



Arsenic enrichment in unconfined sections of the southern Gulf Coast aquifer system, Texas

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ABSTRACT

Groundwater arsenic concentrations exceeding the federal drinking water standard are common in the southern Gulf Coast aquifer system in Texas, including in aerobic, unconfined groundwater which provides much of the municipal and domestic water supplies for the region. The objective of this study was to determine geochemical factors affecting the occurrence and distribution of groundwater As in unconfined portions of the southern Gulf Coast aquifer system through a comparative transect study of groundwater across three major hydrostratigraphic units (the Catahoula Formation, Jasper aquifer and Evangeline aquifer) and analysis of regional water quality data. Results show that As concentrations decrease with increasing distance from the Catahoula Formation, which is consistent with Miocene volcanic ash as the main source of As to groundwater in the region. Arsenic concentrations correlate with V, SiO₂ and K, all of which were released during weathering of volcanic sediments and their degradation products. In all three units, carbonate weathering and active recharge in the unconfined zones result in circum-neutral pH and oxidizing groundwater, which are typically amenable to As immobilization by adsorption of arsenate onto mineral oxides and clays. However, As concentrations exceed 10 µg/L in approximately 30% of wells. Silica that was co-released with As may compete for sorption sites and reduce the capacity for arsenate adsorption.

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1. Introduction

Drinking water is a primary pathway for As intake by humans, and this represents a potential health hazard when As is present at elevated concentrations. Adverse health effects associated with high As intake by humans are well documented (Abernathy et al., 2003; Bates et al., 1995; Chen et al., 1995; Chious et al., 1995; Mazumder et al., 1997; Tsuda et al., 1995; Wu et al., 1989). There are many examples of naturally elevated As concentrations in groundwater worldwide (Smedley and Kinniburgh, 2002). In low-temperature groundwater, they most frequently result from reductive dissolution of metal oxides under reducing conditions or desorption due to elevated pH under oxidizing conditions. In the USA, large-scale water quality assessments have demonstrated the widespread extent of groundwater As occurrence at concentrations exceeding the US Environmental Protection Agency's maximum contaminant level (MCL) of 10 µg/L (Focazio et al., 2000; Ryker, 2003; Welch et al., 2000). This presents difficulties for many public water supply systems which must achieve compliance with national standards, especially in the case of small systems with limited financial and technical resources and where per capita

costs of treatment tend to be significantly higher than for large systems (EPA, 2000; Gurian et al., 2001).

Information about geochemical processes leading to As occurrence may assist public water supply systems in avoiding costly treatment options in some cases. In the common situation where groundwater As concentrations are spatially variable, knowledge of As source distributions and release mechanisms may aid efforts to identify potential zones of low As concentrations locally. Targeting zones of lower groundwater As concentration can allow for achieving compliance by relocating wells or well screens or by mixing multiple groundwater sources. These are typically significantly more cost-effective approaches than chemical treatment for small systems. Given the high degree of spatial variability in groundwater As concentrations commonly found in As-affected aquifers, and the fact that approximately 95% of groundwater As occurrences in the USA above 10 µg/L were between 10 and 50 µg/L (according to NAWQA data; <http://water.usgs.gov/nawqa>), there may be potential for achieving compliance by well relocation, recompletion or mixing in many cases. However, the complexity of As geochemistry in the context of natural groundwater systems can make the circumstances leading to As enrichment difficult to determine. Relatively small geochemical perturbations can have significant effects on As mobility, and chemical evidence for these mechanisms can be obscured by weathering processes, sediment variability and other factors.

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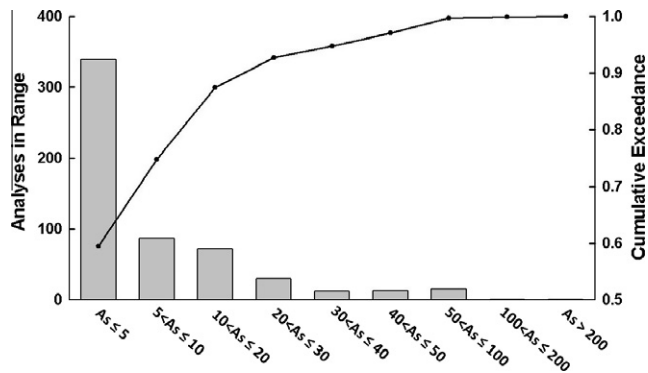


Fig. 1. Summary of groundwater As concentration data in southern Gulf Coast aquifer system based upon the Texas Water Development Board groundwater database (www.twdb.state.tx.us). Concentrations are expressed in µg/L. Data screening procedures are described in Section 3.

This study pertains to an area where As enrichment in groundwater is regionally extensive and subject to high spatial variability. Elevated As concentrations are widespread in the southern Gulf Coast aquifer system in Texas, with approximately 30% of groundwater wells exceeding 10 µg/L (compared to 6% of wells with As >10 µg/L in Texas overall based upon the Texas Water Development Board groundwater database; Scanlon et al., 2005). Although maximum concentrations exceed 100 µg/L, the vast majority of concentrations do not exceed 50 µg/L (Fig. 1). A current challenge is to explain the hydrogeochemical factors underpinning this distribution in order to aid small public water supplies and regulatory agencies in targeting safe groundwater sources. The objective of this study was to address this question using evidence provided by groundwater chemistry. The investigation was based upon chemical analyses of 27 groundwater samples collected from across three hydrologic units of the Gulf Coast aquifer system, as well as data from the Texas Water Development Board groundwater database (more than 500 samples) for comparison of regional patterns with the more detailed localized transect.

The study focused upon As enrichment in unconfined portions of the aquifer system. While a large portion of the Gulf Coast aquifer system is under confined aquifer conditions, this study was restricted to the unconfined cases because the vast majority of domestic wells and public water supply wells in the southern Gulf Coast aquifer system draw from unconfined portions of the aquifer. Therefore the unconfined zones were considered to be the most relevant from a water supply and public health perspective. The reason why most drinking water supply wells are completed in unconfined zones is that sufficient yields can be achieved with relatively shallow groundwater in most localities in the Gulf Coast aquifer system region, so that drilling deeper to confined sections is not necessary for most water supply purposes. Elevated As is known to occur in confined portions also (Henry et al., 1982; Oden et al., 2008) but this is outside the scope of the present study.

2. Study area

The Gulf Coast aquifer system is comprised of sedimentary sequences that have been deposited by alluvial systems draining towards the Gulf of Mexico beginning in the Miocene and continuing to the present. Major units include: (1) the Catahoula Formation, (2) the Oakville Sandstone and Fleming Formation, (3) the Goliad Formation, (4) Pleistocene formations (Willis, Lissie and Beaumont formations), and (5) Quaternary terrace deposits and alluvium (Baker, 1979; Doering, 1935; Figs. 2 and 3). The aquifer system conforms to a layered, dipping bed configuration which thickens toward the coast. Fluvial deposition patterns have resulted in

highly spatially heterogeneous textural compositions, with facies types including channel fill (very coarse), crevasse splay (sandy/silty), floodplain (silty/clayey) and coastal lake (silty). Broadly, the Oakville/Fleming, Goliad and Quaternary units comprise the main aquifers of the Gulf Coast aquifer system: the Jasper, Evangeline and Chicot aquifers, respectively.

