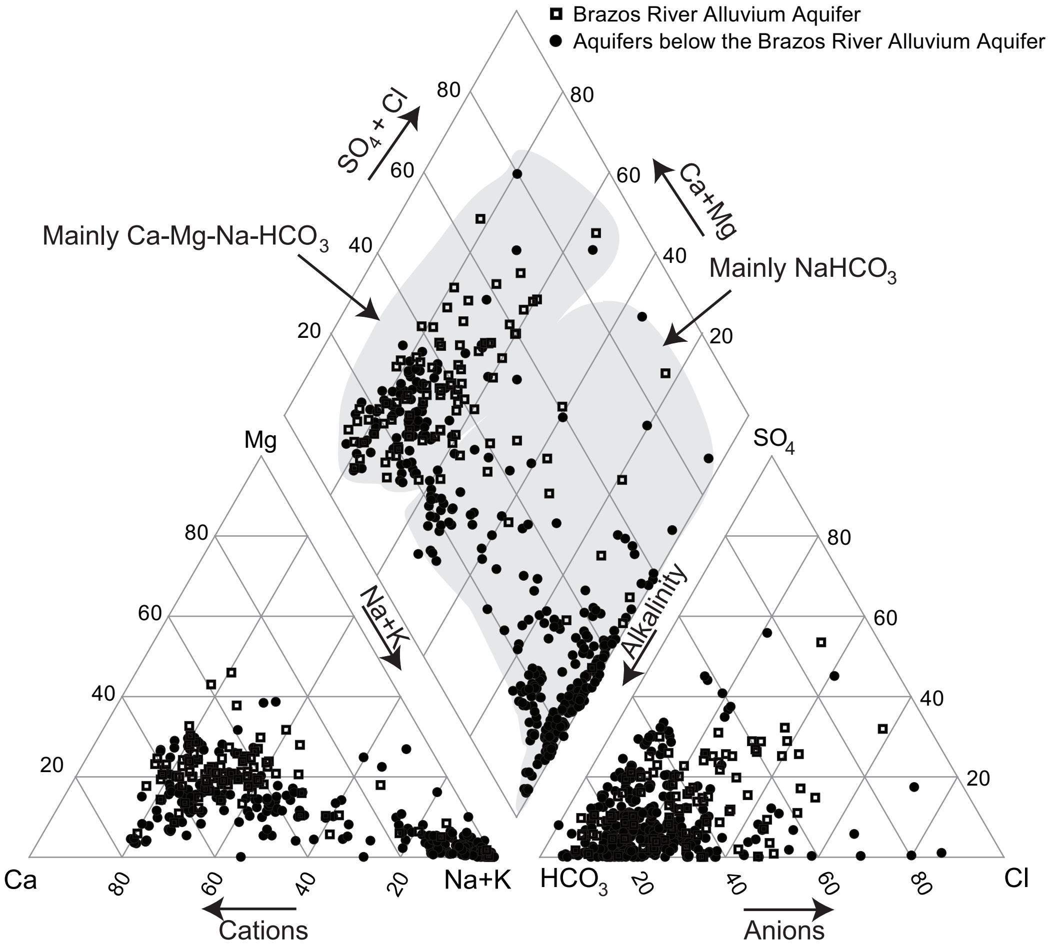

Figure 5-10. Piper plot of groundwater from the Brazos River Alluvium Aquifer and the Queen City, Sparta, and Evangeline aquifers.

Table 5-3. Chemical composition of groundwater selected for isotope analyses.

State well number	Aquifer	Chemical composition (mg/l)							
		Ca	Mg	K	Na	Cl	SO_4	HCO_3	TDS
5920839	Alluvium	236	48	3	79	98	235	687	1,067
5920913	Alluvium	282	62	4	145	205	376	715	1,455
5920923	Alluvium	101	14	1	37	66	42	304	437
5920928	Alluvium	243	54	3	249	348	415	514	1,607
5963802	Alluvium	86	7	2	40	54	12	295	381
6608111	Alluvium	46	13	3	49	61	7	237	321
6608702	Alluvium	99	13	1	59	94	35	308	493
5964701	Evangeline	56	14	5	80	50	1	376	414
6608103	Evangeline	54	16		134	93	35	394	544
5928208	Queen City	39	10	6	240	104	374	198	885

mg/l=milligrams per liter

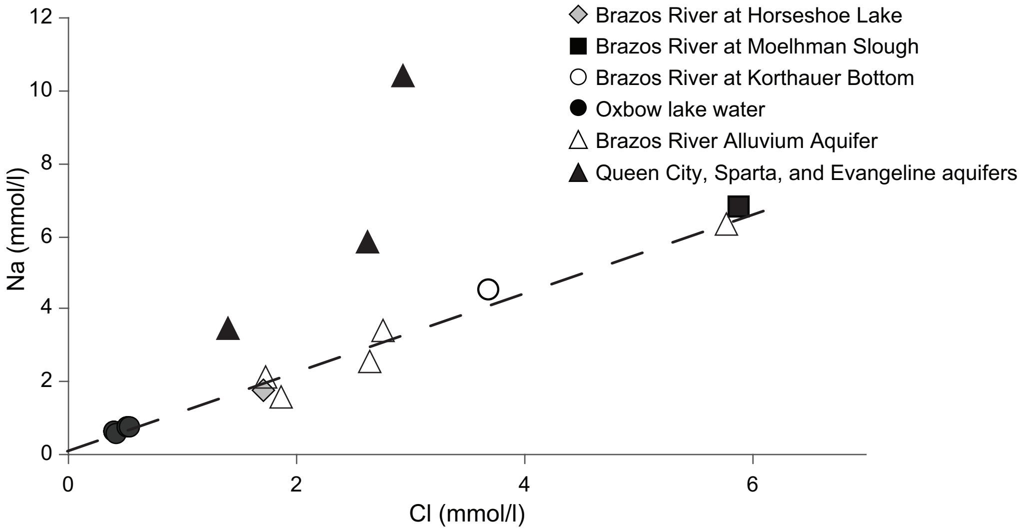

Figure 5-11. Plot of Na versus Cl of surface water from the oxbow lakes and the Brazos River and groundwater from the Brazos River Alluvium Aquifer and Queen City, Sparta, and Evangeline aquifers. Dashed line is the 1:1 line.

mmol/l=millimoles per liter

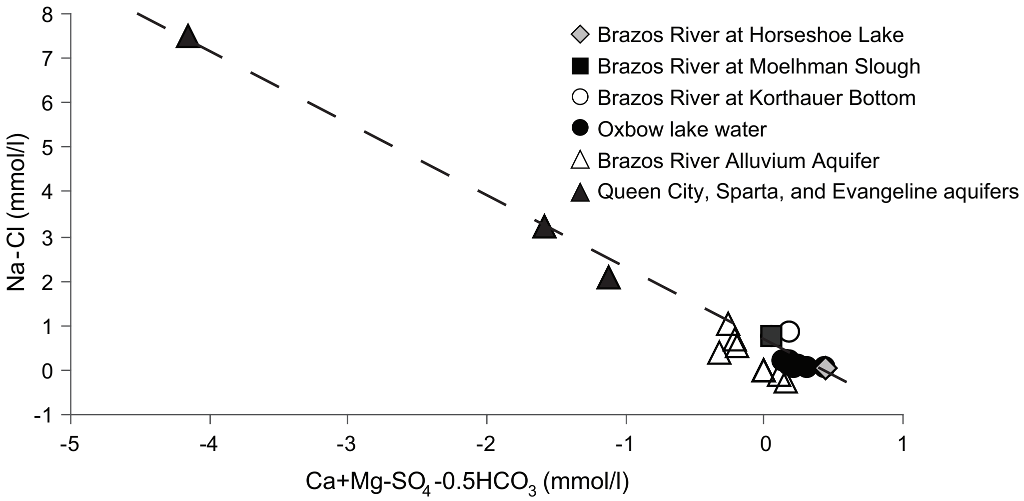

Figure 5-12. Plot of Na-Cl as a function of Ca+Mg-SO_4-0.5HCO_3 of surface water from the oxbow lakes and the Brazos River and groundwater from the Brazos River Alluvium Aquifer and Queen City, Sparta, and Evangeline aquifers. Dashed line is the 2:1 line.

mmol/l=millimoles per liter

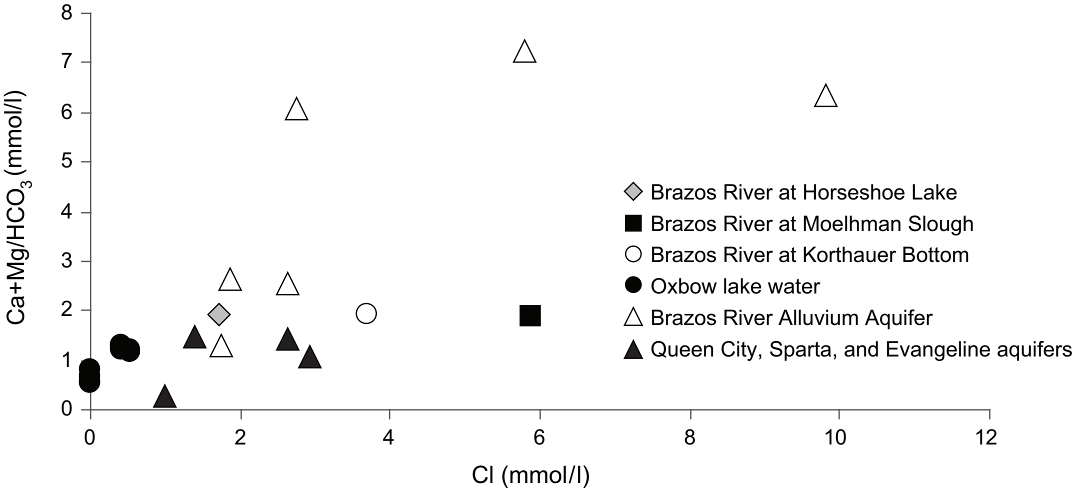

Figure 5-13. Plot of Ca+Mg/HCO_3 as a function of Cl for surface water from the oxbow lakes and the Brazos River and groundwater from the Brazos River Alluvium Aquifer and Queen City, Sparta, and Evangeline aquifers.
mmol/l= millimoles per liter

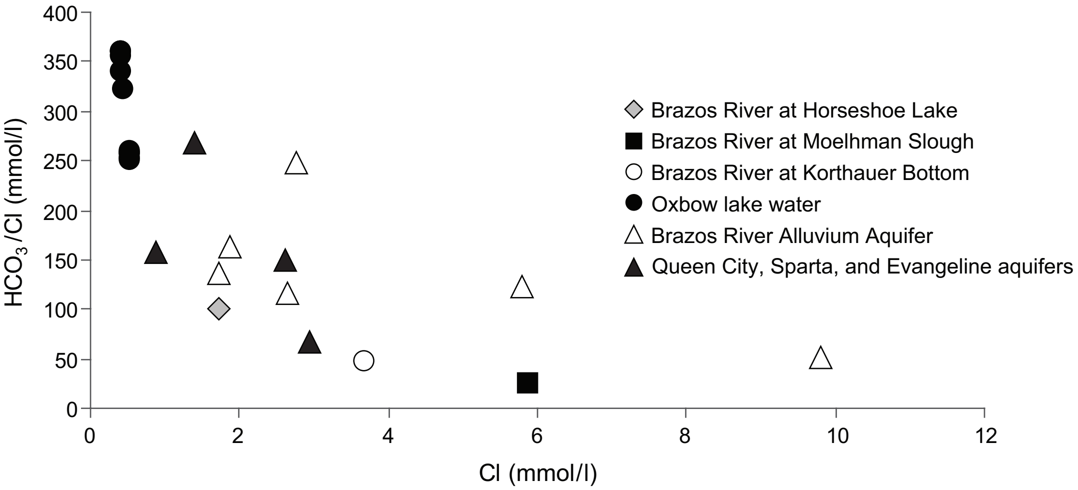

Figure 5-14. Plot of HCO_3/Cl as a function of Cl of surface water from the oxbow lakes and the Brazos River and groundwater from the Brazos River Alluvium Aquifer and Queen City, Sparta, and Evangeline aquifers. Note a progressive decline of HCO_3/Cl with an increase in Cl.
mmol/l=millimoles per liter

The lake water has the lowest ionic concentrations, followed by the river water and the groundwater. For example, total dissolved solids of the lake water range from 21 to 244 milligrams per liter, with an average of 172 milligrams per liter (n = 15). Total dissolved solids of the river water range from about 398 to 572 milligrams per liter, with an average of 556 milligrams per liter (n = 3). Total dissolved solids of the groundwater in the Brazos River Alluvium Aquifer range from about 76 to 2,300 milligrams per liter, with an average of about 1,000 milligrams per liter (n = 74).

