Water Quality in the Carrizo-Wilcox Aquifer, 1990–2006

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Texas Water Development Board
Report 372

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1 *Executive summary*

The Carrizo-Wilcox Aquifer is one of the most prolific groundwater sources in Texas. Sixty Texas counties situated between the Rio Grande and the Red River rely to various degrees on groundwater from this aquifer, predominantly to meet irrigation and municipal water supply needs.

The Carrizo-Wilcox Aquifer consists primarily of sand interbedded with gravel, silt, clay, and lignite deposited in a fluviodeltaic environment. Groundwater in the aquifer is predominantly fresh to slightly saline. Total dissolved solids concentrations are typically below 3,000 milligrams per liter. In 2005 and 2006, the Texas Water Development Board (TWDB) analyzed 331 groundwater samples for major and minor ions, trace elements, and radionuclides. Although the quality of the groundwater was generally good, some of the samples exceeded the maximum contaminant levels and secondary standards for nitrate, lead, fluoride, chloride, sulfate, iron, manganese, and total dissolved solids.

For the most part, groundwater salinity showed little change over time in wells from the northern and central sections of the Carrizo-Wilcox Aquifer, although some changes were noted in wells in the southern section of the aquifer. Most changes in groundwater salinity were moderate, of no more than 100 milligrams per liter over the period of record; however, larger fluctuations were observed at locations in Zavala, Dimmit, and Frio counties. The nitrate in groundwater has generally been within the admissible limits for drinking water.

To determine the age and source of the groundwater, we used radiogenic and stable isotope analysis. Groundwater ages progressively increase along the flow paths from the recharge areas to the downdip areas of the Carrizo-Wilcox. Most of the water originated from precipitation.

Extending from northeastern Mexico into Texas, Arkansas, and Louisiana, the Carrizo-Wilcox Aquifer is the main groundwater supply source for all or parts of 60 Texas counties situated between the Rio Grande and the Red River (Figure 2-1). Of the nearly 450,000 acre-feet of groundwater pumped in 2003 from the aquifer, 42 percent was used for irrigation and 35 percent was used for municipal water supply (TWDB Water Use Survey, 2003). Most of the irrigation pumpage from the aquifer takes place in the Winter Garden region of South Texas, with irrigation pumpage in Zavala, Frio, Atascosa, Wilson, and Dimmit counties accounting for 35 percent of the total water production from the aquifer. Bryan-College Station, Lufkin-Nacogdoches, Bastrop, Tyler, Pflugerville, and Hutto are the major municipalities that rely on groundwater from the Carrizo-Wilcox Aquifer.

Figure 2-1. The Carrizo-Wilcox Aquifer in Texas.

3 Water-bearing formations of the Wilcox and Claiborne groups

The Carrizo-Wilcox Aquifer is contained in the sedimentary deposits of the Wilcox Group and the overlying Carrizo Formation of the Claiborne

2000). The Wilcox Group and the overlying Carrizo Sand are commonly thought to be hydraulically connected. Klemt and others (1976) indicate that "the waters

Series			South Texas	Central Texas	Sabine Uplift
Eocene	Claiborne Group		Weches Fm.	Weches Fm.	Weches Fm.
			Queen City Sand	Queen City Sand	Queen City Sand
			Reklaw Fm.	Reklaw Fm.	Reklaw Fm.
			Carrizo Sand / Upper Wilcox	Carrizo Sand	Carrizo Sand
			Middle Wilcox	Calvert Bluff Fm.	Upper Wilcox
Paleocene	Wilcox Group		Lower Wilcox	Simsboro Fm.	Middle Wilcox
				Hooper Fm.	Lower Wilcox
		Midway Group		Midway Group	Midway Group

☐ Carrizo-Wilcox Aquifer

Figure 3-1. Paleocene to lower Eocene stratigraphic relationships (modified from Mace and others, 2000). Fm=formation

Group (Figure 3-1). It is primarily composed of fluviodeltaic Tertiary sand interbedded with gravel, silt, clay, and lignite.

Beginning 50 to 60 million years ago, the Wilcox and Claiborne groups of the Upper Paleocene and Eocene series were deposited along the edge of the Gulf of Mexico. They overlie the Lower Paleocene Midway Group, a confining unit that constitutes the base of the Carrizo-Wilcox Aquifer. Shales of the Eocene Reklaw Formation bound the upper surface of Upper Wilcox-Carrizo terrigenous sediments and compose the top of the Carrizo-Wilcox Aquifer.

The Paleocene-Eocene Wilcox Group (known as the Indio Formation in outcrop) consists of thin-bedded sandstone, carbonaceous shale, and lignite. Wilcox sediments have a mean sand content of approximately 55 percent (Mace and others,

probably commingle to some degree, although most of the sand beds in the Wilcox Group are less permeable and most contain poorer water quality than the Carrizo Sand."

Three distinct Wilcox Group facies have been identified in South Texas, Central Texas, and the Sabine Uplift, respectively (Figure 3-1). South of the Trinity River and north of the Colorado River, the Wilcox Group consists of the Hooper, Simsboro, and Calvert Bluff formations (Barnes, 1992). The Wilcox Group is undifferentiated north of the Trinity River and south of the Colorado River where the Simsboro Formation is not a distinct unit.

The oldest unit of the overlying Eocene Claiborne Group is the Carrizo Sand. Named for the town of Carrizo Springs in Dimmit County, Texas (Owen, 1889), the Carrizo Sand is composed of

massive, cross-bedded, medium-grained sands ranging in thickness from 150 to 1,200 feet. Interspersed within the sands are fine-textured sediments that form semipermeable hydrologic barriers. The Carrizo Sand crops out in a northeast-trending band between 150 and 200 miles inland from the Gulf of Mexico, dips south to southeast, and thickens toward the Gulf, except near the Sabine Uplift in northeastern Texas. There the units thin or pinch out over the top of the structural dome and dip outward in a radial pattern (Ayers and Lewis, 1985). Because of the high permeability of these laterally connected sand bodies and the large amounts of groundwater contained in them, the Carrizo-Wilcox Aquifer is one of the most productive aquifers in Texas.

