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# Spatial Distribution of Solutes in Aquifer Outcrop Zones along the Brazos River, East-Central Texas

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**ABSTRACT:**Concentrations of several solutes – nitrate, arsenic, sulfate, boron, chloride, and bromide – along with total dissolved solids (TDS) in ten counties bordering the Brazos River in east-central Texas were compiled, mapped, and analyzed relative to regional land use and geology. Agriculture and oil/gas production are major activities and potential sources of groundwater contamination in the study area. Data were compiled from 104 water wells with a median depth of 446 ft (136 m) in the outcrop zones of six sedimentary aquifers: Carizzo-Wilcox, Queen City, Sparta, Yegua-Jackson, Gulf Coast, and Brazos Alluvium. Only two observations surpassed the 44.3 mg/L drinking water standard for nitrate, and four observations exceeded the 10 ug/L standard for arsenic. The median chloride concentration was 53 mg/L; however, the maximum level was almost three times the secondary drinking water standard of 250 mg/L. Chloride, bromide, sulfate, and boron concentrations resembled TDS patterns, with numerous samples exceeding secondary TDS drinking water standards in the Yegua-Jackson Aquifer. Most chloride/bromide ratios were between 100 and 300. Overall, results of this study suggest that natural processes exert a primary control on solute concentrations in the above aquifers, with a potential for modest anthropogenic impacts from agriculture and oil/gas production.

**Key words:** Brazos River, Texas, Groundwater, Agriculture, Oil/gas production

## INTRODUCTION

Agriculture and oil/gas production are significant activities and could impact groundwater in east-central Texas. To further evaluate this potential, this study's objective was to map and evaluate distributions of arsenic, nitrate, sulfate, boron, chloride, and bromide, along with total dissolved solids (TDS) and chloride/bromide ratios, in a ten-county area including outcrop zones of six aquifers (Fig. 1).

Of the six solutes mentioned above, arsenic and nitrate pose the most significant health concerns. Found in groundwater of several countries (WHO, 1999; Welch, 2000), arsenic is associated with cancer, nervous system disorders, cardiovascular problems, kidney and liver disease, diabetes, and respiratory problems (EPA, 2009). The drinking water standard for arsenic is 10 ug/L (EPA, 2009).

Wood preservation and, historically, agriculture are the largest industrial applications for arsenic in the United States (Welch *et al.*, 2000). Arsenic has been applied extensively to cropland, especially cotton fields, as a pesticide and defoliant. Inorganic arsenic, mainly calcium and lead arsenate, was widely applied prior to being banned for pesticide use in the 1980s and 1990s. Arsenic also occurs naturally in rock, especially in association with metal sulfide and oxide deposits.

Worldwide, nitrate is one of the most common contaminants in groundwater (Spalding and Exner, 1993). The drinking water standard for nitrate is 44.3 mg/L (EPA, 2009). Excessive nitrate in drinking water may lead to methemoglobinemia (Johnson *et al.*, 1987) and non-Hodgkin's lymphoma (Ward *et al.*, 1994). Nitrogen compounds originating from several sources are oxidized in aerated soils to soluble nitrate, which can percolate to groundwater. Agricultural nitrogen sources include fertilizer, crop residue, animal waste, and mineralization of soil organic nitrogen; nonagricultural sources include lawn fertilizer, septic systems, municipal and industrial discharge, nitrogen fixation by legumes, and atmospheric deposition.

Sulfate and chloride are common natural components of groundwater; each has a secondary maximum contaminant level (MCL) of 250 mg/L (EPA, 2009). Generally, sulfate is considered beneficial in

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*Corresponding author E-mail: hudak@unt.edu irrigation water (Bouwer, 1978). Chloride concentrations above 150 mg/L are toxic to crops and generally unsuitable for irrigation (Bouwer, 1978).