Concentrations of Ca, Mg, and HCO_3 in the lake water also progressively decrease downstream (Moelhman Slough to Korthauer Bottom to Horseshoe Lake), coinciding with a freshening of the Brazos River Alluvium Aquifer and the river water downstream. This freshening of the river water is probably caused by reduced influx of saline water

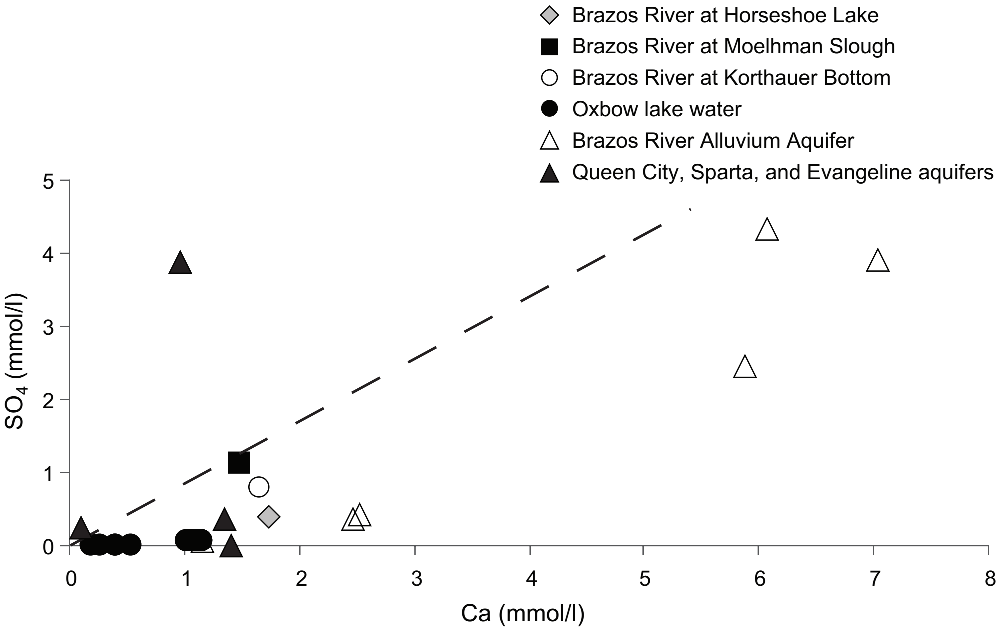

Figure 5-15. Plot of SO_4 as a function of Ca of surface water from the oxbow lakes and the Brazos River and groundwater from the Brazos River Alluvium Aquifer and Queen City, Sparta, and Evangeline aquifers.
mmol/l=millimoles per liter

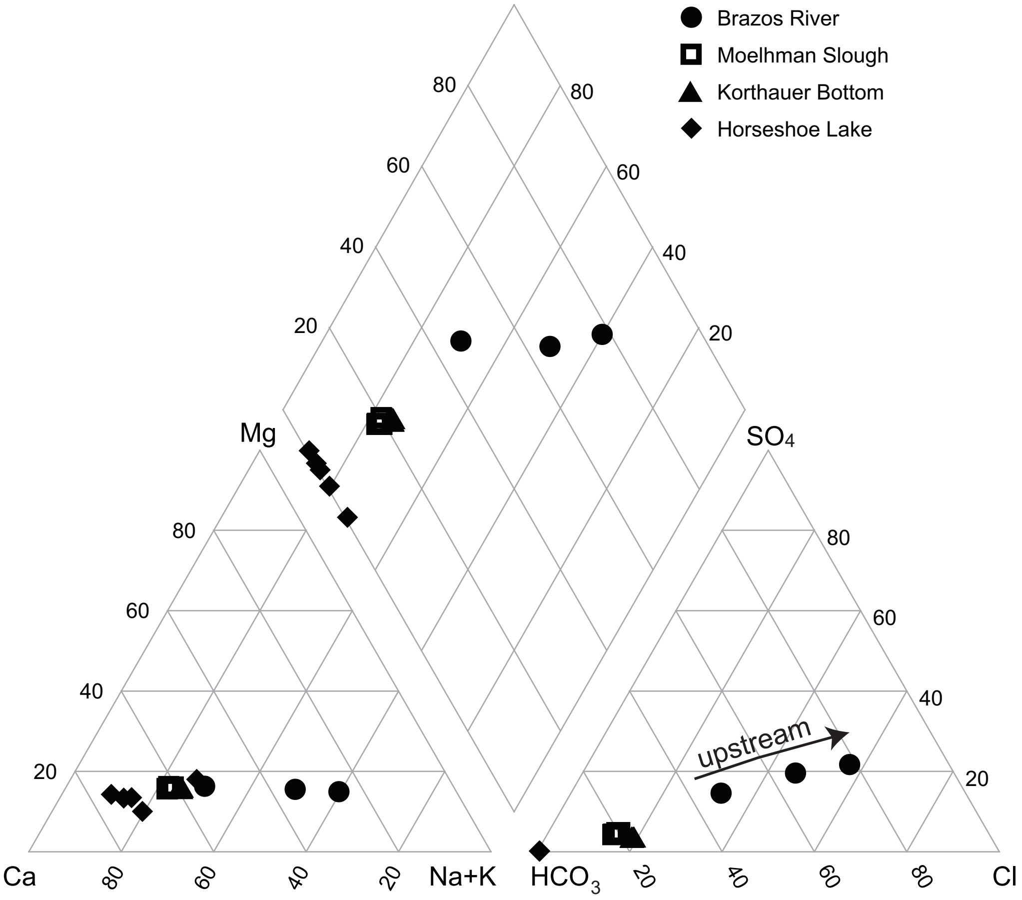

Figure 5-16. Piper plot of surface water from the oxbow lakes and the Brazos River.

Table 5-4. Chemical composition of surface water from the study area.

Site locations	Sample number	Chemical composition (mg/l)						
		Ca	Mg	K	Na	Cl	SO_4	^{a}Alkalinity
Horseshoe Lake	H-1	16.1	1.82	1.51	1.63	0	0	36
Horseshoe Lake	H-2	16.5	1.86	4.25	1.49	0	0	32
Horseshoe Lake	H-3	21.3	2.32	5.14	1.45	0	0	38
Horseshoe Lake	H-4	10.9	0.92	2.9	1.67	0	0	8
Horseshoe Lake	H-5	7.62	1.49	4.5	1.61	0	0	6
Brazos River at Horseshoe Lake	BR-HL-6	69.6	12.5	4.71	40.6	61	36.8	174
Moelhman Slough	M2	43.3	6.83	8.44	13.6	15	6.23	140
Moelhman Slough	M6	46.4	6.99	8.33	13.6	15	5.99	148
Moelhman Slough	M10	46.1	6.89	8.26	13.5	15	5.86	149
Moelhman Slough	M14	46.5	6.96	8.31	13.6	15	5.86	149
Moelhman Slough	M18	44.8	7	8.42	13.1	16	6.3	141
Brazos River at Moelhman Slough	BR-M22	59.8	20.6	5.87	153	209	108	141
Korthauer Bottom	KB02	42.4	6.71	6.2	16.7	19	4.82	137
Korthauer Bottom	KB06	41	6.65	6.02	16.2	19	4.68	135
Korthauer Bottom	KB10	41.8	6.84	6.08	16.5	19	4.69	135
Korthauer Bottom	KB14	42.3	6.85	6.22	16.6	19	4.79	135
Korthauer Bottom	KB18	42.4	6.88	6.07	16.3	19	4.81	136
Brazos River at Korthauer Bottom	BR-KB22	66.6	17.6	5.87	104	131	75.3	172

^{a}Alkalinity as bicarbonate ($CaCO_3$); mg/l=milligram per liter

from upstream and greater fresh water discharges from the alluvial aquifer.

Water chemistry on a global scale is controlled by three main factors: chemistry of the rain water, rock weathering, and evaporation-induced fractional crystallization (Gibbs, 1970). Gibbs used a plot of total dissolved solids as a function of Na/(Na+Ca) to show that most surface water falls along the two axes in the shape of a "boomerang." Herczeg and Edmunds (2000) adopted this to classify groundwater into three zones: precipitation dominated, rock dominated, and evapotranspiration dominated. Very dilute river water is dominated by rainfall composition with higher amounts of Na relative to Ca, which plots on the lower right of the diagram. Because water-rock interaction is widespread in groundwater, groundwater acquires more solutes from the soil zone and aquifer material, generating high HCO_3 and high Ca relative to Na. Groundwater affected by evapotranspiration evolves to higher salinity through removal of Ca and HCO_3 relative to Na and Cl due to precipitation of carbonate minerals (Herczeg and Edmunds, 2000).

Other researchers, however, have contended that the Gibbs model provides only an overly simplistic and general framework to represent general characteristics of surface water chemistry (Kilham, 1990; Eilers and others, 1992). They concluded that much lake water from both the high and low latitudes falls outside the envelope proposed by Gibbs (1970) (Kilham, 1990; Eilers and others, 1992). Baca and Threlkeld (2000) suggested that the bivariate plot fails because it does not consider enough of the ions. Gibbs (1992) responded to the criticism by stating that his model fits most of the major drainage systems of the world, with only some deviation occurring in minor water systems. Gibbs (1992) later expanded the envelope to show the fields for minor water systems (Figure 5-17).

When we plot the groundwater and surface water composition on total dissolved solids versus Na/(Na+Ca) axes, most of the groundwater and Brazos River water falls in the evapotranspiration zone, with a few samples in the precipitation-dominated zone. The groundwater data plot shows a large spread across the zones due to varying rates of evapotranspiration caused by variations in the depth to water table and other chemical reactions noted earlier. Brazos River samples show a progressive decrease in total dissolved solids and Na/(Na+Ca) values downstream due to the inflow of fresher water from the alluvial aquifer (Figure 5-17).