The oldest formation of the Gulf Coast aquifer system is the Miocene Catahoula Formation, which overlies Oligocene sediments of the Jackson Group. The Catahoula Formation is composed of varying proportions of sands, clays and volcanic tuff; sand content ranges from a maximum of about 50% to <10% (Galloway, 1977). The Catahoula Formation is not usually labeled as an aquifer because of its low transmissivity overall. However, it is an aquifer of local importance where sand contents are high. Airborne volcanic ash is abundant in the southern Gulf Coast portion of this unit (Baker, 1979; Galloway, 1977). Bentonite and opalized clay layers and alteration products of volcanic glass (zeolites, montmorillonite, opal, and chalcedony) are present throughout the formation and indicate syndepositional alteration of tuffaceous beds. The Jasper aquifer in the study area includes the Oakville Sandstone and Fleming Formation. Sand percentage in the Jasper is high within paleochannels whereas finer-grained floodplain deposits are more common in the adjacent interchannel environments (Galloway et al., 1986). Fleming Formation sediments are complexly interbedded sands, silts and clays with intermixed volcanoclastic and tuffaceous material. Sand mineralogy of the Jasper aquifer in the study area consists of a mixture of quartz, carbonate rock fragments and volcanic rock fragments, in order of abundance. Chert and feldspar are present in lesser but also considerable amounts (Galloway et al., 1982). Clay mineralogy is dominated by montmorillonite, with minor components of kaolinite and illite. Calcic materials are abundant in association with both fine and coarse grained components. The most common minor constituents include Fe oxyhydroxides. Strike-trending faults associated with the Wilcox fault zone and a deep-seated Cretaceous fault zone intersect the study area and displace the Oakville Sandstone in some locations. The Goliad Formation overlies the Oakville/Fleming formations and has a high proportion of coarse-grained sediments including sands and cobbles, with clays interbedded locally, and is generally similar to the underlying Oakville and Catahoula in mineralogy (Hoel, 1982). The upper part of the Goliad Formation includes fine grained sands that are cemented with CaCO₃ (caliche) (Hosman, 1996).

Information about trace element distributions in aquifer sediments in the study area is available from investigations of the region's U deposits (Galloway, 1977, 1982; Galloway et al., 1982; Henry et al., 1982; Hobday and Galloway, 1999; Smith et al., 1982b). The Oakville Sandstone in particular was a major source of U ore in the 1970s and 1980s. Concentrated U deposits occur as mineralization fronts (roll fronts), which developed when U was leached from volcanic sediments by oxidizing shallow groundwater and was transported down-gradient into a reducing zone of the aquifer where mineral precipitation occurred. Arsenic, Mo and Se accumulated in a similar manner and have been found in high concentrations in the area of U deposits, which are primarily located within sand-rich alluvial axes of high transmissivity (Galloway et al., 1982). There may be a chromatographic separation of Se, U, Mo, As and V in roll front deposits where redox gradients were gradual, but in deposits where the redox gradient was sharp, minerals of these elements are found adjacent to one other (Harshman, 1974).

The selected transect area is located within portions of the Catahoula Formation, Jasper aquifer and Evangeline aquifer, within the vicinity of a high transmissivity paleochannel system (the New Davy Fluvial Axis; Karnes and Goliad Counties; Galloway et al., 1982; Table 1 and Fig. 2). The lateral distribution of high sand

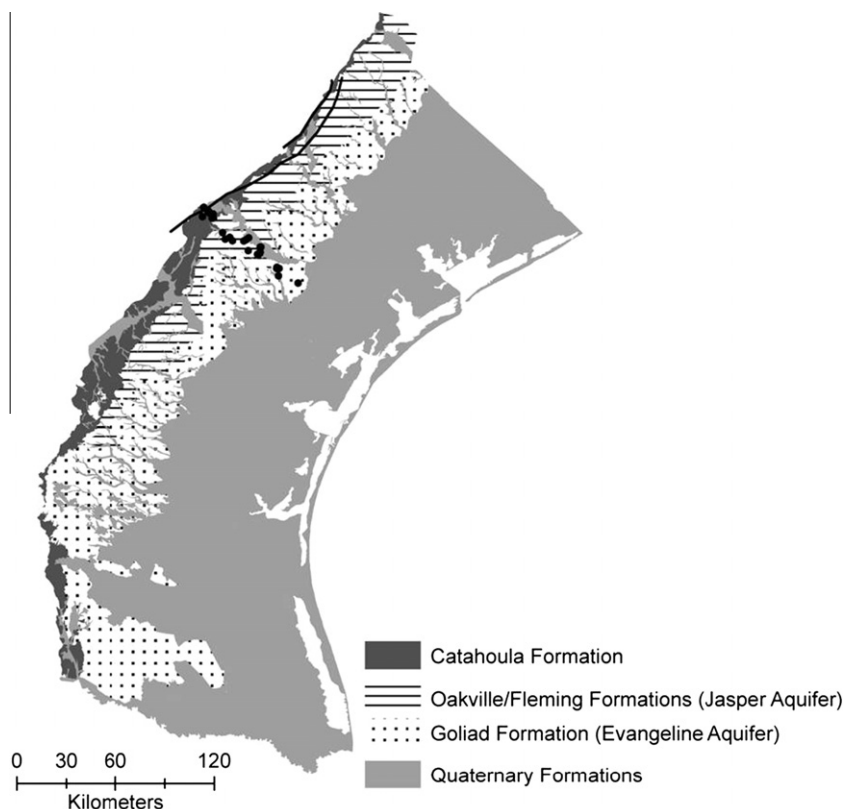


Fig. 2. Map of the southern Gulf Coast aquifer system study area and position of transect samples. The position of a normal fault associated with the Wilcox Fault Zone that intersects the transect in the vicinity of the Catahoula Formation is also shown (Galloway et al., 1983).

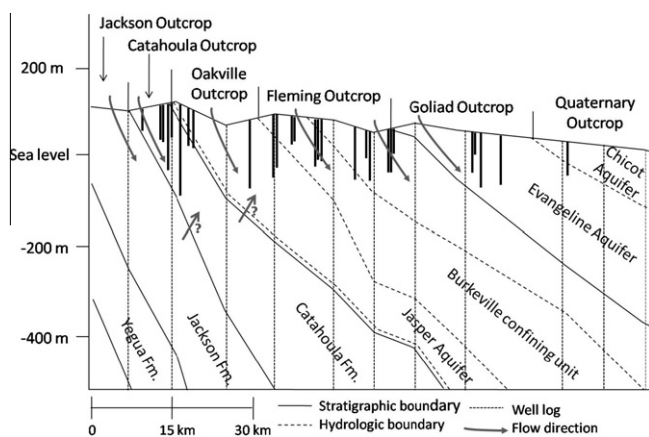


Fig. 3. Cross section of the study area and location of wells sampled; adapted from Baker (1979).

percentage areas is characterized by sinuous, interweaving belts in the downdip direction, typically between 2 and 8 km in width. The most abundant sedimentary facies are conglomeratic bed-load and mixed-load channel fill, and feature a wide range of coarse grain sizes (from sand to conglomerate), interspersed with clay-rich fine grained lenses locally. Sheet splay facies occur in conjunction and are characterized by laterally-broad sheetlike sand deposits with silt interbedded. This results in very heterogeneous but overall highly transmissive conditions in the aquifers.