Several soluble minerals in sedimentary rocks release sulfate and chloride upon dissolution; consequently, groundwater in sedimentary aquifers may have relatively high levels of these constituents (Hem, 1992). Sulfate in groundwater is derived principally from gypsum and anhydrite (Sacks, 1996), whereas chloride often originates from halite and sylvite in sedimentary rocks. These minerals are especially abundant in evaporite sedimentary rocks, which may also produce boron and various other solutes in groundwater. While essential in plant nutrition, high boron concentrations can harm irrigated crops; sensitive, semi tolerant, and tolerant crops can withstand boron concentrations up to approximately 1250, 2500, and 3750 ug/L, respectively (USSL, 1954). Agricultural activity, such as irrigation return flow, may also contribute chloride, sulfate, and boron to aquifers.

In many rural settings, oilfield brine as well as agricultural activity may impact groundwater. High chloride, bromide, and total dissolved solids (TDS) concentrations commonly characterize oilfield pollution of groundwater. Constituents of brine can be toxic to crops and unsafe to drink (TWC, 1989). The secondary drinking water standard for TDS is 500 mg/L (EPA, 2009).

Historically, oilfield brine has been discharged into pits and gullies and applied to dirt roads to reduce dust. Currently, most of the oilfield brine generated in the United States is injected into deep wells; however, brine can potentially leak out of cracked or corroded casings, or migrate upward through nearby abandoned wells. Pits for drilling mud and emergency saltwater storage are still used during oil and gas production; these are also potential sources of groundwater pollution (RCT, 1993).

Whittemore (1995) outlined the application of chloride/bromide ratios to identify sources of groundwater contamination. As both chloride and bromide are conservative in water, their ratio tends not to change significantly between a contaminant source and receptor. Davis et al. (1998) concluded that chloride/bromide ratios generally range from 50-150 in atmospheric precipitation, 300-600 in domestic sewage, 1000-10,000 in dissolved evaporites, 100-300 in oilfield brine (though ratios vary widely), and 100-200 in unimpaired, shallow groundwater. Seawater has a chloride/bromide ratio of approximately 290 (Hem, 1992).

The study area includes ten counties in east-central Texas (Fig. 1, Table 1). Throughout this region, aquifers provide water for irrigation, cities, houses, livestock, and industry (Ashworth and Hopkins, 1995). Aquifer outcrops (unconfined) are relatively vulnerable to contaminants introduced at the land surface (TWC, 1989).

Outcrops of six sedimentary aquifers intersect the study area; from oldest to youngest: Carrizo-Wilcox, Queen City, Sparta, Yegua-Jackson, Gulf Coast, and Brazos Alluvium. Water-bearing deposits of the Brazos Alluvium form a narrow band along the Brazos River (Shah *et al.*, 2007), whereas the other aquifers outcrop in northeast-trending bands and dip underground to the southeast, where they become confined. The aquifers are of Cenozoic age, originally deposited in fluvial, deltaic, and shallow marine environments (TWC, 1989).

The Carrizo-Wilcox and Gulf Coast are major aquifers; wells in these aquifers commonly yield 500 gal/min (1.9 m3/min) or more. The Carrizo-Wilcox consists of sand interbedded with gravel, silt, clay, and lignite. A leaky artesian system, the Gulf Coast complex comprises interbedded clay, silt, sand, and gravel.

Remaining (minor) aquifers in the study area commonly yield less than 200 gal/min (0.8 m3/min) to wells. The Queen City, Sparta, and Yegua-Jackson consist of, respectively: sand, sandstone, and interbedded clay; sand and interbedded clay; and interbedded sand, silt, and clay (Ashworth and Hopkins, 1995). The youngest aquifer in the study area, the Brazos Alluvium, consists of floodplain and terrace deposits of Quaternary Age. Clay, silt, sand, and gravel are principal constituents of the Brazos Alluvium, which is used mostly for irrigation along the Brazos River Valley.