Water from Moelhman Slough and Korthauer Bottom occurs clustered together in the precipitation-dominated zones. However, water from Horseshoe Lake plots in the rock-dominated zone, with some values to the lower left of the precipitation-dominated zone. Compositional differences between the lakes are

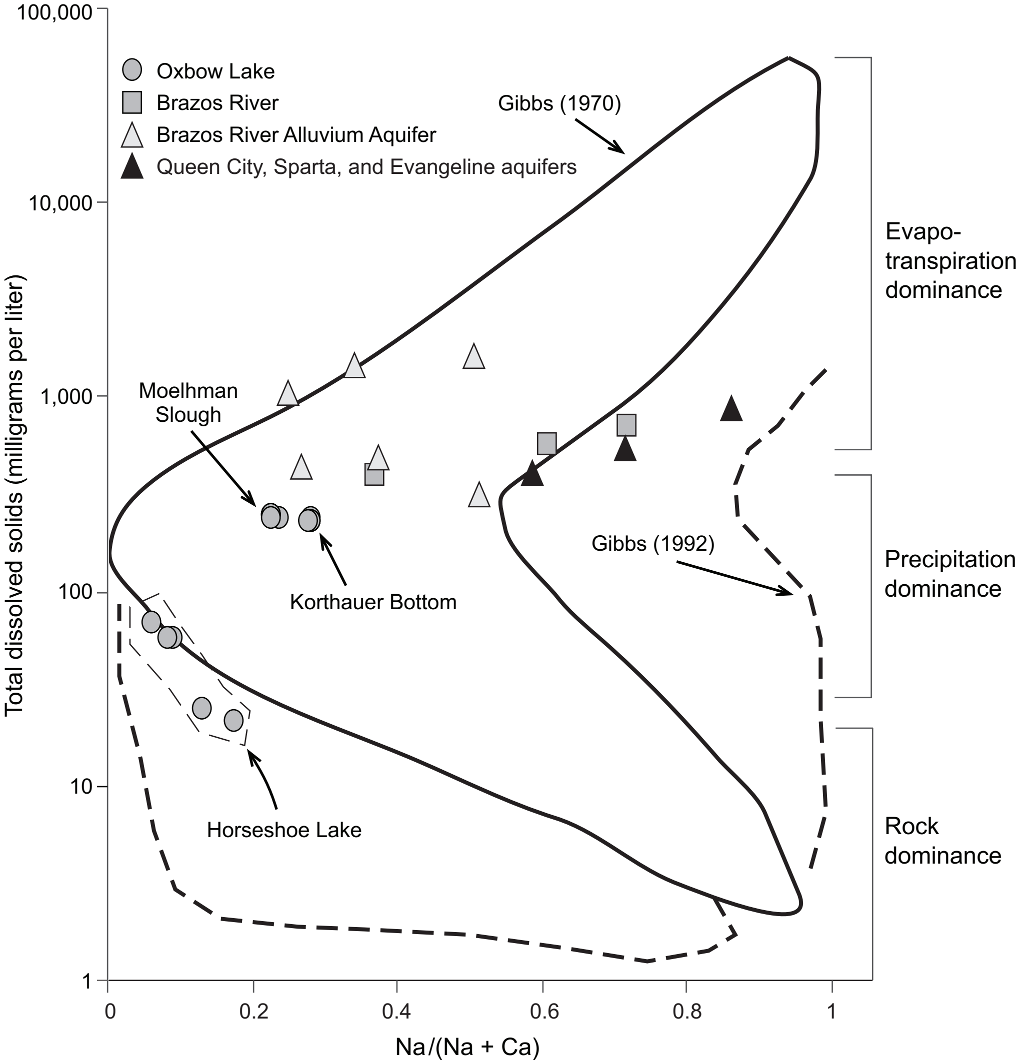

Figure 5-17. Plot of total dissolved solids versus Na/(Na+Ca) ratios of surface water from the oxbow lakes and Brazos River and groundwater (after Gibbs, 1970; 1992). Dashed lines include samples from minor water systems (Gibbs, 1992). Plot modified after Herczeg and Edmunds, 2000.

probably caused by a combination of factors, including lake connection histories with the main channel and differences in the amount and composition of base flow contribution as well as biological activity within the lakes.

The water composition of the Brazos River changes from the winter to the summer (Figure 5-18). In all three sites (Brazos River at U.S. 290, Brazos River at State Highway 105, and Brazos River at Farm to Market 529), sodium, chloride, sulfate, and specific conductance increase in the summer and decrease in the winter. For example, salinity (expressed as specific conductance) may reach a high of 1,400 micro-siemens per centimeter in the summer when temperature rises to about 30°C and a low of 300 micro-siemens per centimeter in the winter when temperature falls to about 5°C. In addition, the salinity of the Brazos River water increases upstream from a total dissolved solids concentration of 398 milligrams per liter near Horseshoe Lake, 572 milligrams per liter near Korthauer Bottom, and 697 milligrams per liter near Moelhman Slough. Other researchers have also observed a similar trend in decreasing salinity downstream, with a total dissolved solids concentration of 896 milligrams per liter below Whitney Dam, 703 milligrams per liter near Highway 21, and 513 milligrams per liter near Richmond (Cronin and Wilson, 1967).

We evaluated rain water composition data from National Trend Network sites TX 10 and TX 56 in Colorado and Wise counties, respectively (Figure 5-19). We compared rain water composition with the groundwater in the Brazos River Alluvium Aquifer and surface water in the Brazos River and the oxbow lakes. Because of stability issues with regard to preserving the water samples stored for more than a week prior to analyses, HCO_3 was not analyzed in the rain water from the National Trend Network sites. However, given the low pH (4 to 5) (Appendix 2) of the rain water, it is likely that HCO_3 would only be present in very small proportions with H_2CO_3 representing dominant carbonate concentrations. Rain water at the two sites is very dilute in ionic concentrations (Appendix 2). Total dissolved solids concentrations of the rain water range from 2.5 to 4.3 milligrams per liter. The rain water from the more inland TX 56 site shows relatively higher concentrations of Ca, SO_4, NH_4, and NO_3. However, the coastal TX 10 site has higher concentrations of Na and Cl.

5.4
ISOTOPIC COMPOSITIONS

Because stable isotopes of deuterium (δ^2H) and oxygen ($\delta^{18}O$) partition predictably during their evolution in a hydrologic cycle, they can provide valuable insights into the origins of the water. For example, vapor mass trajectories over continents, altitude differences, and seasonal changes can have characteristic effects on groundwater isotope values (Clark and Fritz, 1997). Similarly, $\delta^{34}S$ values can reveal the sources of sulfate in groundwater.

5.4.1
Oxygen and deuterium isotopes

Isotopes of δ^2H and $\delta^{18}O$ in freshwater are similar on a global scale and are usually expressed in comparison with the isotopic composition of ocean water, known as the standard mean ocean water. This comparison led to the development of a global meteoric water line defined by this equation (Craig, 1961):

$$\delta^2H = 8\delta^{18}O + 10‰\ (SMOW). \qquad (8)$$

Thus, how isotope values of water in an area are positioned with respect to the global meteoric water line reflects how the water evolved in the hydrologic cycle.

Our analyses of δ^2H and $\delta^{18}O$ isotopes indicate that the different groups of water samples (groundwater, river water, and oxbow lakes) have distinct

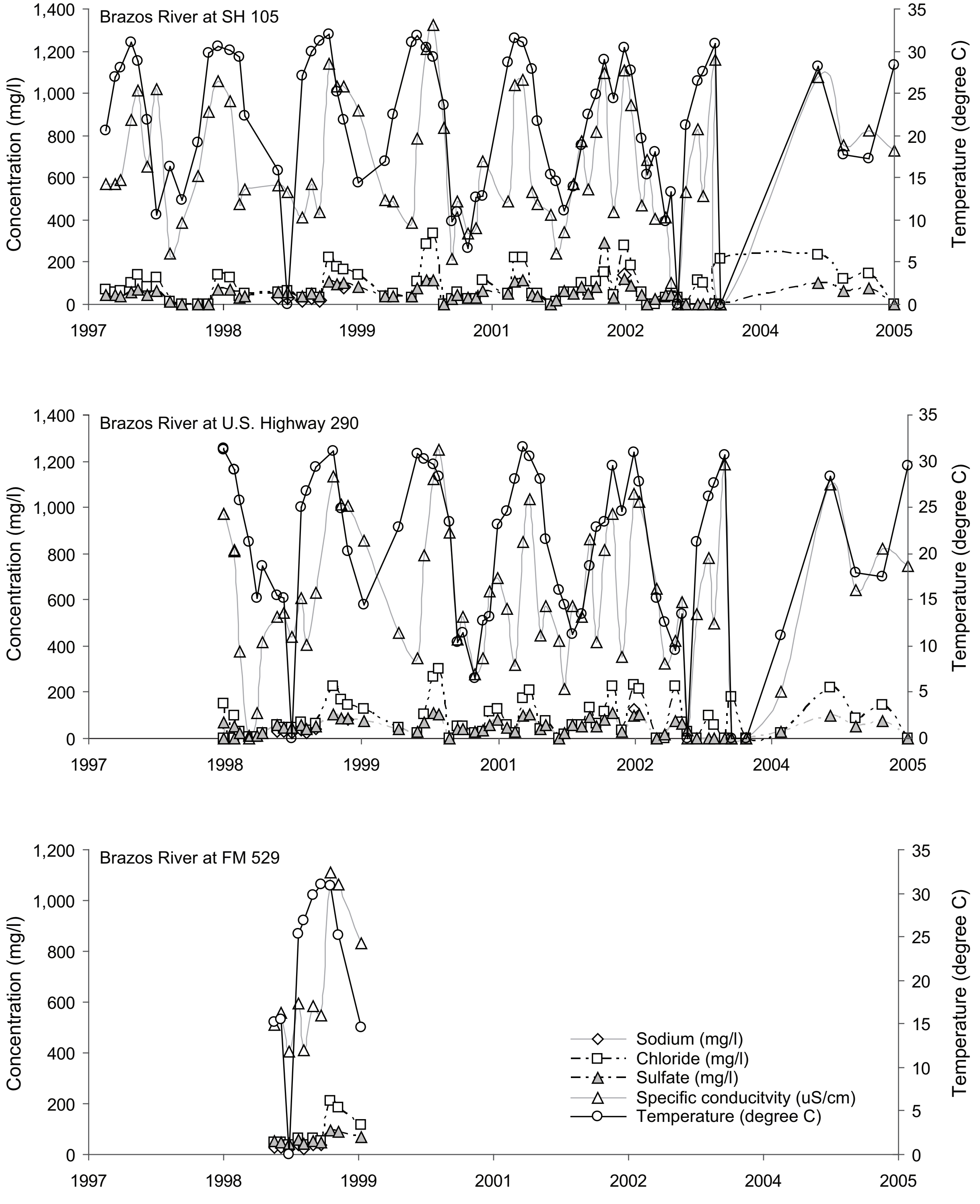

Figure 5-18. Brazos River water composition from three sample sites (Brazos River at State Highway 105, U.S. Highway 290, and Farm to Market 529).

mg/l=milligrams per liter; uS/cm=micro-siemens per centimeter; degree C=degrees Centigrade