Changes in regional deposition patterns through time and faulting impacted the thickness and distribution of Wilcox and Carrizo sediments. The main centers of sedimentary deposition active in Texas during the Paleocene were the Houston and Rio Grande embayments, which were separated by the San Marcos Arch. The Sabine Arch bounds the Houston Embayment to the northeast (Figure 3-2). The presence of structurally high and low areas near the ancient coastline allowed the contemporaneous deposition of both shoreline and fluviodeltaic sediments. The Houston Embayment was the principal depositional center at the time of Wilcox sedimentation, and the Rio Grande Embayment was most active during the Carrizo Sand deposition. This shift in regional sedimentation through time resulted in thicker Wilcox strata north of the Colorado River and thicker Carrizo Sand in South Texas.
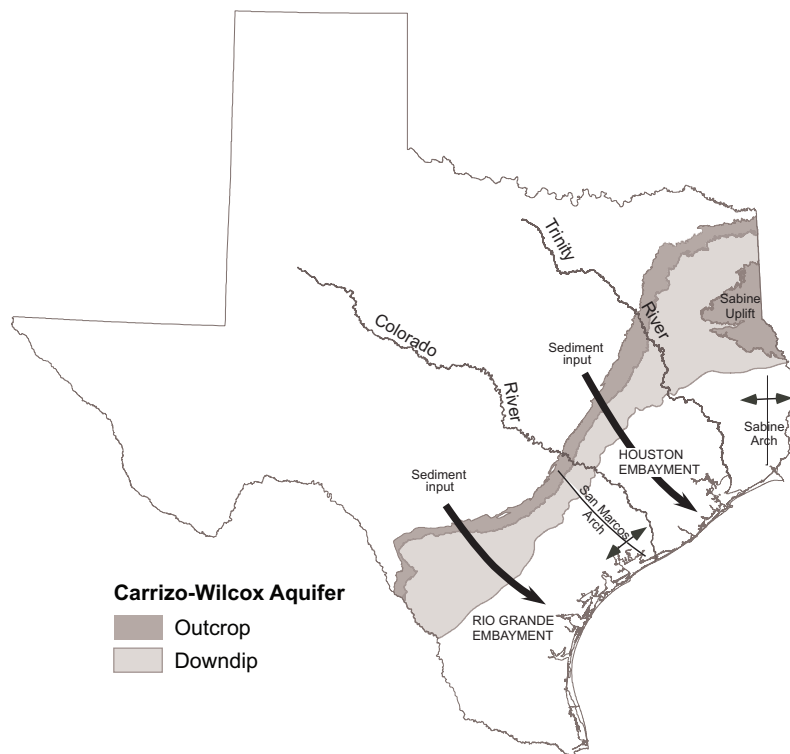

Figure 3-2. Structural elements of the Texas Coastal Plain (modified from Ayers and others, 1985).

4   *General hydrochemistry*

In 2005 and 2006, we analyzed groundwater samples from 331 wells within the Carrizo-Wilcox Aquifer for major and minor ions, trace elements, and radionuclides. Groundwater is predominantly fresh to slightly saline and contains total dissolved solids concentrations below 3,000 milligrams per liter (Figure 4-1). The salinity in the Carrizo-Wilcox Aquifer increases downgradient as freshwater recharge percolates through the aquifer, dissolves minerals along its flow path, and mixes with deep, high-salinity groundwater expulsed along fault zones (Kreitler, 1979).

Of the wells we sampled, two exceeded the Texas Commission on Environmental Quality maximum contaminant level for fluoride, and lead was detected in 20 samples (Table 4-1). Nitrate exceeded the maximum contaminant level in four samples (Figure 4-2).

Twelve samples exceeded the Texas Commission on Environmental Quality's secondary standards for chloride (Figure 4-3). Nine samples exceeded the Commission's secondary standards for sulfate (Figure 4-4). Iron concentrations above the Commission's secondary standard were measured in 85 samples, manganese in 53 samples, and fluoride in 9 samples. Twenty-two samples had total dissolved solids concentrations in excess of the secondary drinking water
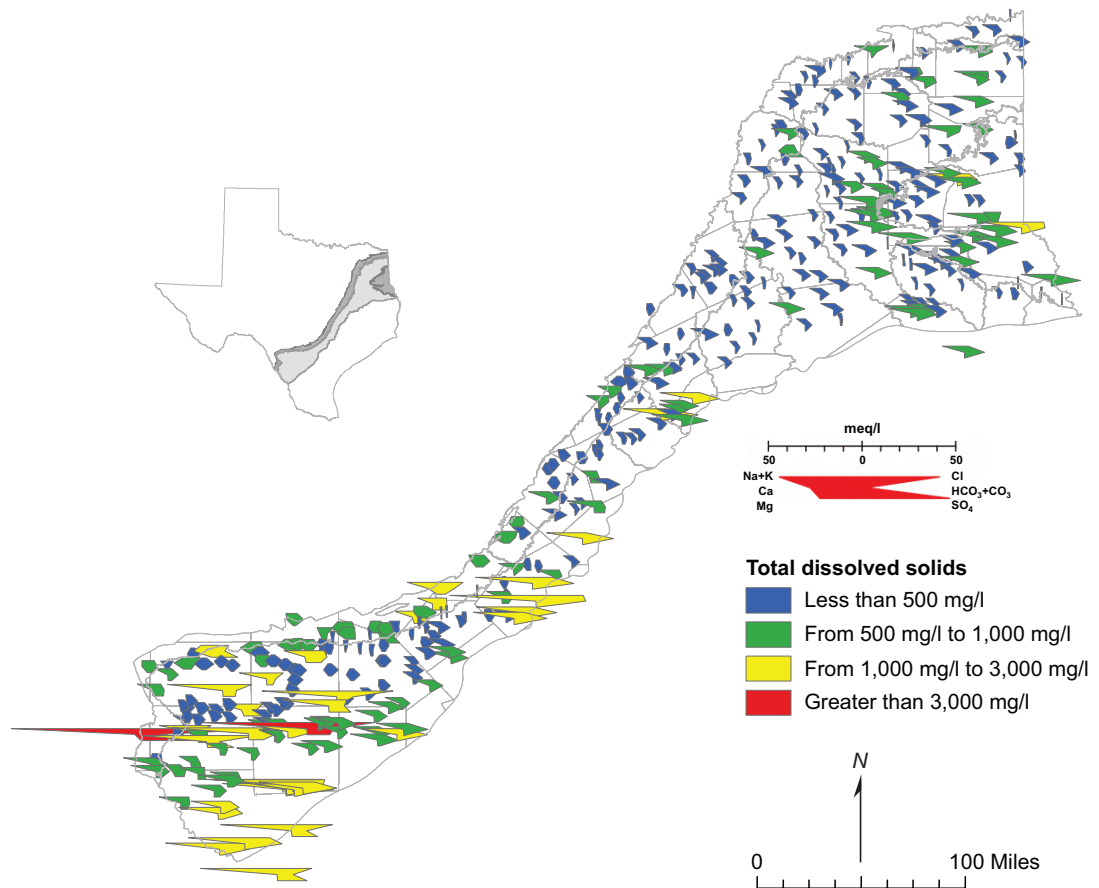

Figure 4-1. General quality of groundwater in the Carrizo-Wilcox Aquifer.

mg/l=milligrams per liter; meq/l=milliequivalents per liter; Na=sodium; K=potassium; Cl=chloride; Ca=calcium; HCO_3=bicarbonate; CO_3=carbonate; Mg=magnesium; SO_4=sulfate

standard of 1,000 milligrams per liter, and the pH of 107 samples was outside the recommended 6.5 to 8.5 range.