Sampling sites were selected to provide a geochemical comparison of unconfined groundwater across the three units at a range of depths that are representative of domestic and public water supply wells in the area. Based on available surface geology mapping and

stratigraphic profiles, all of the transect samples were collected from within or near unconfined aquifer zones associated with outcrops of the Catahoula, Oakville, Fleming and Goliad formations (Fig. 3). Although it parallels the generalized direction of regional flow (SE towards the coast), the transect does not represent a regional groundwater flow path. Because of the proximity of the sample sites to unconfined zones, it is presumed that they are fed by water that has recharged relatively locally and is associated primarily with local rather than regional flow paths. Additional groundwater inputs to the Catahoula and Oakville formations from underlying formations are possible because a section of the transect near the boundary between the Catahoula and Oakville outcrops (Karnes County) crosses a fault network which is thought to serve as a conduit of upward leakage from the Yegua–Jackson aquifer. Galloway et al. (1982) describe temperature anomalies in the area which they attribute to contributions from warmer, deeper fluids mixing with meteoric water along faults. In the vicinity of the transect all four of these units are sand-rich and have high transmissivity associated with a paleochannel system (New Davy; Galloway et al., 1982). Five wells were screened in a portion of the Fleming Formation, which is considered to be a confining unit regionally but is sand-rich locally (Burkeville confining unit; Baker, 1979; Fig. 3).

3. Methods

Existing public water supply wells and domestic wells were selected for analyses based on their location, completion information, and sampling access. Well depths range from 40 to 168 m and mostly have ~6 m (20 ft) screened intervals at the bottom of the well. Water level information was not always available, but water levels were generally less than 70 m and in some cases

Table 1
Transect positions and field parameter results. Transect position is expressed in km from sample C01.

Sample	Unit	Transect position (km)	Well depth (m)	pH	O ₂ (mg/L)	EC (μS/cm)	ORP (mV)	Temp. (°C)
C01	Catahoula	0.0	40	7.0	4.0	1863	356	30.0
C02	Catahoula	3.5	64	6.8	0.6	3985	−8	25.0
C03	Catahoula	3.7	69	6.8	0.8	3189	438	23.7
C04	Catahoula	4.6	122	7.0	4.5	–	448	28.1
C05	Catahoula	5.0	64	7.3	0.8	1607	−9	29.0
C06	Catahoula	6.7	168	7.3	0.9	2719	47	30.4
C07	Catahoula	8.3	46	7.2	6.2	2653	405	27.2
C08	Catahoula	9.2	70	7.2	2.8	1391	214	28.2
J09	Jasper	19.1	126	6.9	5.7	4361	88	27.2
J10	Jasper	23.5	116	6.7	0.2	6185	127	27.8
J11	Jasper	23.9	96	7.0	1.8	2502	93	29.5
J12	Jasper	26.8	53	6.8	5.6	2117	106	26.2
J13	Jasper	27.0	47	6.8	6.1	1768	78	25.3
J14	Jasper	30.7	91	7.3	4.6	1560	35	26.0
J15	Jasper	30.9	75	7.0	5.5	2076	80	26.5
J16	Jasper	31.2	78	7.1	1.9	1430	116	27.6
J17	Jasper	37.7	98	6.9	4.1	1545	46	28.5
J18	Jasper	40.0	51	7.1	2.6	1054	149	26.4
J19	Jasper	40.2	91	7.2	1.8	1078	85	28.2
J20	Jasper	43.2	80	6.9	5.1	1553	49	23.6
J21	Jasper	43.3	80	7.0	2.4	1261	472	25.5
J22	Jasper	43.4	46	7.3	6.6	1579	106	24.1
E23	Evangelina	56.9	76	6.7	7.4	2340	116	23.6
E24	Evangelina	57.0	40	6.9	5.6	2411	53	24.6
E25	Evangelina	58.1	101	6.9	4.6	2503	89	25.1
E26	Evangelina	61.5	91	7.0	2.8	2010	789	23.6
E27	Evangelina	73.0	62	6.8	6.1	1643	96	24.8

<5 m below land surface. Wells were purged prior to sampling to ensure collection of representative samples. Temperature, pH and dissolved O₂ were monitored during this process and sampling began only after stabilization. A multi-parameter meter (Hanna Instruments, Woonsocket, RI) was used to measure dissolved O₂, electrical conductivity, pH, oxidation/reduction potential (ORP) and temperature. Sensors were employed using a low-pressure flow-through cell to minimize groundwater interaction with the atmosphere prior to measurement. Carbonate alkalinity was measured by colorimetric titration (Hach Company, Loveland CO) at each field site. Concentrations of NO₂[−], total and soluble Fe, NH₃ and H₂S were determined by colorimetry (Chemetrics Inc., Calverton, VA). Completion information was obtained from well owners or local groundwater conservation district staff.

Samples for major ion analyses were filtered through 0.45 μm pore diameter disposable filter cartridges (nitrate cellulose) in-line with a flow-through cell, collected into 30 mL HDPE sample bottles, and analyzed with ion chromatography (Dionex ICS-2000; Bureau of Economic Geology, University of Texas at Austin). Samples for trace element analyses were filtered into 30 mL HDPE bottles which had been acid-washed with dilute HNO₃, and analyzed using an ICP-MS (Agilent 7500ce quadrupole; Jackson School of Geosciences, University of Texas at Austin). A 2% high-purity HNO₃ was added to these samples to prevent alteration of dissolved concentrations during storage. Filtered samples were also collected for As speciation analysis (IC-MS; US Geological Survey, Denver, CO). Unfiltered samples were collected for analysis of stable isotopes (IR-MS; University of Arizona Environmental Isotope Laboratory) and ³H (He ingrowth method, University of Utah Noble Gas Laboratory). Samples were immediately chilled and transferred to laboratory cold storage within 48 h in all cases. Acceptability of sampling and analysis was established by examination of blanks, field splits, matrix spikes, standards, repeat analyses and ion balance.

Regional analysis of As and other water quality parameter distributions was undertaken using data from the Texas Water Development Board (TWDB) groundwater database (www.twdb.state.tx.us). Data for the southern Gulf Coast aquifer system were

extracted and screened for applicability to this analysis. Data prior to 1996 were excluded because a large percentage of these data had high detection limits (up to 20 μg/L) for As and other trace elements. Samples were also removed from consideration that did not report As values, had As detection levels >2 μg/L, or had >5% charge balance error. If data from multiple sampling dates were available for a given well then only the most recent sampling date satisfying these conditions was considered. A total of 558 samples met these criteria. Of these, 147 (26%) exceeded 10 μg/L As; 17 (3%) exceeded 50 μg/L; and 167 (30%) were non-detects for As (Fig. 1; Table 2). The highest measured As concentration was 320 μg/L. Pairwise correlations between As and other available water quality parameters were calculated using Spearman's rank coefficient.