Long, hot summers and short, mild winters characterize the climate of the study area. On average, the region receives approximately 101 cm of precipitation a year, whereas annual lake evaporation averages approximately 134 cm (Yang, 2010). Precipitation and seepage from lakes and streams, and from irrigation along the Brazos River Valley, recharge aquifers in the study area. Generally, groundwater beneath the study area flows southeastward, following the slope of water-bearing units into the subsurface. The groundwater discharges to wells and adjacent formations (cross-formational flow); and to streams, springs, seeps, and evapotranspiration in valleys.

The study area is predominantly rural, with farms accounting for approximately 68-91% of the total land area in each county (Table 1). Forage (hay), corn, cotton, and sorghum are primary crops grown in the region. The main livestock raised in the study area include

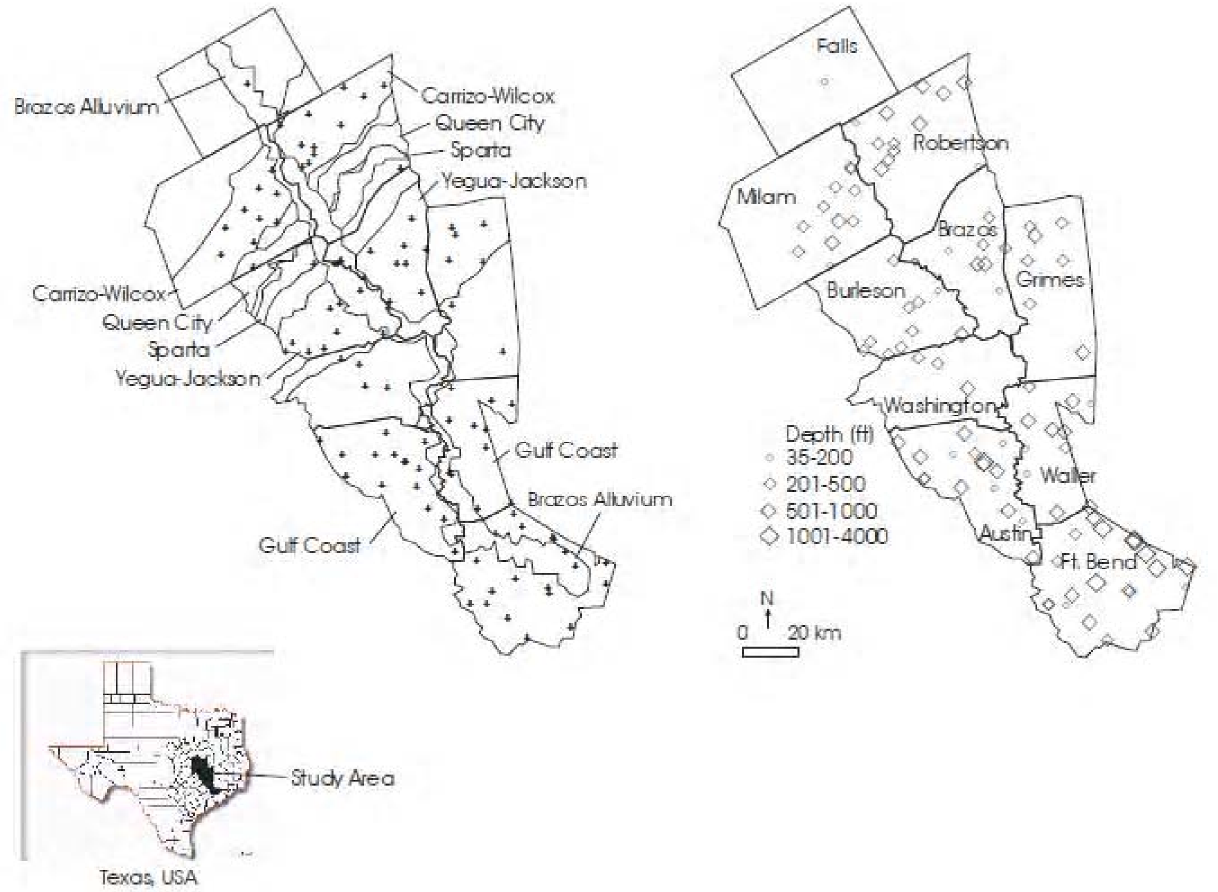

**Fig. 1. Location map showing county boundaries (solid), aquifer outcrop zones (dashed), and sampled water wells (pluses) (left); and county names and well depth classifications (right); 1 ft = 0.305 m**

