Arsenic in Groundwater
Goliad County, Texas

Prepared for **Goliad County Groundwater Conservation District**

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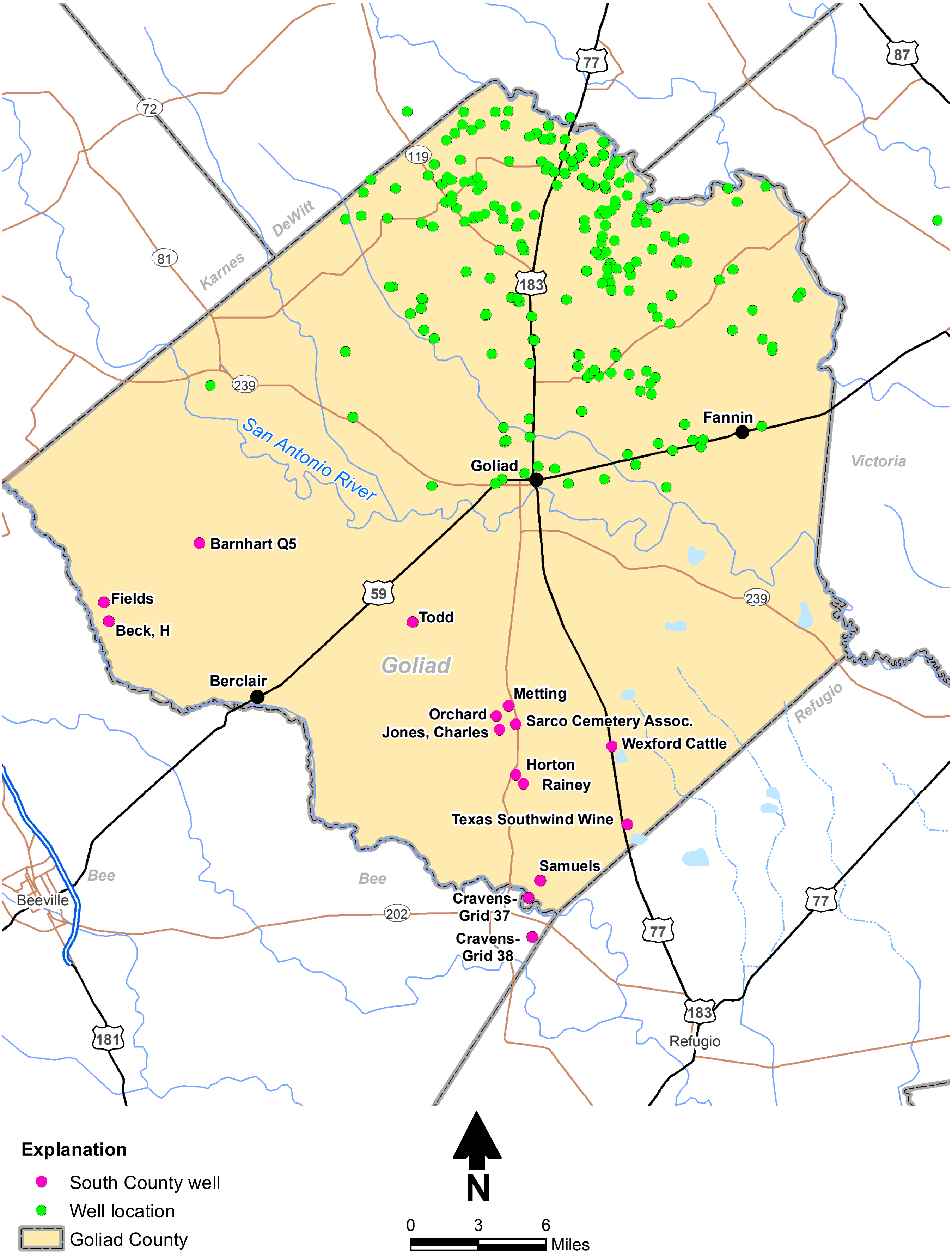
Arsenic in Groundwater
Goliad County, Texas

At the request of the Goliad County Groundwater Conservation District (GCGCD), Daniel B. Stephens & Associates, Inc. (DBS&A) evaluated water quality data to assess whether arsenic concentrations in groundwater are naturally occurring. This report presents information on hydrogeology in Goliad County, arsenic geochemistry, and previous studies, and evaluates water quality data from recent sampling in 2007 to 2013 for wells in the southern portion of the county (Figure 1).