The latest three major aquifer-wide sampling events we conducted for the Carrizo-Wilcox Aquifer took place in 1991 through 1993, in 2002, and again in 2005 through 2006. The number of wells with parameter concentrations in excess of the state primary and secondary standards varied from one sampling event to another (Table 4-1).

Of the three sampling events, 2002 had the highest incidence of noncompliant sites. Contamination by alpha activity,

arsenic, barium, nitrate, beryllium, cadmium, selenium, and thallium was at its lowest in 2005–2006 when some of these analytes never exceeded the maximum contaminant levels. Chloride, manganese, sulfate, and total dissolved solids exceeded secondary standards in 2005–2006 with a frequency comparable to that recorded in 1991–1993, and iron concentrations above the secondary standard were encountered almost as frequently as in 2002. We detected lead in 20 samples during 2005–2006, down from 50 in 2002. The state-prescribed maximum contaminant level for lead has

Table 4-1. Total number of samples exceeding the primary and secondary drinking water standards.

Total number of samples collected by TWDB					
Years of sample collection			**1991–1993**	**2002**	**2005–2006**
			324	386	331
Category	**Constituent**	**MCL**	**Above MCL**	**Above MCL**	**Above MCL**
Primary	Alpha particles	15 pCi/l	6	N/A	0
	Antimony	6 µg/l	N/A	0	0
	Arsenic	10 µg/l	1	0	0
	Barium	2 mg/l	1	0	0
	Beryllium	4 µg/l	N/A	10	0
	Cadmium	5 µg/l	1	10	0
	Chromium	100 µg/l	0	0	0
	Fluoride	4 mg/l	1	5	2
	Lead	Detection	2	50	20
	Nickel	100 µg/l	0	0	N/A
	$NO_2 + NO_3$ (NO_3)	44.3 mg/l	13	5	4
	Selenium	50 µg/l	0	4	0
	Thallium	2 µg/l	0	1	0
Secondary	Chloride	300 mg/l	10	22	12
	Copper	1 mg/l	0	0	0
	Fluoride	2 mg/l	7	9	9
	Iron	0.3 mg/l	41	92	85
	Manganese	50 µg/l	35	66	53
	pH	6.5–8.5	148	75	107
	Sulfate	300 mg/l	5	13	9
	Dissolved solids	1,000 mg/l	22	38	22
	Zinc	5 mg/l	0	0	0

MCL=maximum contaminant level; mg/l=milligrams per liter; µg/l=micrograms per liter; pCi/l=picocuries per liter; N/A=not analyzed; NO_2=nitrite; NO_3=nitrate

changed through time. However, analytical results for all three sampling events presented in Table 4-1 conform to the current standard: any lead detection is treated as an exceedance. The lowering of the maximum contaminant level and laboratory analytical reporting limits for lead in recent years have resulted in more detections in 2002 and later when compared to 1991–1993. This comparison provides only a very general view of the state of the aquifer. Variables, such as the number of samples collected each cycle, their locations, and changes in analytical reporting limits though time, can impact this type of analysis.
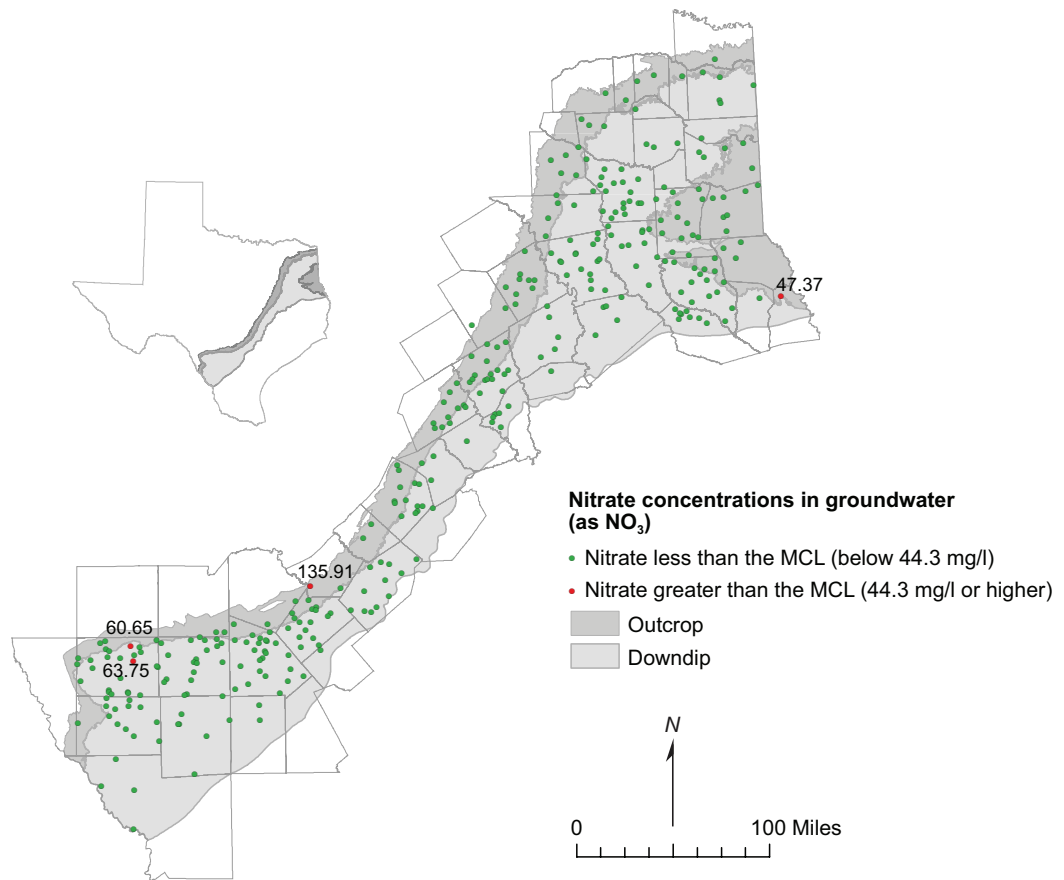