**Table 1. Selected Characteristics of Study Area**

| County | Population[1] | Percent Land in Farms[2] |
|---|---|---|
| Austin | 27,248 | 80 |
| Brazos | 179,992 | 74 |
| Burleson | 16,570 | 85 |
| Falls | 16,782 | 91 |
| Ft. Bend | 556,870 | 68 |
| Grimes | 26,011 | 86 |
| Milam | 24,628 | 83 |
| Robertson | 15,706 | 83 |
| Waller | 36,530 | 82 |
| Washington | 32,893 | 87 |

1U.S. Census Bureau, 2009.

2Census of Agriculture, 2007

chickens, cattle, and horses. Numerous oil and gas wells also occupy the study area, with relatively high concentrations of such wells in Burleson and Brazos Counties (RCT, 2005).

## MATERIALS & METHODS

Solute concentration and water well depth data were obtained from the Texas Water Development Board. Wells were pumped until temperature, conductivity, and pH stabilized (TWDB, 2008). Samples were taken directly from each well, filtered, preserved, and delivered to an analytical laboratory. Samples were collected between 2002 and 2009; most recent samples were retained for wells sampled more than once during this time interval.

Concentrations of arsenic, nitrate, sulfate, boron, chloride, bromide, and total dissolved solids (TDS), along with chloride/bromide ratios, were compiled and mapped for 104 wells in the outcrop zones of the six aquifers: Carrizo-Wilcox (20 wells), Queen City (1 well), Sparta (2 wells), Yegua-Jackson (22 wells), Gulf Coast (49 wells), and Brazos Alluvium (10 wells). These wells supply public (53 wells), domestic (28 wells), irrigation (14 wells), stock (7 wells), and other uses (2 wells). Sampled wells had a median depth of 446 ft (136 m) (Fig. 1). Descriptive statistics were compiled for each solute, TDS, the chloride/bromide ratio, and well depth. ArcView (Environmental Systems Research Institute, Redlands, CA) was used to map well locations and solute concentration categories.

## RESULTS & DISCUSSION

Each solute concentration and well-depth distribution was positively skewed; typical of water-quality data, this pattern reflects more observations at lower than higher concentrations (median concentrations and well depths were closer to minimum than maximum values) (Table 2).

Two relatively shallow wells in the Brazos Alluvium, in the northern part of the study area, registered nitrate levels above the drinking water standard (Fig. 2). These observations reflect possible nitrogen inputs from land-surface sources, such as agriculture. Generally, nitrate concentrations were higher in the Brazos Alluvium, which has shallower wells than the other aquifers; this pattern is consistent with a nitrate origin at or near the land surface (Table 3). However, the median nitrate concentration for the entire study area was only 0.1 mg/L; that is, nitrate is not a significant problem over the study area.

**Table 2. Summary of Solute Concentrations**

| Solute | Number of Observation Observations | Minimum | Maximum | Median |
|---|---|---|---|---|
| Nitrate (mg/L) | 104 | 0.02-0.09 | 85.4 | 0.1 |
| Arsenic (ug/L) | 104 | < 1 | 24.6 | < 2.04 |
| Sulfate (mg/L) | 104 | < 1 | 675 | 16.1 |
| Boron (ug/L) | 104 | < 51 | 6900 | 130 |
| TDS (mg/L) | 104 | 163 | 2568 | 409 |
| Chloride (mg/L) | 104 | 8.2 | 741 | 53 |
| Bromide (mg/L) | 104 | < 0.02 | 3.36 | 0.17-0.21 |
| Chloride/Bromide | 104 | 46-51 | > 1620 | 273-289 |
| Well Depth (ft) | 99 | 35 | 1500 | 446 |

Notes: 1 ft = 0.305 m; ranges reflect uncertainty in values of non-detects.