Because elevated arsenic concentrations in drinking water present a health concern, the U.S. Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) for arsenic concentrations in drinking water of 10 micrograms per liter (µg/L). Note that a concentration of 10 µg/L is equivalent to 0.01 milligrams per liter (mg/L), which are the units used in this report. Arsenic concentrations in 8 of 14 wells sampled in southern Goliad County exceed this MCL.

1. Hydrogeology in Goliad County

Geology along the Gulf Coast of Texas is characterized by a series of exposed sedimentary rocks that outcrop in bands roughly parallel to the coastline. The rocks are younger closer to the coastline and are progressively older with distance from the coastline. Table 1 lists the primary rocks exposed at the surface in Goliad County and their associated aquifer units. Other geologic units that are important to understanding the hydrogeology and water quality in Goliad County, such as the Catahoula Formation, are also included in Table 1. Because the geologic units dip toward the Gulf Coast, each unit becomes progressively deeper below ground surface from the outcrop to the coastline. Depositional environments for these formations are mainly marine, related to transgression and regression cycles of the Gulf of Mexico with typical lithology of sand and mud (silt and clay). Fluvial or river deposits are also common locally where rivers flowed to the coast (Young et al., 2010). Volcanic ash and tuff units are found in the Catahoula Formation (Baker, 1979).



GOLIAD ARSENIC EVALUATION

Well Locations

Figure 1

Daniel B. Stephens & Associates, Inc.

05/07/2014

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Table 1. Geologic and Aquifer Units, Goliad County, Texas

Geologic Age	Geologic Unit	Aquifer Name	Significant Surface Exposure in Goliad County?
Oligocene [23.0–33.9 Ma]	Catahoula Formation	Catahoula Confining System	No
Miocene [5.3–23.0 Ma]	Fleming Group: Oakville and Lagarto Formations	Jasper Aquifer (Oakville Formation, Lower Lagarto Formation, and Burkeville Confining Unit)	Yes
	Fleming Group: Oakville and Lagarto Formations	Evangeline Aquifer (Upper Lagarto and Goliad Formations)	Yes
Pliocene [2.6–5.3 Ma]	Goliad Formation	Evangeline Aquifer (Upper Fleming and Goliad)	Yes
Pleistocene [0.01–2.6 Ma]	Willis Formation	Chicot Aquifer	No
	Lissie Formation	Chicot Aquifer	Yes
	Beaumont Formation	Chicot Aquifer	No

Ma = Million years ago

The Evangeline Aquifer, including the Goliad Formation, is the primary aquifer in Goliad County. The aquifers tend to be predominantly (greater than 60 percent) sandstone, particularly the Upper Goliad Formation (Young et al., 2010). The total dissolved solids (TDS) concentrations of the aquifers tend to increase with depth and distance from the outcrop area, where recharge occurs (Young et al., 2010).

2. Arsenic Geochemistry

Arsenic behavior and solubility in groundwater is strongly influenced by the oxidation/reduction (redox) and pH chemical characteristics of the water. Redox is a measure of how oxidizing the groundwater is. Water with an appreciable amount of dissolved oxygen is considered an oxidizing solution, and is typical of groundwater that was recently recharged. Groundwater will become reducing when it has been disconnected from Earth's atmosphere for an extended period of time, such as groundwater representative of recharge that occurred tens to thousands of years in the past. pH is a measure of the acidic or alkaline nature of the water. Arsenic will occur in two valence states: arsenite [As(III)] and arsenate [As(V)]. Each valence state has different chemical characteristics that determine their mobility in groundwater. Arsenite is the dominant form under reducing conditions, while arsenate is the dominant form under oxidizing conditions. The groundwater redox conditions in the GCGCD samples appear to be oxidizing based on the presence of oxidized ions such as sulfate (SO_4) and nitrate (NO_3).