Figure 4-2. Distribution of nitrate in the Carrizo-Wilcox Aquifer.
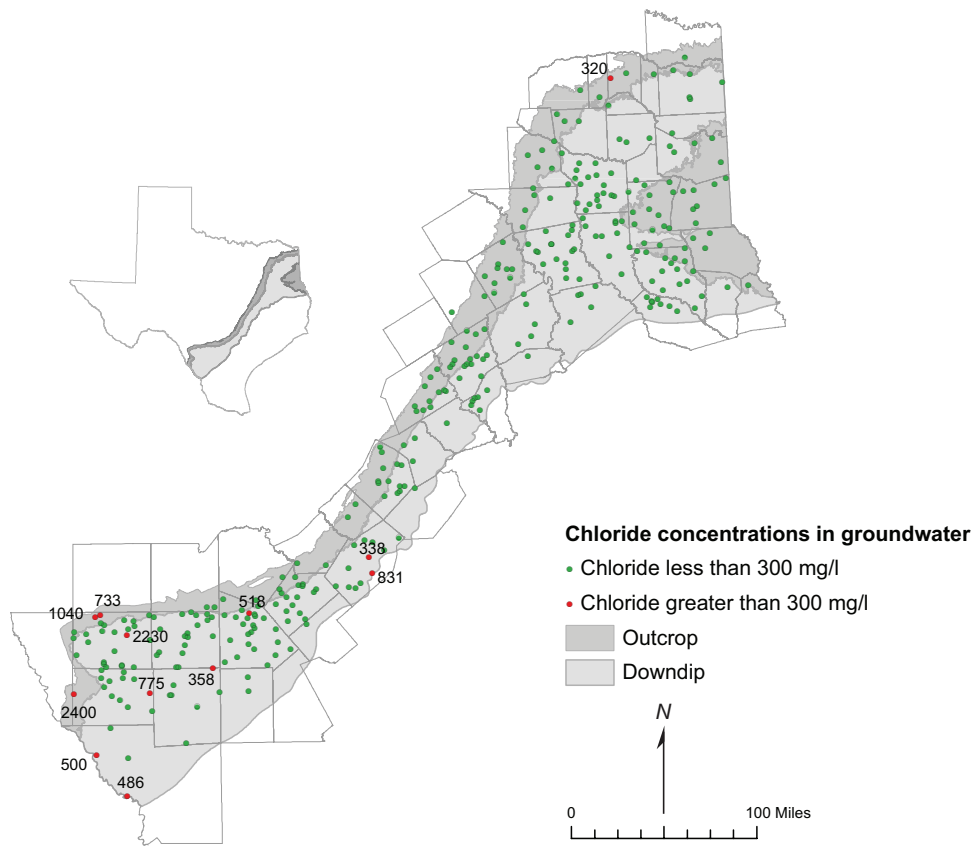mg/l=milligrams per liter; MCL=maximum contaminant level

Figure 4-3. Distribution of chloride in the Carrizo-Wilcox Aquifer.
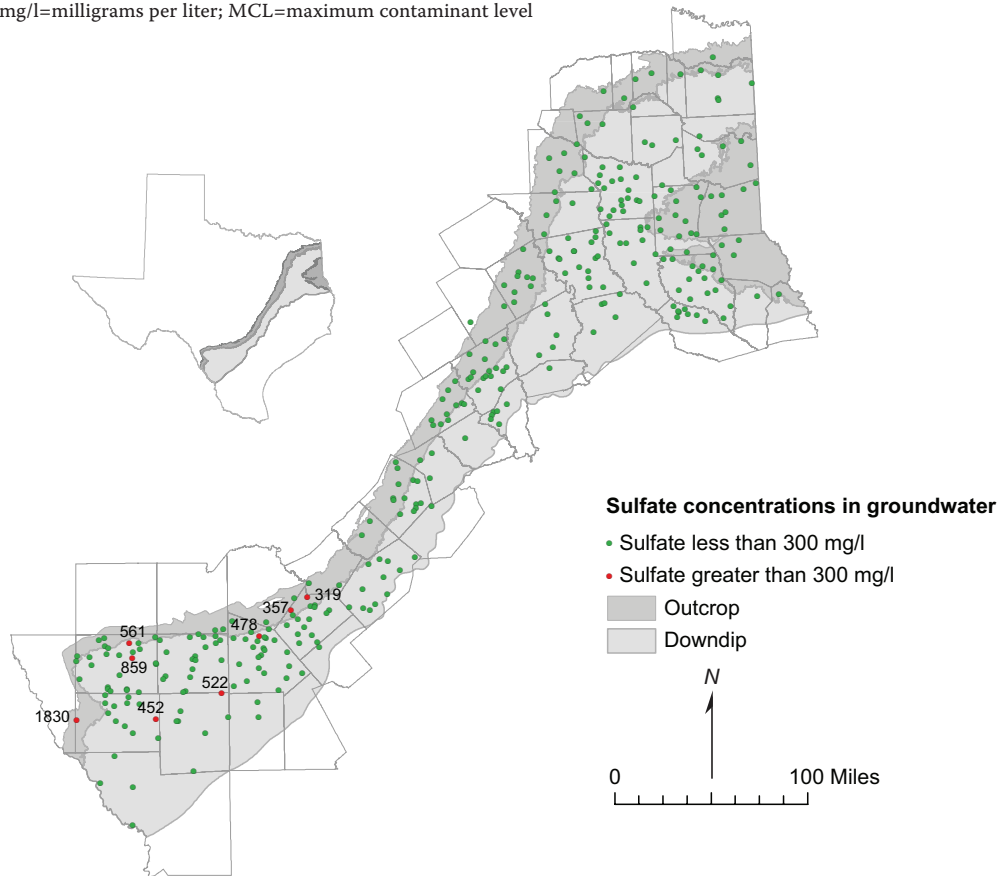mg/l=milligrams per liter; MCL=maximum contaminant level

Figure 4-4. Distribution of sulfate in the Carrizo-Wilcox Aquifer.
mg/l=milligrams per liter

5 _Groundwater types_

To identify groundwater types in the aquifer, we computed the weight of each reported anion and cation to determine total anions and cations. We deemed individual ions dominant when their weight was 50 percent or more of the total. Based on the 2006 water quality data, there were 21 groundwater types in the Carrizo-Wilcox Aquifer. The most common types were calcium-bicarbonate, sodium-bicarbonate, mixed-bicarbonate, and sodium-chloride, accounting for 314 of the 331 samples, or 95 percent (Figure 5-1).