**Table 3. Medians in Each Aquifer**

| Solute | Median | | | |
|---|---|---|---|---|
| | BA | CW | GC | YJ |
| Nitrate (mg/L) | 6.3 | 0.16 | 0.02 | 0.18 |
| Arsenic (ug/L) | 2.2 | < 2 | 2.07 | < 2 |
| Sulfate(mg/L) | 43.6 | 14.4 | 13 | 95.8 |
| Boron (ug/L) | 178.5 | 146.5 | 67 | 1375 |
| TDS (mg/L) | 605 | 339.5 | 376 | 951 |
| Chloride (mg/L) | 80.0 | 34.3 | 48.7 | 127 |
| Bromide (mg/L) | 0.5 | < 0.4 | 0.2 | 0.6 |
| Chloride/Bromide | 171 | 179-277 | 303 | 263 |
| Well Depth (ft) | 55 | 465 | 540 | 400 |

Notes: Medians computed for aquifers with at least five observations; ranges reflect uncertainty in values of non-detects; BA – Brazos Alluvium; CW – Carrizo-Wilcox; GC – Gulf Coast; YJ – Yegua-Jackson

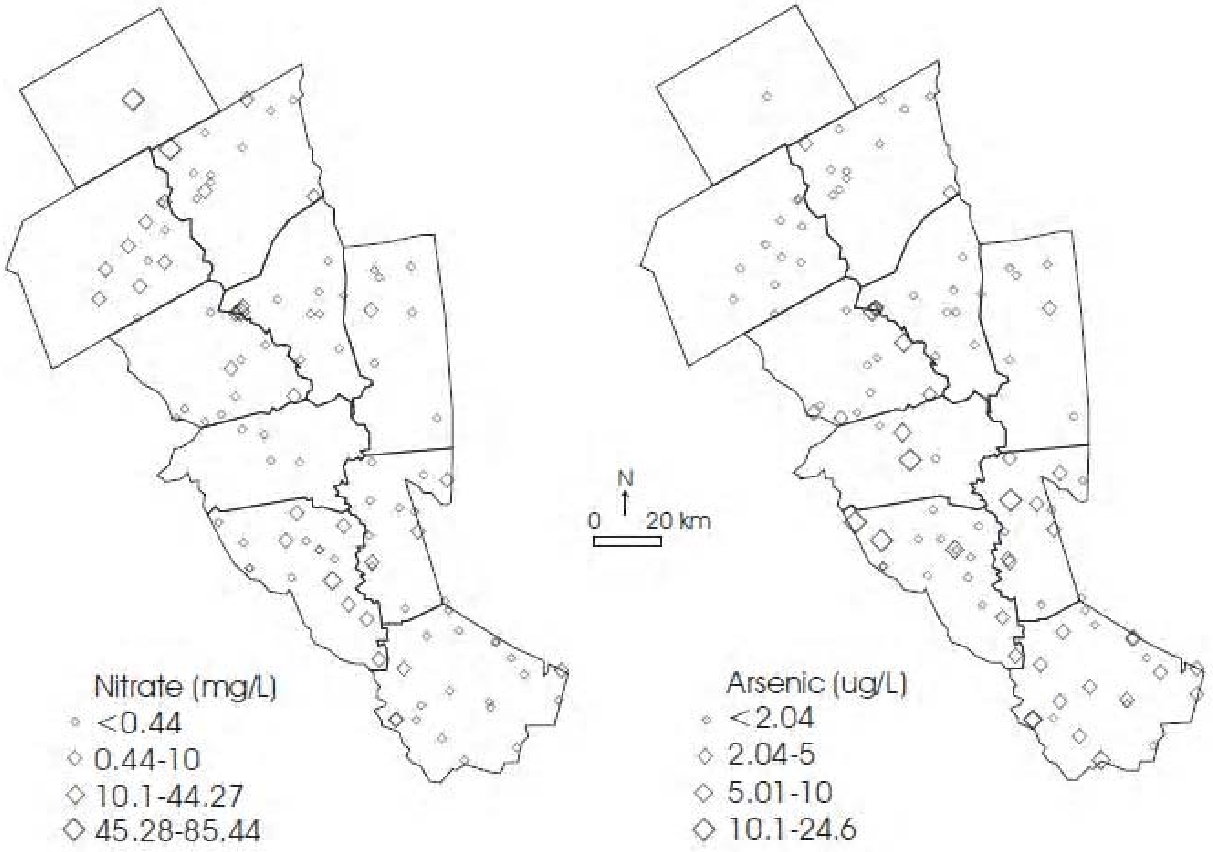

**Fig. 2. Nitrate (left) and arsenic (right) classifications**

Similarly, arsenic concentrations were generally low, with a median concentration of < 2.3 ug/L for each aquifer and for the entire study area (Table 3). Four wells, three relatively deep (> 500 ft, or 152 m) and the other of unknown depth, registered arsenic concentrations above the drinking water standard, with a maximum concentration of 25.6 ug/L. The deep nature of these wells, all in the Gulf Coast Aquifer, suggests predominantly geological rather than anthropogenic sources. Overall low arsenic concentrations may reflect a lack of anthropogenic influence from such sources as arsenic-bearing pesticides and defoliants, reflecting attenuation of arsenic above the water table and/or less intensive cotton farming over the past few decades.