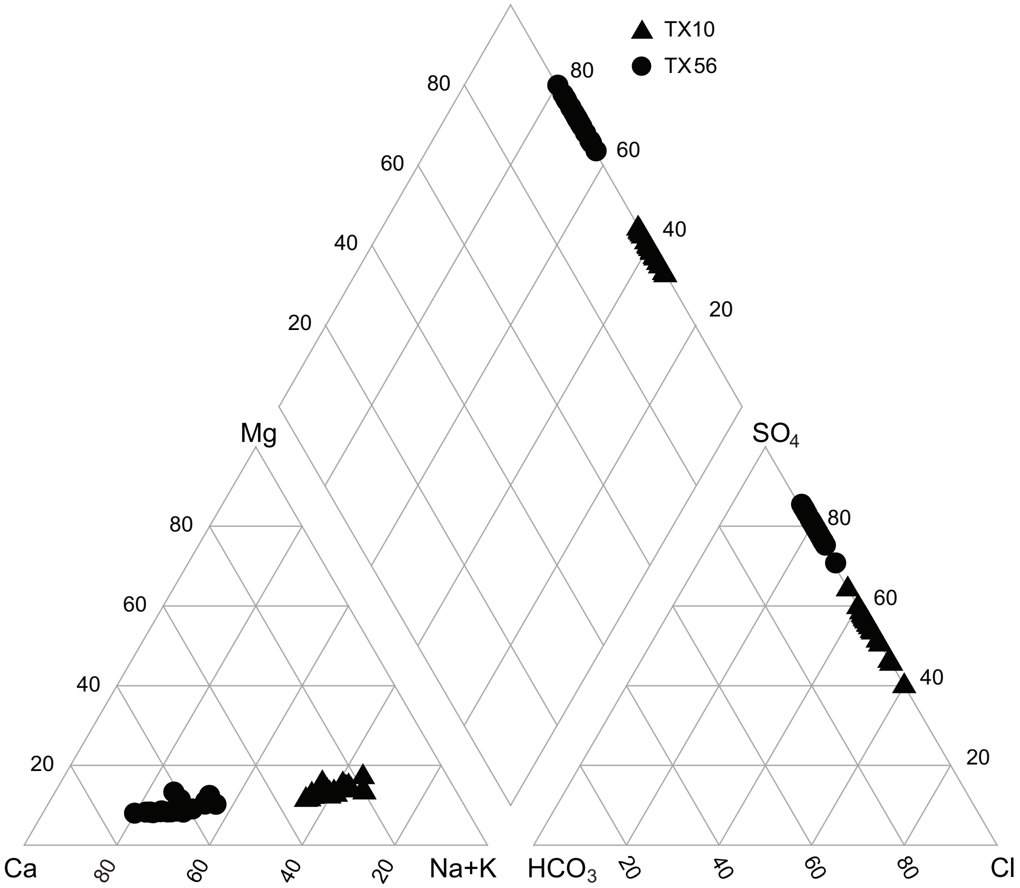

Figure 5-19. Piper plot of precipitation weighted mean rain water composition for National Trend Network sites in Colorado (TX 10) and Wise counties (TX 56). Because no measurements were made on HCO_3 concentrations, HCO_3 was not included in the plot.

isotopic compositions (Table 5-5) (Chowdhury, 2004). For example, the oxbow lake water is enriched in δ^2H and $\delta^{18}O$ isotopes, with values ranging from –3 to +9‰ and +1.6 to + 4.7‰ standard mean ocean water, respectively. Horseshoe Lake water has a wider range of isotope values than water from Moelhman Slough and Korthauer Bottom. For example, δ^2H values in the lake centers and north and south shores vary by about 10‰ standard mean ocean water in Horseshoe Lake, whereas δ^2H values within Moelhman Slough and Korthauer Bottom water are similar.

The second set of enriched samples are from the Brazos River, with δ^2H and $\delta^{18}O$ values ranging from -29 to -11‰ and -3 to -0.2‰ standard mean ocean water, respectively. The river water also becomes progressively depleted in isotopic values downstream. For example, the river water has δ^2H and $\delta^{18}O$ values of -11‰ and -0.2‰ near Moelhman Slough, -17‰ and -1.9‰ near Korthauer Bottom, and -29‰ and -3‰ near Horseshoe Lake. Groundwater from the Brazos River Alluvium Aquifer has more depleted isotopic values than the river and lake water, with δ^2H and $\delta^{18}O$ values that range from -34 to -29‰ and -5.2 to -4.5‰, respectively (Table 5-5). Groundwater from the Queen City, Sparta, and Evangeline aquifers has slightly more depleted $\delta^{18}O$ values than the Brazos River Alluvium Aquifer. A cross plot of δ^2H and $\delta^{18}O$ shows that nearly all the isotope values plot below the global meteoric water line along a linear evaporation trend line (Figure 5-20). Groundwater from the Brazos River Alluvium, Queen City, Sparta, and Evangeline aquifers plots at the bottom of this evaporated trend line. Isotope mass balance using deuterium suggests that about 60 percent of the water in the river may be derived from rain water, with the remaining 40 percent from base flow.

5.4.2
Sulfur isotopes

We sampled water from the oxbow lakes, Brazos River, and the aquifers for $\delta^{34}S$ isotopes (Table 5-5 and Figure 5-21). We found considerable similarities in $\delta^{34}S$ values, with the exception of a larger spread and more positive $\delta^{34}S$ values in the groundwater. Sulfur isotope values range from +0.8 to +5‰ CDT in the oxbow lakes, +2.2 to +6.7‰ CDT in the Brazos River, and -3.9 to +9.8‰ CDT in the groundwater. We also observed two trends from $\delta^{34}S$ and SO_4 plot: (1) a progressive enrichment of $\delta^{34}S$ with an increase in SO_4 and (2) $\delta^{34}S$ enrichment at decreased concentrations of SO_4.

Table 5-5. Isotopic compositions of water from the oxbow lakes, Brazos River, and groundwater.

Sample type	Sample number	Sampling location	δ^2H ‰ (SMOW)	$\delta^{18}O$ ‰ (SMOW)	$\delta^{34}S$ ‰ (CDT)	SO_4 (mg/l)
Moelhman Slough	M17	Northern end of the lake	2	2.4	1.65	6.3
Moelhman Slough	M1	Southern end of the lake	-2	2.1	1.7	6.23
Moelhman Slough	M5	Middle of the lake, east shore	-1	2.1	2.2	5.99
Moelhman Slough	M9	Middle of the lake, lake center, deep pool	-2	1.8	2.5	5.86
Moelhman Slough	M13	Middle of the lake, west shore	-3	1.7	0.8	5.86
Moelhman Slough	BR-MS-M21	Near highway SH21 crossing	-11	-0.2	6.7	108
Korthauer Bottom	KB01	Northern end of the lake	-1	2	5	4.82
Korthauer Bottom	KB17	Southern end of the lake	-2	2	4.1	4.81
Korthauer Bottom	KB13	Middle of the lake, east shore	-3	1.6	3.8	4.79
Korthauer Bottom	KB5	Middle of the lake, lake center, deep pool	-3	1.7	3.6	4.68
Korthauer Bottom	KB9	Middle of the lake, west shore	-2	1.8	4	4.69
Korthauer Bottom	BR-KB-21	Brazos River at Korthauer Bottom	-17	-1.9	6.5	75.3
Horseshoe Lake	H-5-5	Northern end of the lake	4	4.2		0
Horseshoe Lake	H-1-5	Southern end of the lake	10	4.7		0
Horseshoe Lake	H-2-5	Middle of the lake, east shore	0	3.5		0
Horseshoe Lake	H-3-5	Middle of the lake, lake center, deep pool	0.5	3.5		0

Table 5-5 continued.

Sample type	Sample number	Sampling location	δ^{2}H ‰ (SMOW)	δ^{18}O ‰ (SMOW)	δ^{34}S ‰ (CDT)	SO_4 (mg/l)
Horseshoe Lake	H-4-5	Middle of the lake, west shore	9	4.7		0
Horseshoe Lake	BR-H6	Brazos River at Horseshoe Lake near highway SH 159 crossing	-29	-3	2.2	36.8
Brazos River Alluvium Aquifer	59-20-913		-31	-4.5	-0.8	376
Brazos River Alluvium Aquifer	66-08-702		-30	-4.6	-3.9	35.4
Brazos River Alluvium Aquifer	66-08-703		-32	-4.8	6.2	35
Brazos River Alluvium Aquifer	66-08-111		-31	-4.8	8.8	6.81
Brazos River Alluvium Aquifer	59-63-802		-30	-4.6	8.4	N/A
Brazos River Alluvium Aquifer	59-20-928		-33	-4.6	3.4	415
Brazos River Alluvium Aquifer	59-20-839		-32	-4.7	-3	235
Brazos River Alluvium Aquifer	59-20-923		-33	-4.7	2.1	42
Sparta Aquifer	5928209		-34	-5.2	-2.3	14
Queen City Aquifer	5928208	After flooding	-33	-5.2		374
Evangeline Aquifer	6608103		-31	-4.8	9.8	35
Evangeline Aquifer	5964701		-30	-4.9	8.8	1.33

All isotope values are reported in parts per thousand.

SMOW=standard mean ocean water; CDT=Canyon Diablo Troilite; N/A=not analyzed; mg/l=milligrams per liter; SH=state highway

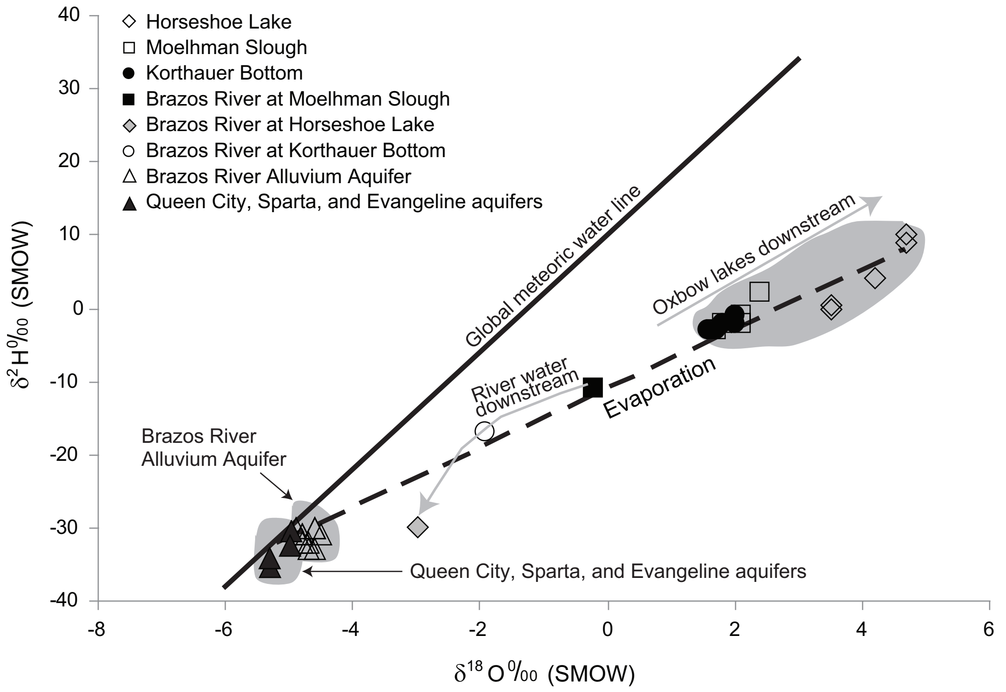

Figure 5-20. Plot of δ^2H and $\delta^{18}O$ values of the oxbow lake water, river water, and groundwater from the study area. The Queen City, Sparta, and Evangeline aquifers have the most depleted isotope values followed by the Brazos River Alluvium Aquifer. The oxbow lakes have the most enriched isotope values. The groundwater samples fall along the global meteoric water line, and the oxbow lakes water plot along or close to an evaporation trend line.
SMOW=standard mean ocean water

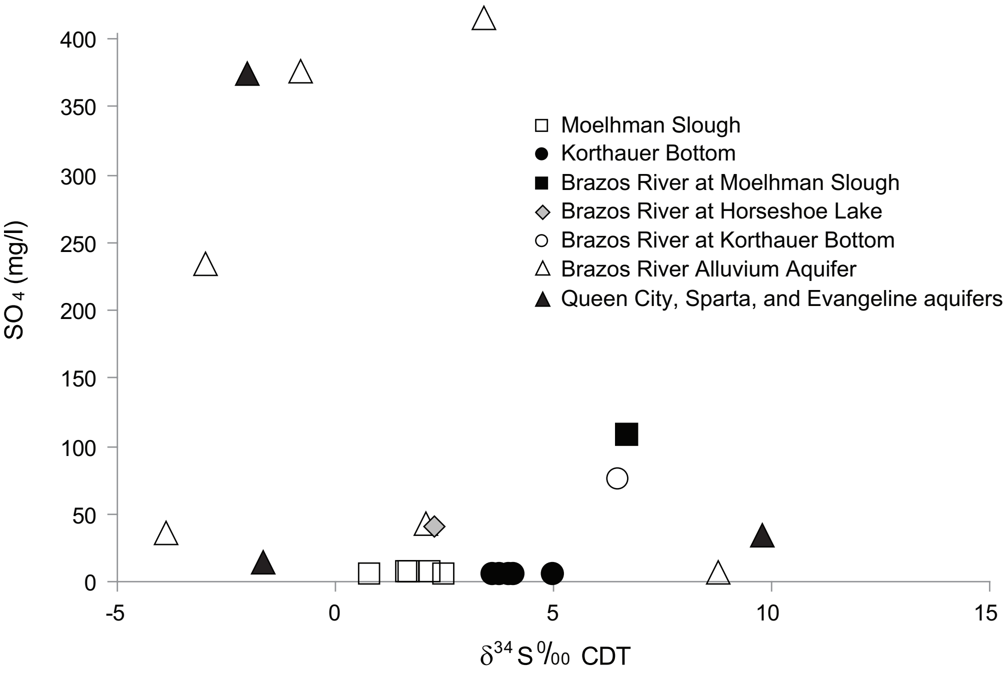

Figure 5-21. Relationship between $\delta^{34}S$ isotope values and SO_4 in the water from the oxbow lakes, Brazos River, and groundwater.