The surface charge of arsenic ions in solution influences the natural process of arsenic removal from groundwater by adsorption and co-precipitation processes. Adsorption occurs when ions such as arsenic are removed from the groundwater solution and chemically or physically bind to the aquifer sediments, including oxide and clay minerals. Co-precipitation is the process where a soluble ion such as arsenic becomes incorporated into the structure of an insoluble mineral such as an iron hydroxide. For example, arsenic may co-precipitate from solution with iron minerals and be incorporated into their crystal structure.

In drinking water aquifers where the groundwater is oxidizing, adsorption to aquifer sediments will be the dominant control on arsenic concentrations. Arsenite has a neutral charge in the pH range of 6 to 9; therefore, it tends to remain in solution and not be adsorbed. In the pH range of 6 to 9, arsenate typically has a negative charge and is readily adsorbed to iron minerals, such as amorphous iron hydroxide [$Fe(OH)_3$], that often form coatings on aquifer sediment grains. Adsorption will also occur on clay minerals in the aquifer sediments. As the pH approaches a value of 8 and higher, the surface charge on the iron and clay minerals changes from positive to negative, and these minerals tend to adsorb less and repel more of the arsenate ion.

3. Previous Water Quality Studies

Arsenic in the Gulf Coast aquifer system has been investigated by the University of Texas Bureau of Economic Geology (Scanlon et al., 2005; Gates et al., 2011). The primary source of arsenic appears to be the Catahoula Formation, which includes Miocene-age (23.0 to 5.3 million years) volcanic ash and tuff. As the volcanic materials weather, trace elements such as arsenic, selenium, vanadium, molybdenum, fluoride, potassium, and silica are released to groundwater (Scanlon et al., 2005; Gates et al., 2011; Nicot et al., 2010). Uranium is enriched locally near outcrops of the Catahoula Formation, and economic deposits are referred to as the South Texas Uranium Province (Nicot et al., 2010). In the past, open-pit mines were developed to mine the uranium ore; recent mining has focused on using in situ techniques. Nicot et al. (2010) suggest that the legacy uranium mining does not appear to have a regional impact on water quality. Gates et al. (2011) also conclude that the localized uranium mining or groundwater leakage from deep aquifers could not have caused the widespread distribution of arsenic observed in the Gulf Coast aquifer system.

Natural conditions tend to enrich uranium and other elements. As water recharges along geologic outcrops, the slightly acidic recharge water tends to mobilize uranium and other elements into solution. The elements remain in groundwater until a chemical change occurs to shift from oxidizing to reducing conditions. When reducing conditions are encountered along a groundwater flow path, the solubility of uranium decreases, and the groundwater cannot maintain the same concentration of uranium; the excess uranium will therefore precipitate from solution. The reducing conditions are usually related to oil, gas, or hydrogen sulfide (H_2S) migrating upward from depth along faults, or the presence of iron sulfide mineral such as pyrite (Nicot et al., 2010). In some cases, reduced portions of an aquifer that contain carbon may change the redox conditions (Nicot et al., 2010). Recurring recharge events over geologic time have allowed significant amounts of uranium and other elements to be mobilized and subsequently concentrated downgradient of the Catahoula Formation outcrops.

Previous investigations provide important insight to arsenic in the Gulf Coast aquifers. Arsenic speciation testing by Gates et al. (2011) indicates that arsenic predominantly occurs in the arsenate oxidation state within the unconfined portion of the local aquifers. They also note that arsenic distribution in groundwater is not well known, but does tend to be enriched along paleoriver (fluvial) systems that would have eroded and transported sediments from the Catahoula Formations toward the Gulf Coast. Elements that tend to occur with arsenic in groundwater and have good statistical correlations include selenium, silica, vanadium, and potassium, which are weathering by-products of volcanic ash such as that found in the Catahoula Formation (Scanlon et al., 2005; Gates et al., 2011).