Calcium-bicarbonate groundwater (the blue dots on map in Figure 5-1) occurs mainly across the Carrizo Sand outcrop in South Texas (Zavala, Frio, Atascosa, and Bexar counties) and Central Texas (Milam, Bastrop, and Caldwell counties). The dissolution of caliche (calcite concretions present in the shallow subsurface) by meteoric recharge water could explain the predominance of calcium ions in this facies. As groundwater moves downdip, it changes to a sodium-dominated chemical composition, owing in part to ion exchange reactions; calcium ions dissolved in groundwater are exchanged for sodium ions bound on clay particles in the aquifer material, resulting in a sodium-bicarbonate facies (the green dots in Figure 5-1).

In the western and central parts of the aquifer, the groundwater composition evolves along flow paths from a sodium-mixed type to a sodium-bicarbonate facies by the addition of bicarbonate at depth. Hamlin (1988) examined the changes in bicarbonate concentrations and pH along groundwater flow paths in the Carrizo Sand of South Texas. He noted that the pH stabilizes at values of around 8.0 to 8.6 at greater depths, whereas the bicarbonate continues to increase. This indicates that an additional source is supplying carbonic acid to the water. The fermentation of methane accompanying deep groundwater expulsed upward along downdip growth faults can supply the additional carbonic acid when mixed with Carrizo-Wilcox groundwater (Hamlin, 1988).

Sodium-chloride water can be the result of evaporite dissolution, ion exchange reactions, irrigation return flow, leakage from underlying water-bearing strata, or local lithologic variations. Sodium-chloride groundwater is found in the Winter Garden area of South Texas where water levels in the Carrizo-Wilcox Aquifer have been lowered due to pumping. This has facilitated the cross-formational flow of saline groundwater into the aquifer in the Crystal City-Carrizo Springs area (the red dots in Figure 5-1).

The composition of groundwater in the Carrizo-Wilcox Aquifer is highly variable in the outcrop and shallow, confined areas but tends to become more uniform with depth. Where the aquifer is shallow, facies dominated by calcium, bicarbonate, and chloride prevail. Downdip, through enrichment in sodium and loss of calcium from ion exchange processes, the water gradually shifts to a sodium-bicarbonate composition. The chemical variability in the Carrizo outcrop is greatest in the southern part of the aquifer, southwest of the Guadalupe River. The presence of heterogeneous, mud-rich overbank sediments interspersed with cleaner sand intervals in the Carrizo-Wilcox Aquifer of South Texas could explain the abrupt facies changes over short distances, as well as the abundance of chloride ions in those samples.
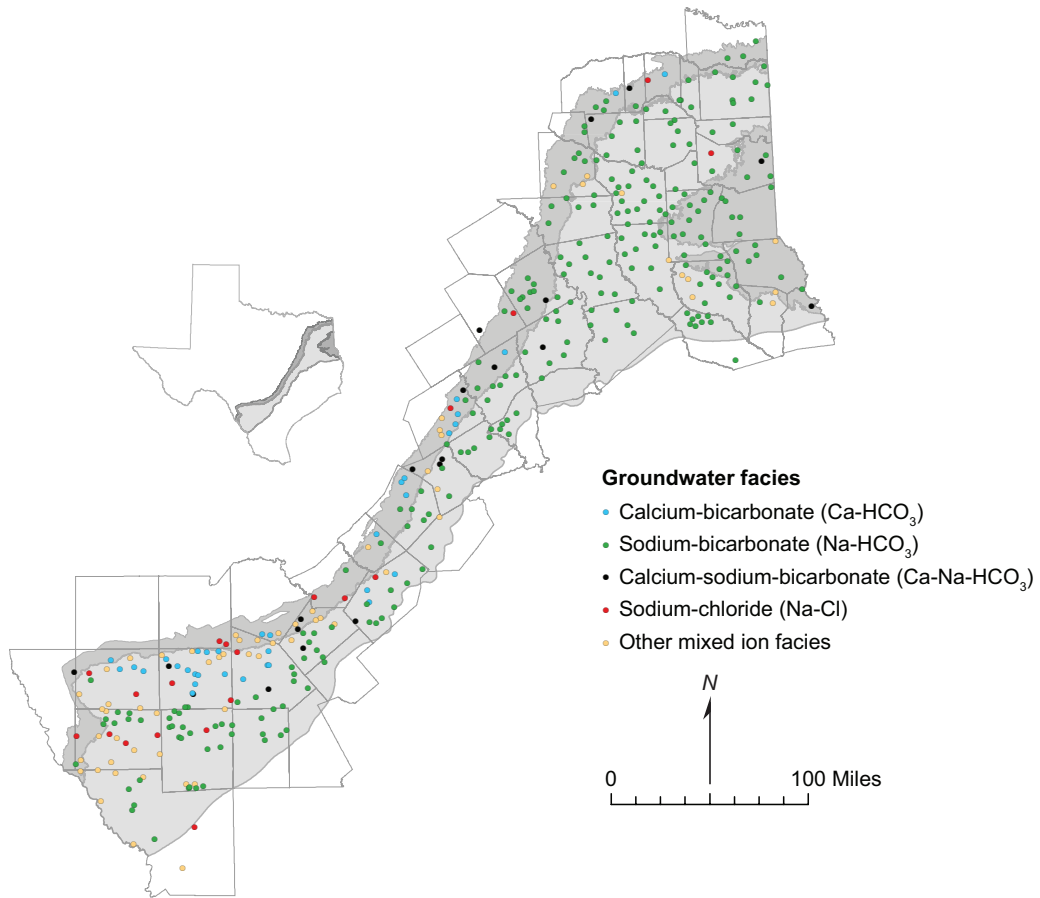
Figure 5-1. Hydrochemical facies map for the Carrizo-Wilcox Aquifer.