6 *Discussion*

Rain water commonly has a wide range of dissolved substances that include sea salt, SO_4, H, NH_4, and NO_3. Sulfuric acid is derived from the oxidation of dimethyl sulfide and hydrogen sulfide, which are produced by biological processes in the ocean (Bonsang and others, 1980). Ammonium and NO_3 are derived from gaseous nitrogen species from terrestrial vegetation (Stallard and Edmond, 1981). Rain water from areas affected by atmospheric pollution commonly is high in SO_2 and a range of nitrogen oxides (Drever, 1988). High concentrations of NH_4 also occur in polluted air (Drever, 1988). Therefore, high SO_4 and NH_4 concentrations in the rain water at the TX 56 site (Wise County) suggest that the area is more influenced by human factors than the TX 10 site (Colorado County). High concentrations of Na and Cl in the rain water at the TX 10 site are probably caused by inputs of sea salts from the Gulf of Mexico.

In comparing rain water compositions with surface water from the oxbow lakes and Brazos River and groundwater from the Brazos River Alluvium, Queen City, Sparta, and Evangeline aquifers, none of the surface water and groundwater compositions match the rain water compositions. The surface water and groundwater are much more saline than the rain water. Therefore, rain water must rapidly change its composition as it travels through the soil and aquifer materials, participates in water-rock interactions in the outcrop and subsurface, and mixes with the river water. None of the water samples we studied plot near the SO_4 vertex in anions and near 50 percent (Na+K) and Ca in cations (Figures 5-10, 5-16, and 5-19) as would be expected if they were strongly influenced by atmospheric precipitation (Baca and Threlkeld, 2000).

Because temperature and precipitation patterns affect isotopic compositions, isotope analysis is useful in determining the origins and recharge of groundwater. Isotopic partition results in depleted isotopic water in cold regions and enriched water in warm regions (Craig, 1961; Clark and Fritz, 1997). The groundwater samples we analyzed for $\delta^{18}O$ isotopes from the Brazos River Alluvium Aquifer closely resemble the weighted mean $\delta^{18}O$ values of about −4.2‰ standard mean ocean water present in the rain water for Central Texas (Barry and Chorley, 1998). However, groundwater from the Queen City, Sparta, and Evangeline aquifers underlying the alluvium is relatively more depleted, which suggests that this water was derived from a different recharge event. Therefore, most of the groundwater in the Brazos River Alluvium Aquifer is not likely mixed with the older groundwater that could flow upward from the aquifers beneath the alluvium under artesian conditions. These differences in isotopic compositions are consistent with the differences in chemical compositions between groundwater from the Brazos River Alluvium, Queen City, Sparta, and Evangeline aquifers.

Water becomes progressively more enriched in $\delta^{18}O$ and $\delta^{2}H$ values during its evaporation (Gonfiantini, 1986). The isotopic values of Brazos River water become progressively depleted downstream (Table 5-5), suggesting relatively greater base flow contribution downstream. This is further supported by greater similarities in water compositions from the alluvial aquifer and the adjacent river water and a higher base flow discharge downstream.

The most enriched $\delta^{2}H$ and $\delta^{18}O$ values occur in Horseshoe Lake in the downstream parts of the Brazos River. The lake water has more enriched isotope values than the groundwater and nearby Brazos River water. These values may suggest that the lake water has not been connected even temporarily to the Brazos River for an extended period of time, allowing continued evaporation of this shallow ponded water.

A literature survey indicates that with continued evaporation, isotope values progressively shift toward more positive values, depending on the mean residence time of the water in a basin and the rate of evaporation (Gonfiantini, 1986). In transient surface water bodies during flushing phases, isotopic compositions approach dilute rain water. However, during the evaporitic phases at low-water stand, isotopic species become enriched (Gat, 1995). In a study of the floodplain lakes in the Amazonia, Martinelli and others (1989) showed that the isotopic composition of many of the lakes changes from depleted isotopic values characteristic of the main stream of the Amazon River and its tributaries to more enriched values due to the increased participation of water from local runoff and rainfall. Our interpretation that the enriched isotopic compositions are due to disconnection of the oxbow lakes from the main river channel for extended periods of time and accumulation of water in the lakes from precipitation and local base flow is consistent with isotopic investigations of other lake water (Martinelli and others, 1989; Gat, 1995).

Sulfur from various sources of sulfate may participate in the geochemical evolution of groundwater and contribute to groundwater salinity. The isotope of δ_{34}S is generally fractionated between sulfur compounds due to biological cycling. Dissolution of gypsum or anhydrite occurs without measurable isotopic fractionation and, therefore, isotopic compositions of SO_4 can be used as a tracer of sulfate origin (Clark and Fritz, 1997). The range of sulfur isotopes (+0.8 to +6.7‰ CDT) we observed in the oxbow lake and river water suggests that the sulfate is mainly derived from human sources. Mayer (1998) reported that sulfate from human sources normally ranges between -3 and +9‰ CDT in rainfall. Sulfate in this water is probably not derived from atmospheric sulfate of marine origin or reduced organic sulfur gases (+15 and +21‰ CDT) (Krouse and Mayer, 2000) or combustion and refining of fossil fuels (-40 to +30‰ CDT) (Newman and Forest, 1991). Isotopes of $\delta^{34}S_{SO4}$ of modern seawater also have a heavier $\delta^{34}S_{SO4}$ value (+21‰ CDT) (Clark and Fritz, 1997).

When we plot δ^{34}S versus SO_4, samples that show a progressive enrichment in δ^{34}S with an increase in dissolved sulfate probably occur under more unconfined conditions in permeable parts of the aquifer where groundwater is more readily recharged (Figure 5-21). On the contrary, δ^{34}S enrichment at the expense of SO_4 suggests groundwater has undergone sulfate reduction in areas containing clay lenses, which provide the necessary anaerobic condition. Negative δ^{34}S values are formed under diagenetic conditions in which reduced sulfur compounds are formed due to biological recycling (Clark and Fritz, 1997).

The net effect of evaporation is to remove water from water bodies, which increases the salinity in the remaining water by increasing the dissolved constituents. As water evaporates, carbonate or sulfate may precipitate, increasing cation (Ca, Na) and decreasing anion (HCO_3, SO_4) concentrations (Eugster and Hardie, 1978). Therefore, the oxbow lakes in the Brazos River that hold the most evaporated water as supported from their isotopic compositions should have higher salinity than the rest of the water unless significant mineral precipitation has occurred. However, the lake waters have lower salinity, with negative saturation indices for most common minerals, which could probably be attributed to dilution effects caused by repeated mixing with river water. However, this explanation does not hold for Horseshoe Lake.

Water compositions within the oxbow lakes are relatively uniform, suggesting an absence of stratification. Water compositions of Horseshoe Lake, however, are considerably different from Moelhman Slough and Korthauer Bottom oxbows, and from rain water and groundwater. No sulfate or chloride is present, and cations occur at reduced concentrations in this lake water. In contrast, the nearby river water has much higher concentrations of chloride and sulfate. Unlike the river and the other two lakes, Horseshoe Lake has dense growths of the aquatic vegetation Eurasian watermilfoil (*Myriphyllum spicatum*), and the water in the lake is very clear. Profuse growth of Eurasian watermilfoil may absorb some of the Ca, Cl, and SO_4, resulting in their reduced concentrations in the water. For example, Wainio and others (2003) observed that *M. spicatum* could potentially be a proficient hyperaccumulator of heavy metals. They noted high concentrations of heavy metals in a lake in Ontario, Canada, where heavy metals in the water were less at the exit of the lake compared to water entering the lake. High concentrations of metals were found in the *M. spicatum* within the lake; they suggested that this accumulation of metals in the *M. spicatum* could result from the plants absorbing metals from the water column through foliar contamination (Wainio and others, 2003). In addition, local reducing conditions from the decay of organic matter and the *M. spicatum* may facilitate sulfate reduction and ion adsorption on organic matter.

Water composition in the Brazos River changes considerably from the winter to the summer. A large fraction of the river water contains relatively more dilute rain water in the winter than the summer because of higher rainfall in the winter. Furthermore, a reduced streamflow and lower river stage caused by increased evapotranspiration and pumping during the summer make the hydraulic gradient steeper and allow more base flow discharge into the river. Base flow nearly always has more dissolved solids than the rain water, which contains only very dilute water (Figure 5-19), particularly in coastal areas.

Average groundwater recharge in the alluvial aquifer estimated from base flow analyses and the chloride mass balance method are in reasonable agreement. For example, the base flow estimate provides average recharge values of 0.74 to 0.95 inches per year, and the chloride mass balance method provides lower average recharge values of 0.33 inches per year. The lower recharge value from the chloride mass balance method could be attributed to dissolved chloride that can accumulate during chemical interaction of the water with the fine-grained aquifer materials. However, the recharge estimate from the chloride mass balance method is similar to groundwater recharge of 0.35 inches per year assigned in the alluvium to calibrate groundwater models for the Queen City, Sparta, Carrizo, and Wilcox aquifers (Dutton and others, 2003).

7 *Conclusions*

We evaluated surface connections for three oxbow lakes with the main channel of the Brazos River using site topography and water surface elevation information. Results indicate that Moelhman Slough connects to the Brazos River at least twice per year, Korthauer Bottom connects to the Brazos River more than once per year, and Horseshoe Lake rarely connects to the Brazos River, even during intense flood events.

Isotopic compositions of the alluvial groundwater, river water, and oxbow lake water show a progressive enrichment in oxygen and deuterium isotopes from continued evaporation of the water. Groundwater from the Queen City, Sparta, and Evangeline aquifers near the lakes has depleted isotopes and a sodium-bicarbonate composition, and the Brazos River Alluvium Aquifer water has a heavier isotope and a calcium-sodium-bicarbonate composition. These differences in chemical and isotopic compositions suggest that there may not be any significant upward discharges from the Queen City, Sparta, and Evangeline aquifers into the Brazos River Alluvium and Brazos River. Water levels and base flow analyses suggest that a substantial portion of the water in the Brazos River is derived from base flow from the shallow alluvial aquifer. Estimated average base flow discharges are significantly higher downstream than upstream. Fresher groundwater composition in the lower parts of the alluvial aquifer also contributes to a fresher river water composition downstream.

We estimated recharge into the Brazos River Alluvium Aquifer using base flow and chloride mass balance methods. We estimate that average recharge into the aquifer ranges from 0.74 to 0.95 inches per year using the base flow method. Using the chloride mass balance method, we estimate average recharge is 0.33 inches per year; however, the chloride mass balance method underestimates recharge due to the possible contribution of non-precipitation chloride in the groundwater.