Sulfate and boron concentrations generally followed trends in TDS, with highest values observed in the Yegua-Jackson Aquifer (Table 3; Fig. 3). In this central part of the study area, numerous sulfate concentrations exceeded the secondary standard of 250 mg/L; several boron observations surpassed 2,000 ug/L; and many TDS values were over 1,000 mg/L (double the secondary drinking water standard). Throughout the entire study area, more than half of the TDS observations exceeded 400 mg/L, and numerous observations exceeded the secondary drinking water standard (Table 3). Aquifer composition strongly influenced TDS concentrations; for example, clusters of relatively high TDS occupy central portions of the study area in the Yegua-Jackson outcrop zone (Fig. 1). Solute concentrations were generally highest in the Yegua-Jackson (Table 3).

Over the study area, the median chloride concentration was 53 mg/L, whereas the maximum concentration was nearly triple the secondary drinking water standard of 250 mg/L (Table 2). A primary constituent of groundwater, chloride closely follows TDS patterns observed in this study (Figures 3-4). Nine chloride observations exceeded the secondary drinking water standard, several of them in them in the Yegua-Jackson, which also produced the highest median chloride concentration (Table 3; Fig. 4). Natural constituents of the Yegua-Jackson, long groundwater residence times in clay beds, and intensive oil production and associated brine may contribute to high chloride concentrations beneath the central part of the study area.

Bromide and chloride have similar chemical characteristics; often groundwater enriched in chloride