4. Results and discussion

4.1. Distributions of arsenic and other trace elements

Arsenic in the transect samples ranged in concentration from <1 to 129 μg/L (median 12 μg/L). Eleven of the 27 samples exceed the US EPA drinking water limit of 10 μg/L (Table 2). The Catahoula Formation was the most prone to high As concentrations in terms of percentages of wells >10 μg/L, followed by the Jasper aquifer and Evangelina aquifer. In the Evangelina aquifer, the maximum As concentration was 20.6 μg/L (sample E27), and the median was 3 μg/L. Only two samples from this unit exceeded 10 μg/L and one sample had As below analytical detection level (sample E24). A range of other trace constituents were detected and include the oxyanion-forming elements U, Se, V and Mo, which generally were present in similar concentration ranges to As (Table 3). With few exceptions, trace elements were found in lower concentrations in Evangelina aquifer samples than in Catahoula Formation or Jasper aquifer samples. Selenium was the only trace element that was highest in the Evangelina aquifer of the three units (median 13 μg/L). The median silica concentration for the transect was 51 mg/L SiO₂, and was highest in the Catahoula Formation (median 90 mg/L). Molybdenum was not detected in any of the Evangelina

Table 2

Summary of As distribution in the Gulf Coast aquifers (TWDB database; www.twdb.state.tx.us).

Unit	% As > 10 µg/L	Median As	n
Catahoula formation	73	23	30
Jasper aquifer	27	3	183
Evangelina aquifer	22	4	196
Chicot aquifer	20	3	149

aquifer samples, in contrast to the Catahoula Formation and Jasper aquifer.

4.2. Redox and arsenic speciation

Five samples with high As concentrations selected for As speciation analysis show that nearly all As occurs as arsenate (one sample with total As concentration of 117 µg/L had arsenite at the detection level of 2 µg/L and all others were non-detects for arsenite; Table 4). Redox indicators suggest that the unconfined conditions along this transect result in predominantly oxidizing conditions. Dissolved O₂ was present in all samples and did not vary systematically with transect distance. However, seven samples had dissolved O₂ < 2 mg/L, which implies significant O₂ consumption and may indicate that some mildly-reducing conditions occur locally (Table 1; Fig. 4a). Two ORP values in the Catahoula Formation were slightly negative (samples C01 and C05) (Table 1). However, no reduced N or S species (NO₂⁻, NH₃ or H₂S) were detected (detection limits 0.25, 0.1 and 0.1 mg/L, respectively). Iron and Mn were low throughout the transect. Nitrate was present in all samples. Unusually high NO₃⁻ was found in several samples in the Catahoula Formation section of the transect (Table 5) and this may suggest leaching of agricultural N. Nitrate in Yegua–Jackson groundwater is typically low and therefore upward leakage is not considered a likely source of the high NO₃⁻ in the Catahoula Formation. Tritium activities confirm that groundwater in this area is relatively young because of active recharge (based on samples C01 and C05; Table 6).

Table 3

Selected trace element concentrations in transect samples.

Sample	SiO ₂ (mg/L)	As (µg/L)	Mn (µg/L)	Mo (µg/L)	Rb (µg/L)	Se (µg/L)	U (µg/L)	V (µg/L)	PO ₄ (µg/L)
C01	90	39	4	112	61	12	12	49	43
C02	88	10	13	<8.5	35	31	31	19	21
C03	92	5	<0.5	<8.5	10	17	21	13	30
C04	88	29	<0.5	12	47	7	18	26	41
C05	90	14	<0.5	<8.5	51	3	34	21	25
C06	86	14	<0.5	10	53	3	15	26	<2
C07	105	89	<0.5	6	28	4	15	33	–
C08	101	129	<0.5	24	20	4	19	71	5
J09	62	44	<0.5	3	31	6	11	41	2
J10	43	4	145	<8.5	24	<1.5	6	22	34
J11	64	30	<0.5	12	25	8	21	29	20
J12	51	6	<0.5	<8.5	6	4	6	28	34
J13	45	4	2	<8.5	4	6	8	31	30
J14	39	5	0	<8.5	5	4	3	26	<2
J15	58	4	<0.5	<8.5	4	6	3	36	2
J16	39	4	2	3	5	2	4	23	2
J17	43	2	<0.5	<8.5	4	7	3	25	<2
J18	30	4	<0.5	<8.5	4	10	10	41	–
J19	30	3	<0.5	<8.5	4	11	11	38	–
J20	49	2	3	<8.5	3	11	6	17	–
J21	34	2	<0.5	<8.5	4	11	13	31	–
J22	43	4	<0.5	<8.5	3	10	8	21	–
E23	51	2	<0.5	<8.5	3	13	8	26	–
E24	56	<1	15	<8.5	3	14	8	15	–
E25	49	1	<0.5	<8.5	3	17	9	20	–
E26	32	15	<0.5	<8.5	3	10	13	49	–
E27	51	21	3	<8.5	2	8	5	43	–

4.3. Controls on major ion chemistry

Major ion compositions of groundwater in the study area are affected by solutes in recharging water, mineral dissolution in the aquifer, and inputs from deeper groundwater. Median total dissolved solids are similar for the three units (medians 1375 mg/L, 1064 mg/L and 1385 mg/L for the Catahoula Formation, Jasper aquifer and Evangeline aquifer samples, respectively). Total dissolved solids are variable in the first half of the transect in the Catahoula Formation and a portion of the Jasper Formation, and are more uniform in Evangeline aquifer samples (Fig. 4b). The most abundant anions are Cl⁻ (median 389 mg/L), HCO₃⁻ (median 278 mg/L), and SO₄²⁻ (median 94 mg/L) (Table 5; Fig. 5). The most abundant major cations are Na⁺ (median 270 mg/L), Ca⁺ (median 116 mg/L) and Mg (median 23 mg/L).

The predominantly brackish, NaCl water type most likely reflects mixing of recharging meteoric water with upward leakage of deep brines from beneath the Gulf Coast aquifer system through the Wilcox fault zone (Henry et al., 1982). Mineral dissolution is considered to be another possible source of Cl⁻ because some evaporate minerals have been documented in the study area associated with playa-floodplain facies (Galloway et al., 1982). There is a positive correlation between Ca⁺ and Cl⁻ ($\rho = 0.83$) which may reflect dissolution of co-occurring halite and gypsum. The highest salinity samples (J09 and J10) have relatively low Br⁻ to Cl⁻ ratios, which is consistent with a Cl⁻ contribution from halite dissolution. However, most samples have ratios between sea water ($\sim 3.5 \times 10^{-3}$, an approximation for the ratio in precipitation) and

Table 4

Arsenic speciation in selected transect samples.