Groundwater facies
- Calcium-bicarbonate (Ca-HCO$_3$)
- Sodium-bicarbonate (Na-HCO$_3$)
- Calcium-sodium-bicarbonate (Ca-Na-HCO$_3$)
- Sodium-chloride (Na-Cl)
- Other mixed ion facies

N

0   100 Miles

6 *Temporal changes in groundwater quality*

Hydrochemical graphs indicate how the overall quality of groundwater in the Carrizo-Wilcox Aquifer has changed through time and display time series concentrations of total dissolved solids (or salinity) and nitrate (as NO3) in 21 wells (see Appendix). As an indicator of the amount of dissolved minerals in the sample, salinity is commonly used to assess the general quality of the water. Nitrate in groundwater is typically associated with the use of nitrogen-based fertilizers and/or animal waste, and indicates agriculture- and/or feedlot-induced contamination. The safe levels recommended by the Texas Commission on Environmental Quality for water potability are 1,000 milligrams per liter for total dissolved solids and 44.3 milligrams per liter for nitrate (as NO3). The well information in the Appendix is from wells predominantly used for public supply that have been chosen from among over 100 sites with water quality records going back at least 20 years.

For the most part, salinity showed little change over time in wells from the northern and central sections of the Carrizo-Wilcox Aquifer while some changes in salinity were noted in wells from the south. The changes were moderate, of no more than 100 milligrams per liter over the period of record, although larger fluctuations were observed at locations in Zavala, Dimmit, and Frio counties. Well 77-35-802, a stock well in Dimmit County, displayed both increases and decreases in salinity of more than 2,000 milligrams per liter from 1985 on. Well 77-02-403, a public water supply well in Zavala County, recorded an increase in total dissolved solids concentration of over 500 milligrams per liter between 1990 and 2002.

Nitrate concentrations have been, with one exception, consistently low, well below the maximum contaminant levels prescribed by the Texas Commission on Environmental Quality. Well 77-02-403 in Zavala County recorded an abrupt increase in nitrate concentration from non-detected levels to 46.93 milligrams per liter in 2000, in excess of the maximum contaminant levels. Pulses of elevated nitrate (up to 9 milligrams per liter) have been recorded in wells in Karnes, Gonzales, Rusk, Cherokee, and Webb counties but returned to the background levels within several years.

Salinization can depend on several factors, including thickness of the freshwater-saturated section, location and pumping rate of the well, depth of the well screen, well construction, mineralogical composition of aquifer material, and lateral and vertical lithological variability. Downward movement of saline groundwater from an overlying brackish zone is responsible for the increase in total dissolved solids concentrations in Well 77-35-802 in Dimmit County. Corrosion of a well casing 250 feet below land surface resulted in brackish water cascading down into the freshwater zone, as documented with the help of a borehole video camera (well owner A. Linnartz, personal communication, 2007). The well has since been cemented, redrilled at a smaller diameter, and relined to seal the contaminating interval. Lateral migration of inferior quality water may account for salinization of other wells not included in this section. Intense pumpage may induce inferior quality water to leak from mud-rich interbeds and move to wells where drawdown cones have reversed the natural hydraulic gradient.

7 Isotope data and implications for groundwater origin and recharge

During 2002, 2004, and 2006, we collected 85 water samples from the Carrizo-Wilcox Aquifer and had them analyzed for various radiogenic and stable isotopes (Figure 7-1 and Table 7-1).

Tritium and carbon-14 are radioisotopes used to determine the apparent or relative age of water. Oxygen-18 and deuterium are stable isotopes used to investigate the source of groundwater.

Isotope samples

- Oxygen-18, deuterium, tritium, and carbon-14
- Tritium
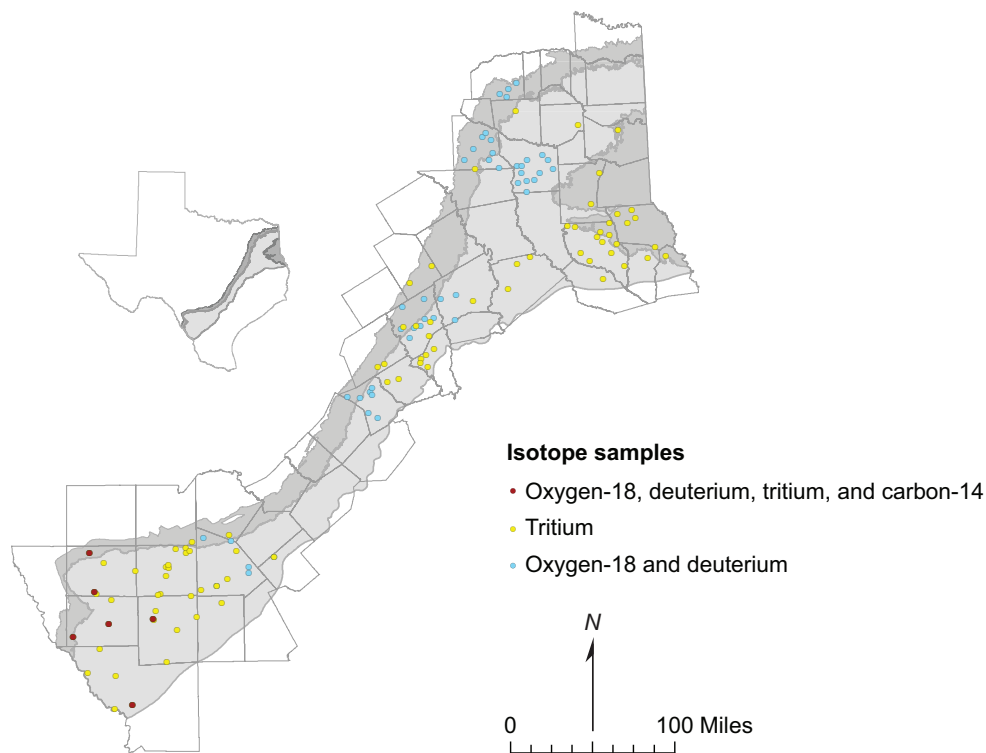- Oxygen-18 and deuterium

N

0   100 Miles

Figure 7-1. Location map for isotope samples collected from the Carrizo-Wilcox Aquifer.

Table 7-1. Isotope composition of groundwater from the Carrizo-Wilcox Aquifer.