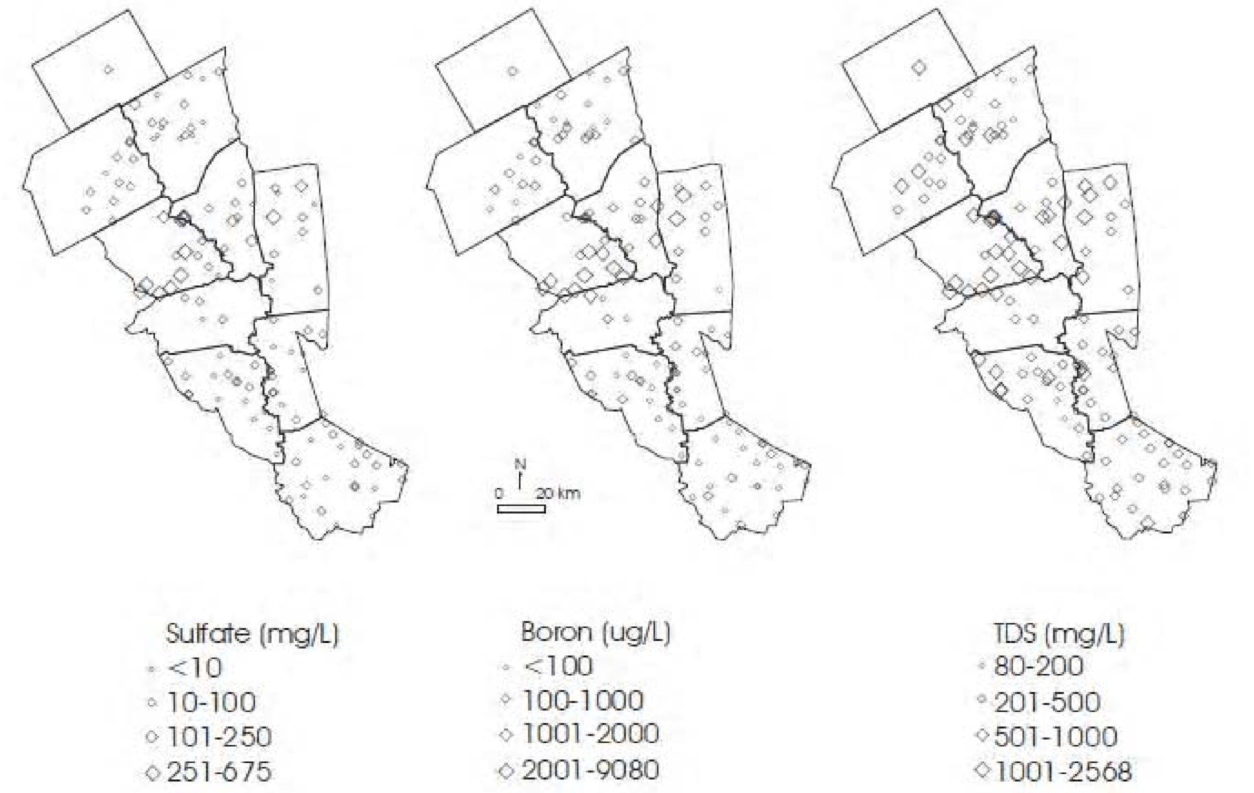

**Fig. 3. Sulfate (left), boron (center), and TDS (right) classifications**

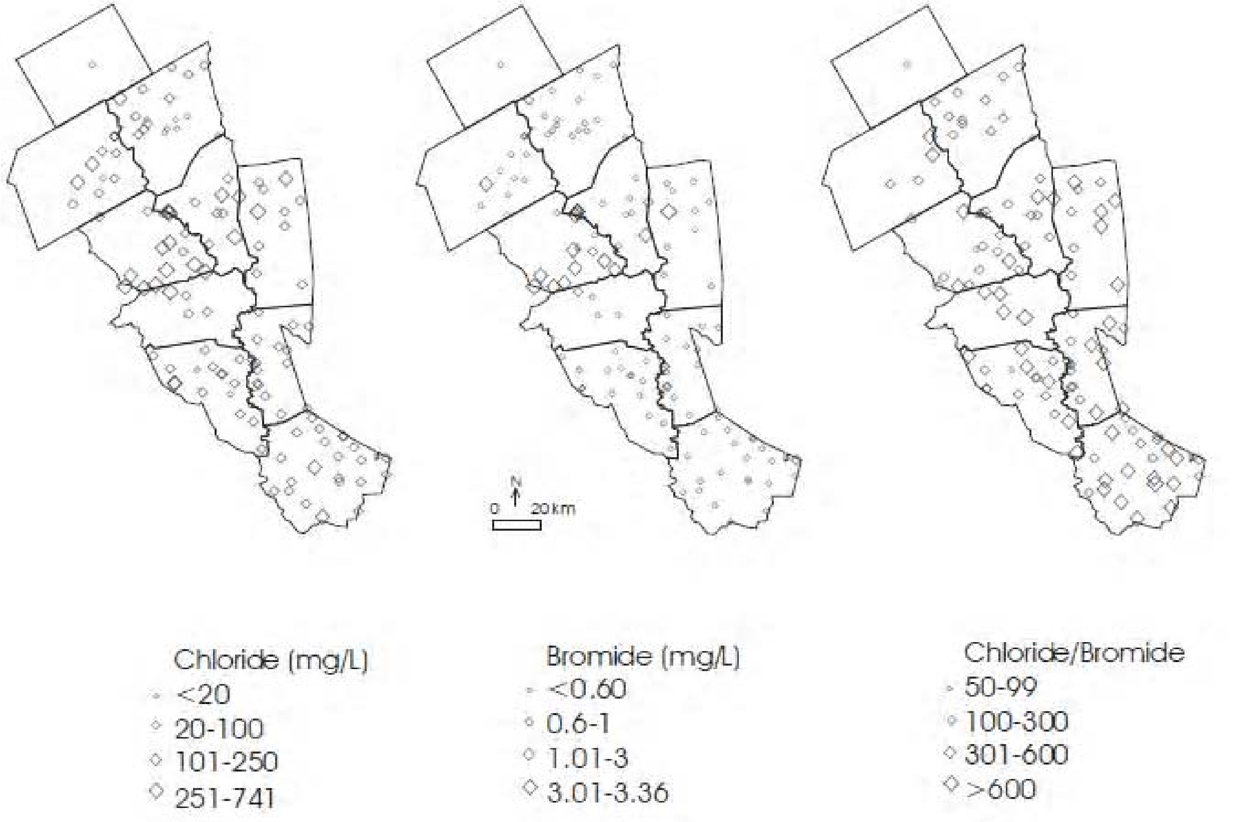

**Fig. 4. Chloride (left), bromide (center), and chloride/bromide (right) classifications; chloride/bromide ratios not assignable to a category, due to non-detectable bromide, excluded from map**

also tends to have above-background bromide concentrations (Hem, 1992). This typical pattern held for the present study, as bromide and chloride concentration maps revealed similar trends (Fig. 4). However, bromide concentrations were low overall (most < 0.3 mg/L) (Table 2). As with chloride, bromide concentrations were generally highest in the Yegua-Jackson.

Reflecting a similar spatial structure for chloride and bromide concentrations, ratios of these constituents showed little variation over the study area (Fig. 4). Chloride/bromide ratios occupied a wide range, though most were between 100 and 300. Several samples in the above range, in the central part of the study area, also had high chloride concentrations consistent with oilfield brine. Two mapped chloride/bromide ratios exceeded 1000, both in the Gulf Coast Aquifer, consistent with evaporite dissolution.

Septic systems, cesspools, and agricultural stock operations may impact groundwater locally within the study area; however, these sources are difficult to detect as they contribute relatively little chloride to groundwater. In sewage, chloride/bromide ratios generally fall between 300 and 600 (Whittemore, 1995). While several observed ratios occupied this range, they could reflect unimpaired groundwater, or groundwater impacted by other sources (such as irrigation return flow or oilfield brine).

## CONCLUSIONS

Recent solute concentration data suggests that natural (geological) sources and, potentially, agricultural and oilfield activity have impacted groundwater quality in the outcrop zones of aquifers in east-central Texas. Several samples compiled in this study exceeded drinking water standards for sulfate, chloride, and TDS, and a few samples were elevated in nitrate and arsenic. However, nitrate and arsenic concentrations were generally low throughout the study area. Several chloride/bromide ratios were consistent with natural sources or oilfield brine, and a few could be explained by dissolution of evaporite deposits. Results presented in this article may be useful for prioritizing more localized groundwater quality investigations.

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