Sample	Total arsenic (µg/L)	Arsenic (III) (µg/L)
C01	35	<2
C07	82	<2
C08	117	2
J09	40	<2
J11	28	<2

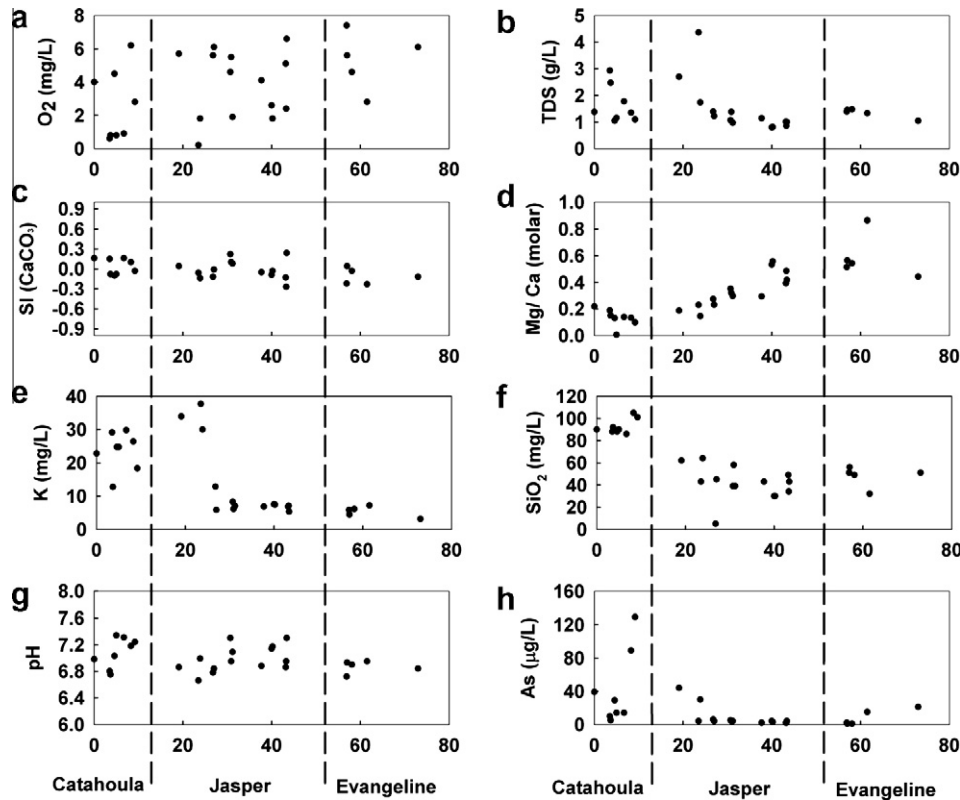


Fig. 4. Variability in selected parameters along the transect (shown as distance in km from the up-dip limit of the Catahoula Formation). Note that the transect is in unconfined aquifer zones fed by local recharge and is not interpreted as geochemical evolution during regional flow.

Table 5
Major ion concentrations (mg/L) in transect samples.

Sample	F	Cl	SO ₄	Br	NO ₃	HCO ₃	Ca	K	Mg	Na
C01	3.5	307.6	172.1	3.8	41.7	372	121.5	22.8	16.0	314.4
C02	0.7	640.8	862.3	4.8	67.1	317	365.8	29.1	41.5	601.9
C03	1.2	392.1	765.2	4.3	119.4	347	214.1	12.7	19.3	596.3
C04	1.0	259.4	125.0	2.9	17.3	253	82.5	24.7	6.5	269.8
C05	0.4	229.8	175.6	2.9	17.2	303	36.4	24.7	0.1	363.2
C06	0.7	666.2	131.4	4.1	51.8	223	97.4	29.8	8.2	559.0
C07	0.8	408.5	121.4	3.5	9.7	285	90.8	26.4	7.3	395.4
C08	0.6	137.5	129.3	3.1	5.8	408	37.4	18.3	2.2	348.1
J09	0.8	1246.5	175.1	5.4	6.1	184	327.3	33.9	37.0	678.7
J10	0.3	1411.7	1018.9	6.0	0.6	263	383.4	37.7	53.3	1186.6
J11	1.0	574.2	156.8	1.5	8.7	328	69.6	30.0	6.1	558.9
J12	0.6	536.6	94.4	3.7	7.2	228	180.9	12.8	30.0	293.3
J13	0.6	371.6	97.1	3.1	6.4	305	151.2	5.8	21.1	259.3
J14	0.8	388.8	35.0	2.9	6.1	230	106.1	8.3	22.6	263.7
J15	1.0	485.7	88.4	3.3	17.2	278	166.3	6.1	32.2	298.9
J16	0.8	306.6	38.9	2.8	3.5	255	106.8	7.0	19.2	228.3
J17	0.7	430.6	42.1	2.9	5.3	229	146.3	6.8	26.0	250.7
J18	0.8	135.5	54.1	0.4	4.1	342	45.9	7.5	14.8	191.4
J19	0.8	134.5	57.0	0.5	3.9	348	46.2	7.4	15.6	191.6
J20	0.7	314.9	74.1	0.7	4.3	280	116.4	6.8	27.6	180.7
J21	0.8	213.9	51.6	0.6	5.4	295	57.8	7.1	17.0	205.4
J22	0.7	346.6	49.2	0.7	3.9	260	105.2	5.3	26.6	200.4
E23	0.7	592.4	94.1	1.2	5.2	225	186.1	5.8	57.9	216.7
E24	0.8	569.2	136.2	1.1	5.9	252	182.7	4.4	62.5	231.6
E25	0.7	634.1	92.1	1.3	5.1	238	171.6	6.1	56.4	268.7
E26	0.6	364.6	88.3	3.5	29.1	400	56.9	7.2	29.8	345.8
E27	0.6	328.9	84.4	0.8	4.1	276	125.0	3.1	33.5	181.52

the median of unsaturated zone samples unaffected by irrigation water (7.3×10^{-2} ; Scanlon et al., 2005), consistent with Cl^- and Br^- inputs mainly from deep brines and meteoric recharge (Fig. 6).

Carbonates are abundant in the study area (Galloway et al., 1982), and all samples are near saturation with respect to calcite ($-0.3 < \text{SI}(\text{CaCO}_3) < +0.3$; Fig. 4c). Groundwater pH values are

generally between 7 and 8 which is consistent with open-system carbonate dissolution (Langmuir, 1971). Incongruent dissolution enriches Mg^{2+} relative to Ca^{2+} and this ratio progressively increases along the transect (Fig. 4d). Silicate weathering also exerts an influence on groundwater quality in the Gulf Coast aquifer system and a strong distinction can be seen along the transect. Potassium and

Table 6
Stable isotope and tritium results for selected transect samples.