State well number	δ^2H (‰) VSMOW	δ^{18}O(‰) VSMOW	Apparent ^{14}C age[a]	pmC	δ^{13}C (‰)	Tritium (TU)
77-18-407	-29	-4.2	10460 ± 80	0.2720	-9.9	0.00
69-57-904	-31	-4.6	32680 ± 1200	0.0100	-11.8	-0.06
85-21-501	-31	-4.5	35490 ± 1500	0.0120	-10.7	-0.02
77-39-407	-31	-4.6	28950 ± 200	0.0270	-9.6	-0.02
77-35-802	-31	-4.4	27600 ± 200	0.0320	-12.1	-0.01
76-48-803	-33	-5.1	1365 ± 80	0.1830	-18.1	-0.14
17-60-804	-33	-5.7	-	-	-	-
17-61-301	-30	-5.2	-	-	-	-
17-61-403	-33	-5.8	-	-	-	-
34-05-102	-30	-5.2	-	-	-	-
34-18-903	-34	-5.8	-	-	-	-
34-19-415	-31	-5.6	-	-	-	-
34-26-407	-32	-5.7	-	-	-	-
34-27-206	-31	-5.5	-	-	-	-
34-27-906	-29	-5.1	-	-	-	-
34-33-401	-33	-5.6	-	-	-	-
34-35-502	-31	-5.4	-	-	-	-
34-38-510	-32	-5.8	-	-	-	-
34-39-302	-32	-5.7	-	-	-	-
34-40-710	-31	-5.6	-	-	-	-
34-44-104	-32	-5.7	-	-	-	-
34-45-206	-35	-5.9	-	-	-	-
34-46-113	-35	-6.0	-	-	-	-
34-46-404	-32	-5.8	-	-	-	-
34-47-504	-31	-5.6	-	-	-	-
34-47-505	-33	-5.8	-	-	-	-
34-48-203	-31	-5.3	-	-	-	-
34-53-302	-36	-5.9	-	-	-	-
34-54-206	-32	-5.6	-	-	-	-
34-54-804	-34	-5.7	-	-	-	-
39-48-701	-32	-5.4	-	-	-	-
39-51-911	-32	-5.5	-	-	-	-
39-53-204	-31	-5.1	-	-	-	-
39-54-306	-32	-5.5	-	-	-	-
39-61-501	-35	-5.8	-	-	-	-
39-62-401	-33	-5.6	-	-	-	-
39-64-705	-32	-5.5	-	-	-	-
58-39-709	-32	-5.5	-	-	-	-
58-40-611	-31	-5.4	-	-	-	-
58-48-114	-30	-5.4	-	-	-	-
58-5-6302	-30	-5.2	-	-	-	-
59-03-203	-32	-5.3	-	-	-	-
59-04-306	-32	-5.4	-	-	-	-

Table 7-1 (continued).

State well number	δ²H (‰) VSMOW	δ¹⁸O(‰) VSMOW	Apparent ¹⁴C ageᵃ	pmC	δ¹³C (‰)	Tritium (TU)
59-04-707	-31	-5.5	-	-	-	-
59-05-103	-32	-5.8	-	-	-	-
59-33-403	-32	-5.7	-	-	-	-
59-33-704	-32	-5.6	-	-	-	-
59-49-509	-30	-5.3	-	-	-	-
68-51-701	-30	-5.1	-	-	-	-
68-53-810	-29	-4.9	-	-	-	-
78-06-903	-29	-4.9	-	-	-	-
78-14-302	-30	-5.0	-	-	-	-
78-20-101	-28	-5.0	-	-	-	-
34-13-308	-	-	-	-	-	0.00
34-42-109	-	-	-	-	-	-0.02
35-18-303	-	-	-	-	-	0.01
35-22-708	-	-	-	-	-	-0.14
35-44-806	-	-	-	-	-	0.05
35-59-902	-	-	-	-	-	0.01
36-25-802	-	-	-	-	-	2.46
37-05-904	-	-	-	-	-	0.11
37-07-403	-	-	-	-	-	0.03
37-09-505	-	-	-	-	-	-0.06
37-10-403	-	-	-	-	-	-0.13
37-12-806	-	-	-	-	-	-0.07
37-13-407	-	-	-	-	-	-0.10
37-14-504	-	-	-	-	-	-0.04
37-15-107	-	-	-	-	-	0.22
37-20-106	-	-	-	-	-	-0.02
37-20-501	-	-	-	-	-	-0.05
37-21-102	-	-	-	-	-	0.00
37-21-904	-	-	-	-	-	0.01
37-26-201	-	-	-	-	-	0.00
37-27-808	-	-	-	-	-	0.07
37-29-406	-	-	-	-	-	0.06
37-32-303	-	-	-	-	-	0.06
37-32-709	-	-	-	-	-	0.01
37-38-404	-	-	-	-	-	-0.17
37-44-202	-	-	-	-	-	0.15
38-29-802	-	-	-	-	-	0.04
38-30-502	-	-	-	-	-	0.06
38-44-505	-	-	-	-	-	0.18
38-49-502	-	-	-	-	-	0.14
39-30-717	-	-	-	-	-	1.17
39-35-907	-	-	-	-	-	0.08
39-62-703	-	-	-	-	-	-0.09

Table 7-1 (continued).

State well number	δ^2H (‰) VSMOW	$\delta^{18}O$(‰) VSMOW	Apparent ^{14}C age[a]	pmC	$\delta^{13}C$ (‰)	Tritium (TU)
59-03-306	-	-	-	-	-	-0.03
59-04-307	-	-	-	-	-	0.05
59-05-901	-	-	-	-	-	0.14
59-14-706	-	-	-	-	-	0.05
59-17-803	-	-	-	-	-	-0.01
59-18-704	-	-	-	-	-	0.11
59-21-205	-	-	-	-	-	-0.02
59-21-411	-	-	-	-	-	-0.04
59-21-732	-	-	-	-	-	0.09
59-21-909	-	-	-	-	-	-0.02
59-27-717	-	-	-	-	-	-0.03
68-53-407	-	-	-	-	-	0.23
68-57-622	-	-	-	-	-	1.34
68-57-918	-	-	-	-	-	0.11
68-58-114	-	-	-	-	-	0.64
68-58-410	-	-	-	-	-	-0.01
69-64-611	-	-	-	-	-	0.01
77-03-401	-	-	-	-	-	0.41
77-08-406	-	-	-	-	-	0.04
77-08-716	-	-	-	-	-	0.09
77-08-814	-	-	-	-	-	0.03
77-13-202	-	-	-	-	-	0.07
77-16-409	-	-	-	-	-	0.02
77-18-807	-	-	-	-	-	0.04
77-23-803	-	-	-	-	-	0.02
77-23-809	-	-	-	-	-	0.08
77-27-304	-	-	-	-	-	0.08
77-31-706	-	-	-	-	-	-0.15
77-39-406	-	-	-	-	-	-0.05
77-48-301	-	-	-	-	-	-0.01
77-50-603	-	-	-	-	-	-0.02
77-64-401	-	-	-	-	-	0.00
78-08-301	-	-	-	-	-	0.07
78-13-705	-	-	-	-	-	0.04
78-18-601	-	-	-	-	-	0.09
78-18-702	-	-	-	-	-	-0.07
78-28-501	-	-	-	-	-	0.04
78-34-205	-	-	-	-	-	0.03
85-01-301	-	-	-	-	-	0.07
85-04-401	-	-	-	-	-	-0.03
85-19-903	-	-	-	-	-	-0.11
59-26-803	-	-	-	-	-	0.35
68-61-905	-	-	-	-	-	0.03

Table 7-1 (continued).