Water levels in wells and base flow discharges show no direct responses with precipitation amounts, suggesting that recharge into the aquifer is delayed due to the presence of clay in or above the alluvium, as documented by earlier geophysical investigations.

As a result of our analyses, we determined that the source water for Moelhman Slough and Korthauer Bottom differs from Horseshoe Lake. The frequency and durations of surface connections of the oxbow lakes with the river in combination with the chemical and isotopic compositions suggest that the water in Moelhman Slough and Korthauer Bottom originated during flood events. In contrast, base flow from the alluvial aquifer is the dominant source of water for Horseshoe Lake. Water in Horseshoe Lake has experienced extensive evaporation, as supported by its enriched deuterium and oxygen isotopic compositions and only one surface connection to the Brazos River over the past 20 years. Although chemical compositions of Horseshoe Lake water should be more saline due to extensive evaporation, the water remains surprisingly fresher than that in the other two lakes and the river. This difference in chemical composition may be caused by biologically mediated filtering of the ions and/or geochemical reactions.

8 *Acknowledgments*

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9 *References*

Allison, G.B., and Hughes, M.W., 1978, The use of environmental chloride and tritium to estimate total recharge to an unconfined aquifer: Australian Journal of Soil Research, v. 16, p. 181–195.

Arnold, J.G., Allen, P.M., Muttiah, R., and Bernhardt, G., 1995, Automated base flow separation and recession analysis techniques: Groundwater, v. 33, p. 1010–1018.

Baca, R.M., and Threlkeld, S.T., 2000, Inland dissolved salt chemistry—statistical evaluation of bivariate and ternary diagram models for surface and subsurface water: Journal of Limnology, v. 59, no. 2, p. 156–166.

Barry, R.G., and Chorley, R.J., 1998, The atmosphere, weather and climate (7th ed.): London, Routledge, 460 p.

Bonsang, B., Nguyen, B.C., Gaudry, A., and Lambert, G., 1980, Sulfate enrichment in marine aerosols owing to biogenic gaseous sulfur compounds: Journal of Geophysical Research, v. 85, p. 7410–7416.

Brazos River Authority, 2005, Annual water quality report: Brazos River Water Authority, 9 p.

Chowdhury, A.H., 2004, Hydraulic interaction between groundwater, oxbow lakes, and the Brazos River: Texas Water Development Board unpublished report, 22 p., www.twdb.state.tx.us/InstreamFlows/pdfs/TWDB_GWBrazosOxbow_Final.pdf.

Clark, I.D., and Fritz, P., 1997, Environmental isotopes in hydrogeology: Boca Raton and New York, Lewis Publishers, 328 p.

Craig, H., 1961, Isotopic variations in meteoric waters: Science, v.133, p. 1702–1703.

Cronin, J.G., and Wilson, C.A., 1967, Groundwater in the flood-plain alluvium of the Brazos River, Whitney Dam to vicinity of Richmond: Texas Water Development Board Report 41, 206 p.

Drever, J.I., 1988, The geochemistry of natural waters (2nd ed.): Englewood Cliff, N.J., Prentice Hall, 438 p.

Dunn, D.D., and Raines, T.H., 2001, Indications and potential sources of change in sand transport in the Brazos River, Texas: U.S. Geological Survey Water Resources Investigations Report 01-4057, 38 p.

Dutton, A.D., Harden, B., Nicot, J.P., and O'Rourke, D., 2003, Groundwater availability model for the central part of the Carrizo-Wilcox aquifer in Texas: final technical report prepared for the Texas Water Development Board under contract 2001-483-378, 295 p.

Eilers, J.M., Brakke, D.F., and Henriksen, A., 1992, The inapplicability of the Gibbs model of world water chemistry for dilute lakes: Limnology Oceanography, v. 37, p. 1335–1337.

Epstein, S., and Mayeda, T.K., 1953, Variations of the $^{18}O/^{16}O$ in natural waters: Geochimica and Cosmochimica Acta, v. 4, p. 213.

Eugster, H.P., and Hardie, L.A., 1978, Saline lakes, *in* Lerman, A., ed., Lakes—Chemistry, geology, physics: New York, Springer Verlag, p. 237–293.

Gat, J.R., 1995, Stable isotopes of fresh and saline lakes, *in* Lerman, A., and others, eds., Physics and chemistry of lakes: New York, Springer Verlag, p. 139–165.

Gibbs, R.J., 1970, Mechanisms controlling world water chemistry: Science, v. 170, p. 1088–1090.

Gibbs, R.J., 1992, A reply to the comment of Eilers et al.: Limnology Oceanography, v. 37, p. 1338–1339.

Gonfiantini,R.,1986, Environmental isotopes in lake studies, in Fritz, P., and Fontes, J-Ch., eds., Handbook of environmental isotope geochemistry—The terrestrial environment, v. 2,: Amsterdam, Elsevier-Verlag, p. 113–168.

Hendrickson, K., 2001, Brazos River, The handbook of Texas online, www.tshaonline.org/handbook/online/articles/BB/rnb7.html

Herczeg, A.L., and Edmunds, W.M., 2000, Inorganic ions as tracers, *in* Cook, P.G., and Herczeg, A.L., eds., Environmental tracers in subsurface hydrology: Boston, Kluwer Academic Publishers, p. 31–77.

Kilham, P., 1990, Mechanisms controlling the chemical composition of lakes and rivers—Data from Africa: Limnology Oceanography, v. 35, p. 80–83.

Krouse, H.R., and Mayer, B., 2000, Sulfur and oxygen isotopes in sulfate, *in* Cook, P.G., and Herczeg, A.L., eds., Environmental tracers in subsurface hydrology: Boston, Kluwer Academic Publishers, p. 195–231.

Lyne, V., and Hollick, M., 1979, Stochastic time-variable rainfall runoff modeling, *in* Hydrology and water resources symposium, Perth, 1979, Proceedings: Australia, National Committee on Hydrology and Water Resources of the Institution of Engineers, p. 89–92.

Martinelli, L.A., Victoria, R.L., and Matsui, E., 1989, The use of oxygen isotopic composition to study water dynamics in Amazon floodplain lakes, *in* Isotopes hydrology investigations in Latin America: Vienna, International Atomic Energy Association, Tecdoc - 502, p. 91–101.

Mayer, B., 1998, Potential and limitations of sulfur isotope abundance ratios as an indicator for natural and anthropogenic induced environmental change, *in* Isotope techniques in the study of past and current environmental changes in the hydrosphere and atmosphere: Vienna, International Atomic Energy Association p. 423–435.

Narasimham, B., Srinvasin, R., Quiring, S., and Neilson-Gammon, J., 2005, Digital climate atlas of Texas: College Station, Texas A&M University, Project report prepared for the Texas Water Development Board under contract no. 2005-483-559, 108 p.

Nathan, R.J., and McMahon, T.A., 1990, Evaluation of automated techniques for baseflow and recession analyses: Water Resources Research, v. 26, p. 1465–1473.

Newman, L., and Forrest, J., 1991, Sulfur isotope measurements relevant to power plant emissions in the northeastern United States, *in* Krouse, H.R., and Grienko, V.A., eds., Natural and anthropogenic sulfur in the environment, SCOPE 43: Chicester, Wiley and Sons, p. 87–91.

Osting, T., Furnans, J., and Mathews, R., 2004a, Surface connectivity between six oxbow lakes and the Brazos River, Texas: Texas Water Development Board unpublished report, 63 p., www.twdb.state.tx.us/instreamflows/pdfs/TWDB_SurfaceBrazosOxbowsFinal_20041207.pdf.

Osting, T., Mathews, R., and Austin, B., 2004b, Analysis of instream flows for the Lower Brazos River—hydrology, hydraulics, and fish habitat utilization: Texas Water Development Board unpublished report, 161 p.

Philips, F.M., 1994, Environmental tracers for water movement in desert soils of the American Southwest: Soil Science Society American Journal, v. 58, p. 14–24.

Ryder, P., 1996, Groundwater atlas of the United States, Oklahoma and Texas: U.S. Geological Survey Publication HA-730E.

Scanlon, B., 1991, Evaluation of moisture flux from chloride data in desert soils: Journal of Hydrology, v. 128, p. 137–156.

Scanlon, B., 2000, Uncertainties in water fluxes and residence times using environmental tracers in an arid unsaturated zone: Water Resources Research, v. 36, p. 395–409.

Scanlon, B., Dutton, A., and Sophocleus, M., 2002, Groundwater recharge in Texas: Bureau of Economic Geology unpublished report prepared for the Texas Water Development Board, 84 p.

Shah, S.D., Houston, N.A., and Braun, C.L., 2007a, Hydrogeologic characterization of the Brazos River Alluvial Aquifer, Bosque County to Fort Bend County, Texas: U.S. Geological Survey Scientific Investigations Map 2007-2989, 17 p.

Shah, S.D., Kress, W.H., and Legchenko, A., 2007b, Application of magnetic resonance soundings and other surface geophysical methods to characterize the hydrostratigraphy of the Brazos River Alluvial Aquifer, College Station, Texas—A pilot study: U.S. Geological Survey Scientific Investigations Report 2007-5203, 34 p.

Stallard, R.F., and Edmond, J.M., 1981, Geochemistry of the Amazon— Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge: Journal of Geophysical Research, v. 86, p. 9844–9858.

TWDB (Texas Water Development Board), 2001, Surveys of irrigation in Texas 1958, 1964, 1969, 1974, 1979, 1984, 1989, 1994, and 2000: Texas Water Development Board Report 347, 102 p.

Van Den Brink, F.W.B., Van Der Velde, G., Buijse, A.D., and Klink, A.G., 1996, Biodiversity in the Lower Rhine and Meuse river-floodplains—Its significance for ecological river management: Aquatic Ecology, v. 30, p. 129–149.

Wainio, S.E., Beckett, P.J., Pearson, D.A.B., and Courtin, G.M., 2003, A potential remediation strategy using wetland vegetation and aquatic macrophytes in Kelley lake, Sudbury, Ontario, variously paginated.

White, K., and Sloto, R.A., 1990, Base flow frequency characteristics of selected Pennsylvanian streams: U.S. Geological Survey Water Resources Investigation Report 90-4160, 66 p.