Sample	Sample	$\delta^{18}\text{O}$ (‰ VSMOW)	$\delta^2\text{H}$ (‰ VSMOW)	^3H (TU)
C01	KAR10	–	–	1.44
C05	KAR11	–	–	1.49
C06	KAR04	–4.1	–24	0.02
C07	KAR01	–4.1	–24	–
C08	KAR02	–5.0	–29	–
J09	KAR03	–4.0	–24	0.06
J13	KAR16	–	–	0.04
J14	KAR08	–4.3	–27	–
J15	KAR07	–4.1	–26	–
J16	KAR06	–4.7	–26	–
J17	KAR05	–4.3	–24	0.02
J18	GOL03	–4.7	–28	–
J19	GOL04	–4.6	–27	–
J20	GOL09	–4.3	–24	–
J21	GOL01	–4.7	–26	–
J22	GOL02	–4.5	–26	–
E23	GOL08	–4.0	–25	–
E24	GOL06	–4.3	–26	–
E25	GOL05	–4.1	–24	–
E26	GOL10	–3.9	–22	–
E27	GOL07	–4.5	–25	–

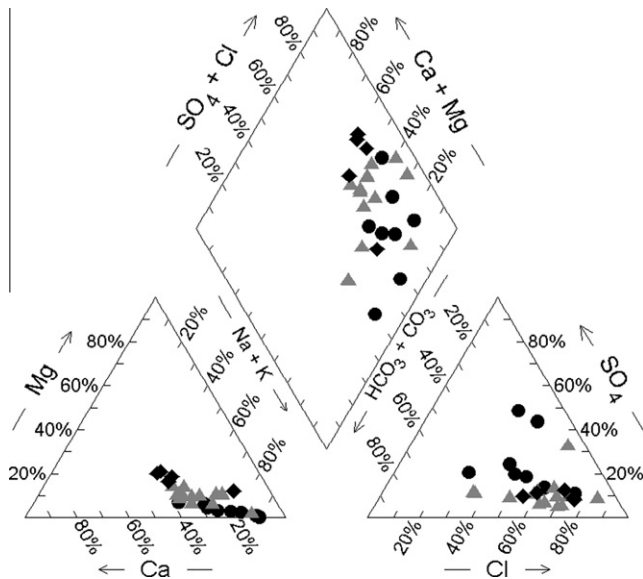


Fig. 5. Piper diagram of samples from the transect (black circles = Catahoula Formation; grey triangles = Jasper aquifer; black diamonds = Evangeline aquifer).

SiO_2 , in particular, are derived from silicate weathering and are highest in the Catahoula Formation, decrease across the Jasper aquifer, and are relatively low in the Evangeline aquifer (Fig. 4e and f). Source availability distributions are considered to be the most likely factor contributing to the variation. Solubility may also play a role, but saturation indices with respect to amorphous SiO_2 are in the sub-saturation range (–0.59 to –0.05). Upward leakage from the Yegua–Jackson aquifer is also not considered to be a likely factor because K concentrations in the Yegua–Jackson aquifer (median 5 mg/L in the Texas Water Development Board database) are generally lower than those observed in the Catahoula Formation portion of the transect.

4.4. Arsenic sources

Volcanic ash in the aquifer matrix is considered to be a probable original source of As to the region. The Catahoula Formation in particular is rich in volcanic ash and rock fragments and their

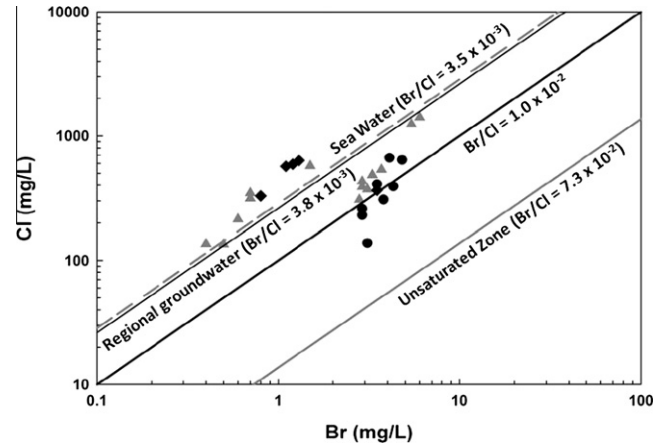


Fig. 6. Bromide versus chloride in transect samples (black circles = Catahoula Formation; grey triangles = Jasper aquifer; black diamonds = Evangeline aquifer).

diagenetic alteration products. The original volcanic materials likely derive from Oligocene–Miocene volcanism in the area of northwestern Mexico and southwestern USA (Galloway, 1977; McBride et al., 1968; Parker et al., 1988). These volcanic sediments are also considered to be the regional source of U, which has been subject to economic extraction in several locations within the study area (Eargle et al., 1975; Galloway, 1977). Original As concentrations in the volcanic sediments are not known. In general volcanic sediments are not particularly enriched in As (Ure and Berrow, 1982), but fresh volcanic ash can have significantly elevated concentrations in some instances (Boyle and Jonasson, 1973) and is susceptible to rapid leaching of trace elements by oxidizing groundwater (Smith et al., 1982a; Stewart et al., 2006). Based upon available petrographic data, current As concentrations in ash layers in the Catahoula, Fleming, and Oakville formations are low (Henry and Kapadia, 1980). Therefore the current source of As to groundwater may be As that was leached from volcanic ash after deposition and is now primarily adsorbed onto metal oxides and clays.

Apart from the immediate vicinities of economic U deposits, the current spatial distribution of As in southern Gulf Coast aquifer system sediments is not well known. The spatial distribution in groundwater illustrates that many As enrichment occurrences are located further coastward than the original volcanoclastic deposition area (e.g. in the Evangeline and Chicot aquifers). That pattern suggests that a degree of redistribution of As from the Catahoula Formation deposits toward the coast took place. By analogy with studies of U geochemistry in the study area, leaching by dissolution would have occurred soon after deposition in the near surface during pedogenesis, and dissolution that took place in the near surface or vadose zone may have allowed for long-distance redistribution by erosion and subsequent coastward transportation by rivers and streams, either as adsorbed As or incompletely weathered volcanic silicates (Walton et al., 1981). Many high groundwater As occurrences further coastward than the original volcanoclastic deposition area are clustered around rivers or their alluvial deposits (for example near the Guadalupe River in Victoria County; the Rio Grande in Starr, Hidalgo and Cameron counties; and the network of alluvium in Duval County). The distribution of As available to groundwater may be related to characteristics of the paleo-fluvial systems. However, this is difficult to test without better characterization of the highly heterogeneous alluvial deposits.

Regional As data show that median groundwater As concentrations and frequency of high groundwater As occurrences both generally decrease with increasing distance from the Catahoula

Formation (Table 2). This is consistent with the volcanic ash as the original source, and subsequent transport toward the coast. Furthermore, the highest analyte correlation coefficients for As are with V ($\rho = 0.45$), K ($\rho = 0.43$) and SiO_2 ($\rho = 0.39$) (Table 7), all of which are associated with volcanic silicates.

There are several other potential sources of As to groundwater in the study area; however, available evidence suggests that none are capable of explaining the observed As distributions at the regional scale:

- (i) *Upward leakage of saline fluids from the underlying Yegua–Jackson aquifer.* The Yegua–Jackson is a source of salinity to the Jasper aquifer through upward leakage within fractures (Galloway et al., 1982). However, water quality data for the Yegua–Jackson aquifer beneath the Southern Gulf Coast aquifer system show uniformly low As concentrations. Out of 124 available water quality analyses, only 18 have detectable As (detection limits were mostly 2 $\mu\text{g/L}$) and the median of detected As concentrations is 3 $\mu\text{g/L}$ (TWDB data). Therefore, while the focal point of high salinity in the study area is near the zone of highest groundwater As, the two are not likely to be causally linked.
- (ii) *Anthropogenic sources.* Anthropogenic inputs are also possible in some locations, but they do not spatially correlate with groundwater As enrichment. Possible contamination by leaching of arsenical pesticides used in cotton production has previously been examined (Reedy et al., 2007; Scanlon et al., 2005). Unsaturated zone profiles showed that As is largely immobile in agricultural soils examined due to strong sorption. Furthermore some areas of the Gulf Coast aquifer system that have relatively high levels of As enrichment have not been subject to any cotton production (Live Oak and Duval Counties).