4. Water Quality Evaluation

Based on the pH range of 7.01 to 7.9 and oxidizing conditions in GCGCD samples (Table 2), arsenate is expected to be the dominant arsenic species in the groundwater (similar to

Table 2. Water Quality Data for Southern Goliad County

Name	Grid #	Well Location (from GPS)	Date Tested	Well Depth (ft bgs)	Concentration (mg/L)								Activity (pCi/L)			pH (s.u.)	Electrical Conductivity (µS/cm)	Temperature (°C)
					Chloride	Sulfate	Nitrate	TDS	Arsenic	Iron	Selenium	Uranium	Gross Alpha	Radium-226	Radon-222			
Texas Southwind Winery	38	28.44548 –97.32322	11/27/2012	178	255	82.8	0.774	891	0.013	0.1	0.004	0.0121	11.6 ± 3.3	0.5 ± 0.2	742 ± 278	7.9	—	21.7
			12/17/2013	178	263	85.9	0.796	874	0.01	0.1	0.004	0.011	29.9 ± 4.8	0.4 ± 0.1	219 ± 46.8	7.65	—	23.6
Horton (rent house)	37	28.478502 –97.40392	11/27/2012	—	355	102	1.13	1,040	0.018	—	0.004	0.0087	12.6 ± 4.8	0.2 ± 0.1	373 ± 276	7.7	1,696	23.5
			12/17/2013	—	359	103	1.16	1,040	0.013	—	0.004	0.0075	17.4 ± 4.9	0.3 ± 0.1	184 ± 46.6	7.4	—	22.1
Rainey	37	28.47263 –97.39823	11/27/2012	—	363	94.7	1.14	1,040	0.016	—	0.004	0.0091	17.1 ± 4.8	0.3 ± 0.1	483 ± 276	7.78	1,727	24.5
			12/17/2013	—	360	93.9	1.17	1,050	0.012	—	0.004	0.0079	18 ± 4.9	0.4 ± 0.1	212 ± 47.1	7.09	—	24.6
Sarco Cemetery Assoc.	29	28.51115 –97.4033	6/26/2012	—	150	36.8	2.14	711	0.013	0.73	0.002	0.0023	5.7 ± 6.2	0.2 ± 0.1	234 ± 107	7.41	1,186	24.2
			12/17/2013	—	153	28.7	1.25	664	0.014	0.79	0.002	0.0019	7.1 ± 2.2	0.2 ± 0.1	59.5 ± 44.8	7.43	—	24.6
Todd	21	28 34.656 –97 28.654	3/02/2010	320	100	48	0.511	537	ND	ND	0.003	0.0061	8.8 ± 3.3	0.16 ± 0.13	200 ± 37	—	—	—
Barnhart Q5	27	28 37.797 –97 37.949	5/21/2007	276	226	40.4	5	620	<0.002	<0.01	0.004	0.006	4.5 ± 0.5	ND	300 ± 48.5	—	—	—
			5/21/2007	—	243	38.9	5.2	720	<0.002	<0.01	0.008	0.005	3.8 ± 0.6	ND	205 ± 47.4	—	—	—
			5/21/2001	—	145	45.3	32	666	0.023	0.1	—	0.003	2.5 ± 0.4	ND	109 ± 46	—	—	—
Beck, H	27	28 34.825 –97 41.950	3/22/2011	—	505	93.7	1.17	1,320	0.004	ND	0.009	0.0033	16.2 ± 7.5	0.68 ± 0.15	236 ± 91.8	—	—	—
Fields	27	28 35.558 –97 42.151	1/20/2009	245	715	54.7	0.816	1,450	0.002	2.01	0.009	0.0034	8.2 ± 6.1	0.63 ± 0.19	259 ± 61.9	—	—	—
Metting	29	28 31.385 –97 24.505	2/14/2007	278	452	63	1.1	1,160	0.011	—	0.008	0.0066	7.6 ± 0.8	1.2 ± 0.4	238 ± 48.3	—	—	—
Jones, Charles	29	28 30.463 –97 24.902	8/07/2012	—	92.4	30.2	1.32	556	0.015	ND	0.001	0.0016	0.6 ± 2.4	0.1 ± 0.1	344 ± 125	—	—	—
Orchard	29	28 30.993 –97 25.034	8/07/2012	—	544	91.4	0.876	1,460	0.011	0.07	0.005	0.0059	(-)2 ± 6.5	0.4 ± 0.1	550 ± 129	—	—	—
Cravens	37	28.39955 –97.39585	6/26/2012	186	360	94	1.17	1,018	0.004	ND	0.005	0.016	22.9 ± 5.2	0.5 ± 0.2	924 ± 115	7.5	1,796	24.3
Samuels	37	28 24.629 –97 23.219	7/17/2012	150	450	122	0.835	1,220	0.007	0.18	0.016	0.0127	(-)5 ± 6.9	0.4 ± 0.1	462 ± 114	7.59	1,941	24.2
Cravens	38	28.374183 –97.393583	6/26/2012	—	276	90.7	1.18	921	0.005	ND	0.005	0.0184	11.8 ± 3.7	0.7 ± 0.2	748 ± 112	7.54	1,420	24.7