Winemiller, K.O., Gelwick, F.P., Bonner, T., Zeug, S., and Williams, C., 2004, Response of oxbow lake biota to hydrologic exchanges with the Brazos River Channel: Final project report submitted to the Texas Water Development Board, 232 p., www.twdb.state.tx.us/rwpg/rpgm_rpts/2003483493.doc

10 *Appendix 1: Surface water composition from the Brazos River*

County	Location	Latitude	Longitude	Collection date	Temp.	Specific conductivity	DO	DO saturation	pH	Salinity	Na	K	Mg	Ca	TSS	Cl	SO_4	Nitrate
					°C	µS/cm	mg/l	%		ppt	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l N as NO_3
Brazos	Brazos River at SH 105	30.36	-96.15	5/13/1997	20.55	567	7.36	83.10	7.82	0.30					377.14	67.27	45.70	1.08
Brazos	Brazos River at SH 105	30.36	-96.15	6/19/1997	26.86	572	7.03	87.90	7.99	0.30					291.30	57.81	41.22	0.62
Brazos	Brazos River at SH 105	30.36	-96.15	7/9/1997	28.09	589	8.69	76.60	7.91	0.40					570.00	65.03	40.42	0.22
Brazos	Brazos River at SH 105	30.36	-96.15	8/18/1997	31.03	872	10.03	135.60	8.11	0.50					74.05	100.72	56.54	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	9/10/1997	28.80	1013	6.82	88.80	7.97	0.50					40.86	140.94	71.46	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	10/14/1997	21.83	654	6.99	80.10	7.82	0.30					313.20	79.29	44.12	0.37
Brazos	Brazos River at SH 105	30.36	-96.15	11/19/1997	10.66	1020	11.26	101.50	8.12	0.50					21.00	129.67	66.39	1.28
Brazos	Brazos River at SH 105	30.36	-96.15	1/7/1998	16.35	238	7.41	77.30	7.81	0.10					<4.00	10.05	13.85	0.54
Brazos	Brazos River at SH 105	30.36	-96.15	2/23/1998	12.30	386	9.54	89.20	8.03	0.20					962.00			
Brazos	Brazos River at SH 105	30.36	-96.15	4/21/1998	19.19	605	7.90	86.80	7.81	0.30					116.00			
Brazos	Brazos River at SH 105	30.36	-96.15	6/3/1998	29.84	911	7.07	93.40	8.13	0.50					54.00			
Brazos	Brazos River at SH 105	30.36	-96.15	7/8/1998	30.51	1060	8.31	110.70	7.79	0.60						139.33	72.10	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	8/20/1998	30.02	962	7.92	106.60	8.09	0.50					30.00	125.14	69.07	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	9/23/1998	29.26	472	5.23	67.60	7.82	0.20					146.00	36.17	28.66	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	10/14/1998	22.36	542	7.87	91.80	7.69	0.30					51.00	48.09	37.42	0.75
Brazos	Brazos River at SH 105	30.36	-96.15	2/16/1999	15.81	566	9.30	94.30	8.03	0.30	30.17	3.50	8.31	63.00	55.00	55.02	54.77	1.14
Brazos	Brazos River at SH 105	30.36	-96.15	3/24/1999		529	8.65	94.10	7.82	0.30	31.90	3.70	6.99	61.60	262.00	62.34	55.86	1.80
Brazos	Brazos River at SH 105	30.36	-96.15	5/18/1999	27.01	414	7.22	90.80	8.02	0.20	18.78	3.66	5.64	56.70	297.00	33.74	35.83	1.34
Brazos	Brazos River at SH 105	30.36	-96.15	6/21/1999	29.90	568	8.31	113.60	8.22	0.30	31.56	3.54	9.51	64.30	67.00	51.13	52.24	1.57
Brazos	Brazos River at SH 105	30.36	-96.15	7/21/1999	31.13	434	8.45	115.00	8.30	0.20	21.90	3.58	6.84	56.20	78.00	32.88	34.94	0.94
Brazos	Brazos River at SH 105	30.36	-96.15	8/24/1999	31.94	1138	6.27	85.20	8.04	0.60				71.50	45.00	223.76	107.09	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	9/22/1999	25.23	1031	9.69	117.60	8.05	0.50				72.30	22.00	176.61	96.16	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	10/18/1999	21.87	1030	8.48	97.10	7.91	0.50	82.28	3.88	17.61	70.50	23.00	166.62	100.51	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	12/13/1999	14.40	917	11.23	110.10	8.09	0.50				67.00	66.00	138.99	83.91	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	3/21/2000	16.98	497			7.83	0.30				45.60	97.00	36.63	37.83	1.00
Brazos	Brazos River at SH 105	30.36	-96.15	4/18/2000	22.48	485	7.18	81.20	7.95	0.20				56.90	148.00	53.70	40.29	1.68
Brazos	Brazos River at SH 105	30.36	-96.15	6/28/2000	31.05	389	9.25	119.00	8.48	0.20					41.00	29.42	36.81	0.57
Brazos	Brazos River at SH 105	30.36	-96.15	7/19/2000	31.76	785	7.82	106.80	8.22	0.40					18.00	106.49	77.72	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	8/23/2000	30.44	1208	6.30	83.80	8.23	0.60					41.00	286.82	115.47	0.28
Brazos	Brazos River at SH 105	30.36	-96.15	9/13/2000	29.26	1321	6.09	81.70	7.90	0.70					13.00	336.18	115.98	<0.05
Brazos	Brazos River at SH 105	30.36	-96.15	10/24/2000	23.60	838	7.64	88.50	7.99	0.40								
Brazos	Brazos River at SH 105	30.36	-96.15	11/21/2000	9.74	216	11.24	97.00	7.74	0.10					880.00	23.63	27.60	1.25
Brazos	Brazos River at SH 105	30.36	-96.15	12/12/2000	10.95	488	15.94	99.50	7.97	0.18					65.00	57.56	46.29	1.63
Brazos	Brazos River at SH 105	30.36	-96.15	1/23/2001	6.71	338	10.63	60.90	7.82	0.20					1397.00	25.11	32.52	1.54
Brazos	Brazos River at SH 105	30.36	-96.15	2/21/2001	12.68	362	10.00	92.90	7.85	0.18					310.00	24.88	30.25	2.53
Brazos	Brazos River at SH 105	30.36	-96.15	3/20/2001	12.85	677	10.19	95.40	8.03	0.34					388.00	114.08	63.63	0.99
Brazos	Brazos River at SII 105	30.36	-96.15	6/19/2001	28.64	488	5.92	74.19	7.53	0.25					1200.00	49.68	49.09	1.77
Brazos	Brazos River at SH 105	30.36	-96.15	7/17/2001	31.45	1041	6.63	89.50	7.94	0.55					31.00	223.60	108.08	<0.05

Temp. = temperature, °C = degrees centigrade, µS/cm = micro-siemens per centimeter, DO = dissolved oxygen, mg/l = milligrams per liter, ppt = parts per thousand, and % = percent, SH = state highway.

County	Location	Latitude	Longitude	Collection date	Temp.	Specific conductivity	DO	DO saturation	pH	Salinity	Na	K	Mg	Ca	TSS	Cl	SO$_4$	Nitrate
					°C	µS/cm	mg/l	%		ppt	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l N as NO$_3$
Waller	Brazos River at US 290	30.12	-96.18	12/8/1998	18.67	415	7.72	81.80	7.77	0.20					284.00	20.70	24.30	0.57
Waller	Brazos River at US 290	30.12	-96.18	1/28/1999	15.49	528	9.75	97.40	7.84	0.30	29.30	3.10	7.74	54.30	44.00	54.96	56.15	0.69
Waller	Brazos River at US 290	30.12	-96.18	2/24/1999	15.25	542	10.82	108.30	8.08	0.30	26.69	3.50	8.21	62.00	38.00	45.21	48.25	0.86
Waller	Brazos River at US 290	30.12	-96.18	3/24/1999		441	7.75	84.90	7.71	0.20	24.90	3.72	5.48	55.50	320.00	48.01	48.80	1.62
Waller	Brazos River at US 290	30.12	-96.18	4/26/1999	25.05	606	10.48	121.00	8.04	0.30	36.35	3.18	10.89	57.70	50.00	66.95	57.93	0.11
Waller	Brazos River at US 290	30.12	-96.18	5/18/1999	26.80	407	6.77	84.70	7.98	0.20	20.62	4.05	5.12	55.10	491.00	35.78	38.17	1.48
Waller	Brazos River at US 290	30.12	-96.18	6/21/1999	29.41	633	10.51	137.60	8.49	0.30	39.01	3.32	12.21	63.20	64.00	63.68	53.90	0.61
Waller	Brazos River at US 290	30.12	-96.18	8/24/1999	31.15	1135	7.74	104.80	8.32	0.60				71.30	67.00	225.87	103.08	<0.05
Waller	Brazos River at US 290	30.12	-96.18	9/22/1999	24.84	1015	8.24	99.50	8.07	0.50				76.80	32.00	165.23	87.29	<0.05
Waller	Brazos River at US 290	30.12	-96.18	10/18/1999	20.21	1005	8.81	97.50	8.00	0.50	78.77	3.89	16.62	74.60	23.00	145.79	87.08	<0.05
Waller	Brazos River at US 290	30.12	-96.18	12/14/1999	14.44	854	12.67	123.80	8.27	0.40				70.60	24.00	125.96	72.70	0.81
Waller	Brazos River at US 290	30.12	-96.18	4/18/2000	22.84	457	7.18	83.30	7.95	0.20				56.00	332.00	46.33	41.02	2.11
Waller	Brazos River at US 290	30.12	-96.18	6/28/2000	30.87	350	8.89	113.90	8.40	0.20					116.00	25.03	28.67	0.57
Waller	Brazos River at US 290	30.12	-96.18	7/19/2000	30.21	791	6.82	90.60	8.29	0.40					39.00	104.20	71.32	<0.05
Waller	Brazos River at US 290	30.12	-96.18	8/23/2000	29.69	1121	7.53	97.40	8.42	0.60					53.00	263.43	110.05	<0.05
Waller	Brazos River at US 290	30.12	-96.18	9/13/2000	28.37	1251	6.41	80.90	8.30	0.70					55.00	299.57	106.75	<0.05
Waller	Brazos River at US 290	30.12	-96.18	10/24/2000	23.38	891	7.58	88.60	8.18	0.50								
Waller	Brazos River at US 290	30.12	-96.18	11/21/2000	10.48	427	9.38	81.70	7.71	0.21					516.00	50.27	39.52	1.19
Waller	Brazos River at US 290	30.12	-96.18	12/12/2000	11.39	524	8.29	74.80	7.83	0.27					56.00	50.49	42.81	1.46
Waller	Brazos River at US 290	30.12	-96.18	1/23/2001	6.50	277	11.26	88.40	7.76	0.10					269.00	20.47	27.72	1.03
Waller	Brazos River at US 290	30.12	-96.18	2/21/2001	12.78	347.5	10.41	93.80	7.72	0.17					535.00	29.08	36.49	2.86
Waller	Brazos River at US 290	30.12	-96.18	3/20/2001	13.14	634.5	9.40	87.50	7.73	0.33					353.00	116.62	60.43	0.63
Waller	Brazos River at US 290	30.12	-96.18	4/17/2001	23.17	696.5	6.17	70.30	8.14	0.36					205.00	124.86	78.11	1.23
Waller	Brazos River at US 290	30.12	-96.18	5/22/2001	24.60	563.59	7.55	90.90	7.98	0.28					157.00	57.00	44.31	1.00
Waller	Brazos River at US 290	30.12	-96.18	6/19/2001	28.00	319.7	5.03	63.40	7.57	0.15					555.00	21.46	28.14	1.36
Waller	Brazos River at US 290	30.12	-96.18	7/17/2001	31.46	852.5	6.07	80.00	8.17	0.43					55.00	172.33	97.63	<0.05
Waller	Brazos River at US 290	30.12	-96.18	8/14/2001	30.50	1034	4.42	61.09	7.98	0.54					65.00	206.52	105.44	<0.05
Waller	Brazos River at US 290	30.12	-96.18	9/19/2001	28.00	445.2	6.40	81.60	8.10	0.20					138.00	41.90	38.00	0.70
Waller	Brazos River at US 290	30.12	-96.18	10/9/2001	21.60	575.4	6.90	76.50	7.90	0.30					73.00	73.70	55.70	1.00
Waller	Brazos River at US 290	30.12	-96.18	11/28/2001	16.10	419.7	8.50	86.80	7.90	0.20								
Waller	Brazos River at US 290	30.12	-96.18	12/18/2001	14.40	211.6	8.10	78.30	7.80	0.10					2520.00	17.60	23.70	1.00
Waller	Brazos River at US 290	30.12	-96.18	1/15/2002	11.30	573.5	10.70	95.30	7.80	0.30					82.00	57.30	59.50	1.10
Waller	Brazos River at US 290	30.12	-96.18	2/20/2002	13.49	525.1	10.24	98.20	7.88	0.27					84.00	58.47	49.44	0.97
Waller	Brazos River at US 290	30.12	-96.18	3/21/2002	18.61	861.5	8.56	90.20	8.20	0.45					24.00	134.24	92.94	0.96
Waller	Brazos River at US 290	30.12	-96.18	4/16/2002	22.82	417.1	8.37	97.10	8.02	0.21					233.00	64.45	50.18	1.05
Waller	Brazos River at US 290	30.12	-96.18	5/14/2002	23.49	817.7	7.72	90.20	7.94	0.42					32.00	113.64	81.33	0.17
Waller	Brazos River at US 290	30.12	-96.18	6/11/2002	29.45	973.4	5.01	67.00	8.25	0.51					85.00	228.04	111.03	<0.02
Waller	Brazos River at US 290	30.12	-96.18	7/17/2002	24.54	352	6.50	74.40	7.91	0.17					836.00	34.99	26.09	0.46

Temp. = temperature, °C = degrees centigrade, µS/cm = micro-siemens per centimeter, DO = dissolved oxygen, mg/l = milligrams per liter, ppt = parts per thousand, and % = percent, US = United States.