Open pit U mining has occurred in the southern Gulf Coast aquifer system including in the vicinity of the transect. Studies of soils and mine spoils before reclamation showed aqueous concentrations averaging 30 $\mu\text{g/L}$ despite high TDS and U (Nugent et al., 1994). Brandenberger et al. (2004) found that mine tailings have little impact on the regional surface water quality (Lake Corpus Christi). Henry et al. (1982) note that the chemical composition of groundwater in the vicinity of ore bodies matches that of the regional aquifer except in the middle of the ore body. Solution mining of U (in situ leach) has also been employed in the southern Gulf Coast aquifer system, and can lead to aquifer contamination where hydraulic control of the leachates is not adequate. This has the potential to adversely affect groundwater quality, but as with pit mining, solution mining is not sufficiently widespread to account for the broad geographic distribution of elevated As.

- (iii) *Concentration by evapotranspiration.* Stable isotopes of water show that evaporative enrichment has not affected the groundwater to a significant degree, suggesting that rainfall

deposited As can be considered negligible (Fig. 7). Groundwater isotopic compositions fall within the range of the annual weighted rainfall means, consistent with modern rainfall being the dominant source of recharge to the aquifer. The samples are slightly displaced from the local meteoric water line (slope 4.85; $r^2 = 0.71$ for $n = 8$), indicating some evaporation prior to recharge. The small amount of displacement indicates that evaporative enrichment is not sufficient to account for the elevated As concentrations.

4.5. Mobilization

Although heterogeneous source availability may be an important underlying factor in observed groundwater As distributions, sorption/desorption processes are also likely to play a key role. Arsenic concentrations in sedimentary aquifers with low-temperature groundwater are usually controlled by partitioning between adsorbed and dissolved phases because of affinity for adsorption to mineral oxides or clay (Smedley and Kinniburgh, 2002), which are abundant in the Gulf Coast aquifer system (Galloway et al., 1982). Sorption of arsenate is strongest at near-neutral pH, and weakens as pH values increase, with adsorption rapidly weakening above pH ~ 8.5 (Goldberg and Johnston, 2001; Masscheleyn et al., 1991). As such, pH increase associated with evapoconcentration or cation exchange can lead to As release. However, transect results show consistently circum-neutral pH values which are not strongly affected by evapoconcentration and are buffered by open-system carbonate dissolution (Table 1). pH does not vary systematically

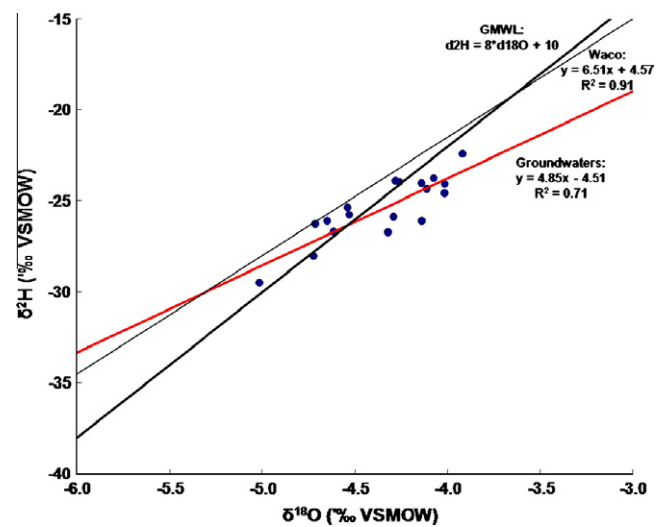


Fig. 7. Isotopic compositions of groundwater are compared to the meteoric water line for Waco (IAEA/WMO, 2010). Annual weighted mean isotopic compositions of rainfall events (for 8 a between 1962 and 1976) range between -31 and -17 $\delta^2\text{H}$ ($\delta^2\text{H} = 6.51 * \delta^{18}\text{O} + 4.57$; $r^2 = 0.91$; $n = 96$).

Table 7

Spearman's rank correlation coefficients with As for selected constituents ($n = 558$). Source: TWDB database.

Constituent	Spearman's ρ	Constituent	Spearman's ρ	Constituent	Spearman's ρ
V	0.45	Na	0.29	pH	0.05
K	0.43	Li	0.26	Ba	0.04
Si	0.39	NO_3	0.26	O_2	0.04
B	0.37	Se	0.25	HCO_3	-0.04
TDS	0.37	Temp	0.22	Fe	-0.05
SO_4	0.35	Sr	0.23	Mn	-0.06
F	0.33	Mg	0.17		
Cl	0.32	Ca	0.12		

with position along the transect (Fig. 4g). Also, correlation between As and pH is weak in both the regional database ($\rho = 0.05$) and in the transect study ($\rho = 0.33$).

Ion competition effects are capable of desorbing arsenate without high pH conditions. Several studies on As remediation demonstrate these effects, and desorption by competitive ions has been invoked in some natural systems as well (Stollenwerk, 2003). Phosphate is known to be an effective competitor for arsenate sorption sites on a range of materials including Fe oxides (Jain and Loeppert, 2000; Jeong et al., 2007; Manning and Goldberg, 1996), and PO_4^{3-} concentrations in transect samples are of a similar magnitude to As. However, there is no correlation between As and PO_4^{3-} concentrations in the transect (Table 3). Arsenic adsorption onto some oxides and clays has also been shown to be altered in the presence of elevated SiO_2 , HCO_3^- , V and Se concentrations in solution (Jeong et al., 2007). Major ion concentrations and compositions can also affect As sorption in some cases (Masue et al., 2007; Smith et al., 2002).

Based on spatial correlations with As and previous experimental evidence on ion competition effects, SiO_2 and V are the only two constituents that are both correlated with As in the Gulf Coast aquifer system and known to be sorption competitors with arsenate. Silica and V both have a positive statistical relationship with As regionally as well as within the transect (Fig. 8). Arsenic, V and SiO_2 have a common original source in weathering of volcanic sediments. Potassium, also derived from ash weathering, is strongly correlated with As but not known to be a sorption competitor for As. The correlations may be partially attributable to the common source distribution. However, SiO_2 concentrations are high (median 51 mg/L and maximum 105 mg/L SiO_2 in the transect), and may have prevented a proportion of dissolved As from adsorbing or resulted in desorption after further weathering. Therefore the combination of common source materials and competition for sorption sites is likely to be responsible for the observed statistical relationship between As and SiO_2 . Correlation with V also likely stems from common source material distributions (Smith et al., 1982a) and the fact that V has similar adsorption behavior to As, which frequently leads to covariance of As and V in groundwater (Nicolli et al., 1989; Robertson, 1989). Competitive desorption of As by V has been invoked in natural systems, for example in Argentina where V concentrations are up to 5.4 mg/L (Smedley et al., 2005). However, concentrations in the southern Gulf Coast aquifer system (median = 26 $\mu\text{g/L}$; maximum = 71 $\mu\text{g/L}$) are not likely to be sufficient to result in widespread As mobilization.