ft bgs = Feet below ground surface
mg/L = Milligrams per liter
TDS = Total dissolved solids

pCi/L = Picocuries per liter
s.u. = Standard units
µS/cm = Microsiemens per centimeter

°C = Degrees Celsius
— = Not analyzed
ND = Not detected

Gates et al., 2011). As the pH approaches 8, iron minerals in the aquifer will still adsorb arsenate, but the overall adsorption capacity will begin to diminish.

Table 2 presents water quality data for southern Goliad County. Insufficient data were available to create stiff or Piper diagrams, as these diagrams require data for the major ions sodium, potassium, calcium, magnesium, chloride, sulfate, and alkalinity. Arsenic concentrations in groundwater in southern Goliad County range from non-detect (less than 0.0022 mg/L) to 0.023 mg/L. Of the 20 samples analyzed, 8 contained arsenic concentrations below the MCL of 0.01 mg/L (Table 2). Uranium concentrations in all 20 samples were below the MCL of 0.03 mg/L (Table 2).

Although data for silica, vanadium, and potassium are not available for samples presented in Table 2, a correlation between selenium and arsenic is evident, with a correlation coefficient (R^2) of 0.34 that is similar but slightly less than coefficients calculated by Gates et al. (2011) for silica, vanadium, and potassium. The water quality data for arsenic in southern Goliad County indicate that the arsenic is most likely naturally occurring, and probably is not anthropogenic in origin.

5. Arsenic Treatment

Due to the variable distribution of arsenic concentrations that exceed the MCL in southern Goliad County, careful selection of new well locations may help avoid centralized water treatment for water systems. However, as the majority of wells are for domestic purposes, household systems may be the best choice to reduce exposure of residents to arsenic in drinking water. Household systems are designed to be either a point of entry (POE) system, which treats water entering the home, or point of use (POU) system, which treats water at one tap in the household, typically in the kitchen.

The types of treatment available to consumers are reverse osmosis (RO) or adsorptive media, including iron oxide or activated alumina. Both types will provide water with arsenic concentrations below the MCL. If a significant amount of arsenic is present as arsenite, a pre-oxidation step may be required. This pre-oxidation step usually consists of oxidation with hypochlorite ion (bleach type solution). Some iron oxide adsorptive media is designed to remove arsenite so that pre-treatment is not necessary.

RO will remove other constituents such as sulfate and metals, but requires regular maintenance. Adsorptive media systems require less maintenance than RO systems, and usually consist of media replacement every 2 to 3 years depending on use.

6. Conclusions

Arsenic in groundwater in southern Goliad County appears to be naturally occurring, and is related to weathering of volcanic ash in the Catahoula Formation. Arsenic concentrations exceed the MCL for drinking water in some wells, and distribution is irregular in the Evangeline aquifer. Household systems are readily available to remove arsenic from drinking water.

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