County	Location	Latitude	Longitude	Collection date	Temp.	Specific conductivity	DO	DO saturation	pH	Salinity	Na	K	Mg	Ca	TSS	Cl	SO$_4$	Nitrate
					°C	µS/cm	mg/l	%		ppt	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l N as NO$_3$
Waller	Brazos River at US 290	30.12	-96.18	8/27/2002	30.98	1061.00	6.12	82.50	8.27	0.56	129.20	6.16	18.18		69.00	229.09	99.11	
Waller	Brazos River at US 290	30.12	-96.18	9/19/2002	27.82	1023.00	5.31	67.90	8.30	0.53					194.00	214.85	101.34	0.67
Waller	Brazos River at US 290	30.12	-96.18	11/21/2002	15.22	647.00	8.21	80.70	7.79	0.41					129.00			0.42
Waller	Brazos River at US 290	30.12	-96.18	12/17/2002	12.57	324.70	9.12	86.00	8.07	0.16					330.00		20.19	0.48
Waller	Brazos River at US 290	30.12	-96.18	1/28/2003	9.56	422.80	13.24	108.70	7.89	0.21					77.00	226.94	76.38	7.45
Waller	Brazos River at US 290	30.12	-96.18	2/19/2003	13.47	590.50	9.68	92.20	7.86	0.30					110.00	69.25	65.62	1.50
Waller	Brazos River at US 290	30.12	-96.18	3/12/2003												28.66	35.75	1.22
Waller	Brazos River at US 290	30.12	-96.18	4/15/2003	21.31	537.00	8.62	98.60	8.05	0.27								
Waller	Brazos River at US 290	30.12	-96.18	5/28/2003	26.23	781.40	8.10	100.00	7.90	0.40						99.20		0.23
Waller	Brazos River at US 290	30.12	-96.18	6/18/2003	27.68	497.60	5.48	66.30	7.45	0.25					209.00	58.28		1.40
Waller	Brazos River at US 290	30.12	-96.18	7/29/2003	30.60	1186.00	6.93	90.30	8.01	0.62					33.00			
Waller	Brazos River at US 290	30.12	-96.18	8/19/2003											44.00	181.60		0.20
Waller	Brazos River at US 290	30.12	-96.18	10/15/2003														
Waller	Brazos River at US 290	30.12	-96.18	2/19/2004	11.17	200.00			7.68	0.09					36.00	22.73	30.38	1.75
Waller	Brazos River at US 290	30.12	-96.18	8/19/2004	28.30	1099.00	5.98	77.40	8.11	0.58					82.00	221.41	97.13	0.06
Waller	Brazos River at US 290	30.12	-96.18	11/18/2004	17.87	644.00	9.10	93.50	7.55	0.33					168.00	88.15	54.12	0.76
Waller	Brazos River at US 290	30.12	-96.18	2/24/2005	17.49	818.90	8.72	93.40	8.00	0.42					151.00	143.95	73.39	0.58
Waller	Brazos River at US 290	30.12	-96.18	5/26/2005	29.45	743.60	8.53	112.90	7.44	0.38								
Waller	Brazos River at FM 529	29.91	-96.11	1/28/1999	15.17	512.00	9.19	92.90	7.76	0.30	28.32	3.08	7.38	53.00	82.00	49.68	54.52	0.92
Waller	Brazos River at FM 529	29.91	-96.11	2/24/1999	15.56	559.00	10.81	109.40	8.07	0.30	26.77	3.30	8.52	65.40	36.00	45.13	48.45	0.84
Waller	Brazos River at FM 529	29.91	-96.11	3/24/1999		404.00	7.33	80.00	7.71	0.20	21.81	3.73	5.22	58.40	856.00	37.27	44.69	1.90
Waller	Brazos River at FM 529	29.91	-96.11	4/26/1999	25.34	593.00	10.11	123.40	8.19	0.30	34.77	3.09	10.75	57.60	47.00	61.90	56.90	<0.05
Waller	Brazos River at FM 529	29.91	-96.11	5/18/1999	26.82	409.00	6.64	83.20	7.95	0.20	21.72	4.03	5.23	55.20	585.00	37.47	39.67	1.68
Waller	Brazos River at FM 529	29.91	-96.11	6/21/1999	29.71	586.00	9.11	119.60	8.54	0.30	37.02	3.35	10.89	58.50	94.00	61.18	54.40	0.08
Waller	Brazos River at FM 529	29.91	-96.11	7/21/1999	30.96	550.00	9.30	124.50	8.55	0.30	38.96	4.40	9.72	62.40	83.00	53.44	49.50	1.09
Waller	Brazos River at FM 529	29.91	-96.11	8/24/1999	30.80	1112.00	7.20	96.90	8.13	0.60				74.60	51.00	209.53	96.92	<0.05
Waller	Brazos River at FM 529	29.91	-96.11	9/22/1999	25.24	1062.00	8.82	108.00	8.12	0.60				83.80	38.00	184.09	87.75	<0.05
Waller	Brazos River at FM 529	29.91	-96.11	12/14/1999	14.64	833.00	12.85	126.50	8.43	0.40				72.90	34.00	115.10	66.54	<0.05

Temp. = temperature, °C = degrees centigrade, µS/cm = micro-siemens per centimeter, DO = dissolved oxygen, mg/l = milligrams per liter, ppt = parts per thousand, and % = percent, US = United States.

Appendix 2

Precipitation weighted mean rain water composition for the National Trends Network TX 10 site (Colorado County) and TX 56 site (Wise County). Data and station locations downloaded from the National Atmospheric Water Deposition Web site at http://nadp.sws.uiuc.edu/.

Station ID	Year	Chemical composition (mg/l)									
		Ca	Mg	K	Na	NH_4	NO_3	Cl	SO_4	pH	HCO_3
TX10	1984	0.21	0.09	0.04	0.60	0.14	0.64	1.05	0.97	5.07	N/A
TX10	1985	0.13	0.05	0.03	0.29	0.14	0.62	0.51	0.97	4.89	N/A
TX10	1986	0.11	0.05	0.03	0.31	0.17	0.76	0.55	0.98	4.88	N/A
TX10	1987	0.12	0.05	0.04	0.36	0.29	0.78	0.66	1.21	4.86	N/A
TX10	1988	0.22	0.07	0.04	0.51	0.17	1.00	0.89	1.44	4.82	N/A
TX10	1989	0.14	0.04	0.04	0.26	0.24	0.62	0.46	0.95	5.05	N/A
TX10	1990	0.18	0.07	0.05	0.52	0.28	0.96	0.91	1.45	4.86	N/A
TX10	1991	0.13	0.04	0.05	0.31	0.18	0.79	0.55	0.98	4.86	N/A
TX10	1992	0.07	0.03	0.04	0.25	0.16	0.69	0.40	1.00	4.83	N/A
TX10	1993	0.15	0.05	0.04	0.37	0.20	0.69	0.61	0.99	4.98	N/A
TX10	1994	0.11	0.04	0.04	0.34	0.24	0.80	0.57	0.98	4.84	N/A
TX10	1995	0.18	0.04	0.03	0.34	0.20	0.77	0.58	1.05	4.81	N/A
TX10	1996	0.11	0.07	0.03	0.43	0.20	0.69	0.74	0.86	4.94	N/A
TX10	1997	0.12	0.05	0.03	0.35	0.19	0.75	0.61	1.12	4.78	N/A
TX10	1998	0.20	0.05	0.03	0.38	0.22	0.65	0.66	0.93	4.90	N/A
TX10	1999	0.21	0.06	0.04	0.49	0.28	0.91	0.81	1.40	4.77	N/A
TX10	2000	0.20	0.06	0.04	0.46	0.22	0.82	0.77	1.13	4.86	N/A
TX10	2001	0.15	0.03	0.02	0.28	0.17	0.63	0.49	0.96	4.91	N/A
TX10	2002	0.16	0.04	0.02	0.29	0.14	0.56	0.50	0.84	4.96	N/A
TX10	2003	0.15	0.04	0.03	0.31	0.22	0.78	0.54	1.01	4.87	N/A
TX10	2004	0.12	0.05	0.03	0.44	0.21	0.67	0.76	0.91	4.96	N/A
TX56	1983	0.57	0.04	0.03	0.20	0.23	0.97	0.31	1.32	5.10	N/A
TX56	1984	0.42	0.05	0.04	0.20	0.26	1.05	0.29	1.29	5.01	N/A
TX56	1985	0.27	0.04	0.04	0.17	0.25	0.86	0.28	1.14	5.01	N/A
TX56	1986	0.24	0.03	0.03	0.15	0.20	0.76	0.24	1.02	5.04	N/A
TX56	1987	0.27	0.03	0.05	0.16	0.24	0.91	0.25	1.22	4.93	N/A
TX56	1988	0.40	0.03	0.02	0.15	0.12	0.80	0.20	1.16	5.05	N/A
TX56	1989	0.49	0.04	0.08	0.20	0.40	1.19	0.31	1.43	5.14	N/A
TX56	1990	0.28	0.03	0.03	0.17	0.36	0.90	0.28	1.21	5.09	N/A
TX56	1991	0.26	0.02	0.03	0.12	0.24	0.92	0.18	1.03	5.01	N/A
TX56	1992	0.24	0.02	0.03	0.10	0.30	0.90	0.14	1.04	4.94	N/A
TX56	1993	0.24	0.03	0.03	0.16	0.21	0.75	0.28	0.91	5.10	N/A
TX56	1994	0.31	0.02	0.03	0.12	0.27	1.04	0.18	1.08	4.93	N/A
TX56	1995	0.49	0.03	0.04	0.13	0.34	1.15	0.19	1.25	4.99	N/A
TX56	1996	0.34	0.03	0.03	0.15	0.31	1.16	0.22	1.21	4.83	N/A
TX56	1997	0.20	0.02	0.03	0.09	0.30	1.04	0.14	1.10	4.84	N/A
TX56	1998	0.31	0.02	0.03	0.10	0.34	0.95	0.17	1.24	4.93	N/A
TX56	1999	0.45	0.04	0.05	0.21	0.37	1.25	0.34	1.46	4.98	N/A
TX56	2000	0.48	0.06	0.09	0.17	0.31	1.15	0.25	1.22	5.13	N/A
TX56	2001	0.38	0.03	0.03	0.14	0.31	1.03	0.22	1.13	5.09	N/A
TX56	2002	0.33	0.03	0.08	0.13	0.29	0.95	0.21	1.09	5.21	N/A
TX56	2003	0.33	0.02	0.04	0.10	0.41	1.07	0.15	1.05	5.31	N/A
TX56	2004	0.20	0.02	0.03	0.11	0.24	0.87	0.17	0.90	4.96	N/A

N/A = data not available.