4.6. Comparison of regional and local data

A brief comparison of regional and local transect data is made in order to evaluate how inferences regarding controls on groundwater As concentration based on the transect may be relevant across the southern Gulf Coast aquifer system region. However, the transect study is focused on oxidizing groundwater, and the degree to which the regional database reflects oxidizing groundwater is not clear. While most records in the database are expected to pertain to oxidizing groundwater because most are completed in unconfined aquifer portions, few redox indicator data are available to confirm this. The presence of elevated Fe suggests that a considerable subset of this data set represents groundwater under reducing conditions (for example, total dissolved Fe >0.5 mg/L in 9% of samples). Therefore, this comparison must carry the qualification that differing geochemical controls may be affecting a portion of the regional data set. Also, the transect has significantly higher median As (12 $\mu\text{g/L}$) than the regional data set (4 $\mu\text{g/L}$). Nonetheless, similarity between regional and local (transect) data exists in terms of several constituent correlation coefficients with As, as well as

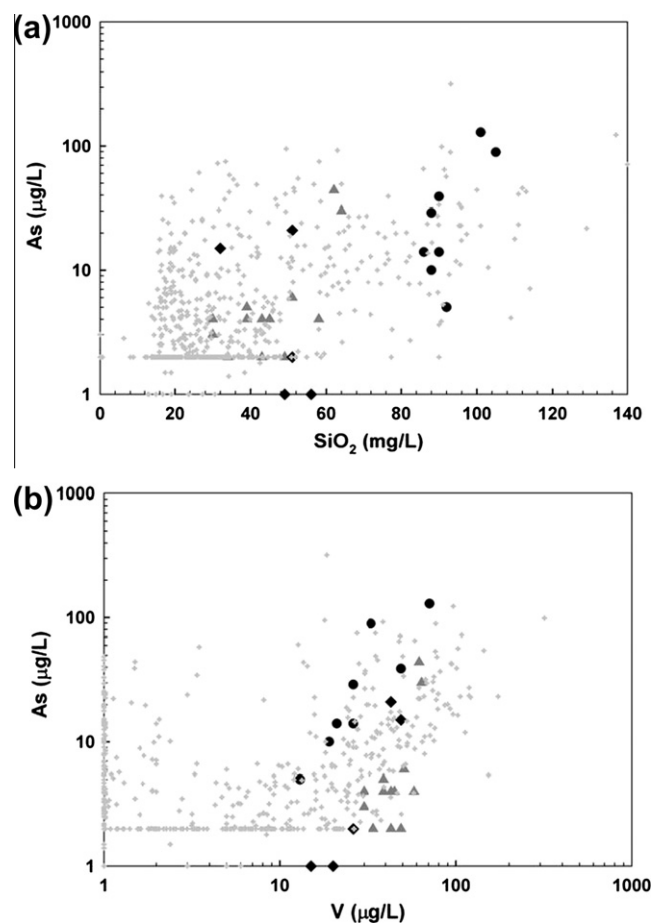


Fig. 8. Arsenic versus silica (a) and vanadium (b) in the transect (black circles = Catahoula Formation; grey triangles = Jasper aquifer; black diamonds = Evangeline aquifer) and the TWDB database (grey circles). Non-detects are plotted at their analytical detection limit.

spatial distributions. The highest correlation coefficients in both cases were with V, K and SiO_2 . (In the regional database, $\rho = 0.45$ with V; $\rho = 0.43$ for K, and $\rho = 0.39$ for SiO_2 . In the transect, $\rho = 0.67$ with V; $\rho = 0.39$ for K, and $\rho = 0.64$ for SiO_2 .) Arsenic generally decreases coastward in both the local and regional case (highest in the Catahoula Formation and decreasing with increasing distance from it). These two similarities suggest that source sediment distribution is similarly relevant on the regional scale.

5. Conclusions

In summary, major and trace elements, As speciation and isotopes were used to provide evidence regarding As sources and occurrence in groundwater within unconfined areas of the southern Gulf Coast aquifer system. Spatial distributions within the local transect and the region overall are consistent with volcanic ash as the main source of As to groundwater in the region. Trace element leaching and transportation likely occurred soon after ash deposition, so the current As source to groundwater is likely to be desorption from metal oxides and clays. Early redistribution may help to explain why elevated concentrations of As in groundwater, while most common nearest to the Catahoula Formation, also occur further coastward. Major ion and dissolved O_2 analyses from the transect indicate that carbonate weathering and active recharge in the unconfined zones yield pH and redox conditions that promote adsorption of arsenate (near-neutral pH and oxidizing). However, it is also shown that As concentrations commonly exceed 10 $\mu\text{g/L}$

in oxidizing groundwater in the study area. The elevated groundwater As concentrations in this area may be related to competitive desorption. A potential competitor is dissolved SiO₂, which is present in high concentrations and correlates with As concentrations in both the local transect and regional database. Salinity appears to result both from upward leakage and from evaporate dissolution, and the area of the transect with highest salinity coincides with the highest As concentrations, but there is no evidence to suggest that the two are causally linked. Experimental studies using Gulf Coast aquifer system sediments are desirable to confirm these conclusions. In particular, the evidence for competitive desorption by SiO₂ is ambiguous without further experimental support because the common sediment source for As and SiO₂ could also account for their covariance.

This information may be relevant to public water supply systems and others wishing to minimize As risk. For one, because most wells that draw groundwater from the Catahoula Formation have elevated As concentrations, this unit should be avoided by new wells where any other alternatives are available. In the Jasper, Evangeline and Chicot aquifers, concentrations are highly variable spatially and the present results do not provide a sufficient basis for predicting As distribution. Silica, K and V are positively correlated with As, but the relationships are not strong enough for these constituents to be considered reliable predictors of As. Nonetheless, high concentrations of SiO₂ or other potential sorption competitors may be considered a warning sign for high As in oxidizing sections of the Gulf Coast aquifer system. Arsenate is apparently not sufficiently adsorbed at pH 7–8 and this may be related to the competition effects. Especially outside of the Catahoula Formation, there is high spatial variability in As concentrations, which allows for the possibility for some small public water supplies which currently have high As concentrations to reduce concentrations using mixing to minimize the need for costly chemical treatment. While this study has demonstrated lateral variability, spatial variability most likely extends to the vertical dimension also. In such cases, wells with long screens might be amended to avoid high As-bearing depth intervals.

Results may also be valuable for comparison with other occurrences of arsenate enrichment in natural groundwater systems. Arsenate-enrichment affects oxidizing groundwater in numerous locations worldwide, including Argentina (Bundschuh et al., 2004; Nicolli et al., 1989) and elsewhere in the USA, most proximately in northwestern Texas (Nativ and Smith, 1987; Scanlon et al., 2009) and also in the northern High Plains (Gosselin et al., 2006) and elsewhere (Robertson, 1989; Smedley and Kinniburgh, 2002). As noted by Schreiber et al. (2003), multiple lines of evidence from water chemistry, isotopes, mineralogy and hydrogeology are necessary for discerning As sources and mobilization mechanisms in complex natural settings. Improved knowledge of source distributions, competitive ion effects and other factors can then inform efforts to obtain low As drinking water sources in a cost effective fashion.

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