State well number	δ^2H (‰) VSMOW	δ^{18}O(‰) VSMOW	Apparent ^{14}C age[a]	pmC	δ^{13}C (‰)	Tritium (TU)
69-57-904	-	-	-	-	-	0.00
76-48-803	-	-	-	-	-	0.00
77-35-802	-	-	-	-	-	0.00
77-39-407	-	-	-	-	-	0.00
78-20-101	-	-	-	-	-	0.01
85-21-501	-	-	-	-	-	0.00

[a]Reported as radiocarbon years before present ("present"=1950 A.D.)

δ^2H=deuterium; δ^{18}O=oxygen-18; ^{14}C=carbon-14; ^{3}H=tritium; pmC=percent modern carbon;δ^{13}C=carbon-13; TU=tritium units; VSMOW=Vienna standard mean ocean water; ‰=per mil, indicates parts per thousand.

7.1

TRITIUM AND CARBON-14

Tritium concentrations in groundwater ranged from zero to 2.46 tritium units. Most of the samples showed concentrations below 0.5 tritium units, which suggests the water was recharged before 1952 (Mazor, 2004). Three samples had tritium concentrations greater than 0.5 tritium units, indicating a component of post-1952 water. The carbon-14 activities, where analyzed, were very low, which is typical for older water in slow-moving flow systems with limited active recharge. These low carbon-14 values indicate the groundwater was recharged several thousands of years ago. Highly accurate age estimates based exclusively on carbon isotopes, however, are difficult to derive because of the complex nature of carbon chemistry in groundwater systems. Geochemical processes, such as dilution and isotope exchange, can strongly alter the initial carbon-14 activity in groundwater, resulting in an artificial aging of groundwater. We did not correct our apparent ages for radiocarbon dilution; these ages are assumed to represent maximum limits (Table 7-1). Previous work by Pearson and White (1967) showed that the age of groundwater in the Carrizo Sands in Atascosa and neighboring counties ranged from zero at the outcrop to 27,000 years downdip and that average groundwater velocities ranged from 5.2 feet per year to 7.8 feet per year.

The results of the TWDB radiocarbon and tritium sampling in areas of South Texas generally agree with the findings of Pearson and White (1967). Radiocarbon activities decreased from 27 percent modern carbon in shallower wells in the aquifer outcrop to 1 percent modern carbon in deep, downdip samples. However, a shallow water sample with high total dissolved solids from Zavala County yielded very low carbon-14 values and no measurable tritium despite its location in the aquifer recharge area. Bicarbonate concentrations ranging from 615 milligrams per liter to 732 milligrams per liter have been measured in groundwater from this well (Well 69-57-904). Such values are typical of deeper parts of the flow system where mixing between meteoric water and formation water takes place (Hamlin, 1988).

7.2

OXYGEN-18 AND DEUTERIUM

Because water consists of hydrogen and oxygen, the various isotopes of these two elements can be found in water molecules. The ratios of stable isotopes of hydrogen (deuterium to hydrogen)

and of oxygen (oxygen-18 to oxygen-16) can provide valuable insights into the origins of the water. For example, in precipitation these ratios vary according to elevation and distance from the ocean. An altitude difference of 820 feet produces a clear and measurable change in the two stable isotope ratios, a change that is preserved once the precipitation percolates into the aquifer. Although some mixing of groundwater in the aquifer is inevitable, often water from different sources is separated because of the aquifer's physical characteristics. Thus, the hydrogen and oxygen stable isotope ratios can be used to determine the recharge location for groundwater and to discriminate among multiple water sources within an aquifer.

The isotopic composition of water is usually expressed in comparison with the isotopic composition of ocean water. By international agreement, the standard mean ocean water (SMOW) has been selected to serve as a reference against which all water samples are reported (Craig, 1961). The isotopic composition of water is expressed in per mil (‰) deviation from the standard mean ocean water. The deviation is shown as δD (also expressed as $\delta^2 H$) for deuterium and $\delta^{18}O$ for oxygen-18:

$$\delta D‰ = \frac{(D/H)_{sample} - (D/H)_{SMOW}}{(D/H)_{SMOW}} \, x \, 1000$$

and

$$\delta^{18}O‰ = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}} \, x \, 1000,$$

where D = deuterium, or ^2H, H = hydrogen, or ^1H, ^{18}O = oxygen-18, and ^{16}O = oxygen-16.

In this report, we use the expression "oxygen-18" to mean $\delta^{18}O$ expressed as per mil (‰) and the expression "deuterium" to mean δD expressed as per mil (‰).

Meteorological processes affect the stable oxygen and hydrogen isotopes of water during the hydrologic cycle and

provide a distinctive fingerprint of their origin. This fingerprint is fundamental to investigating the origin of groundwater.

Craig (1961) discovered a linear correlation between oxygen-18 and deuterium measured in freshwater worldwide. This line is termed "global meteoric water line" and is described by the equation below:

$$\delta^2 H = 8 \, \delta^{18}O + 10,$$

where $\delta^2 H$ is deuterium and $\delta^{18}O$ is oxygen-18.

The global meteoric water line is, in fact, an average of many local meteoric water lines, which are different from the global line due to local climatic and geographic factors.

Most of the groundwater deuterium and oxygen-18 data from the Carrizo-Wilcox Aquifer samples plot tightly around the global meteoric water line, which suggests this water originated from precipitation (Figure 7-2). Several data points, representing six South Texas samples, plot below the global meteoric water line where they form a well-defined linear trend with a very good coefficient of determination (R^2 = 0.97). The slope of the line of best fit (S = 4.9) could indicate that evaporative isotope enrichment occurred prior to recharge (Clark and Fritz, 1997). Given the old ages of this groundwater, however, it is more likely that water-rock interactions have modified their original isotopic signature.

Groundwater temperatures at these locations range from 27°C to 43°C, not hot enough to explain the positive oxygen-18 shift from the global line as high-temperature exchange between the fluids and the rocks. However, cases of oxygen-18 enrichment accompanied by minor deuterium enrichment at low temperatures have been documented in formation water in the Gulf Coast and other sedimentary basins around the world (Clayton and others, 1966; Fleischer and others, 1977). The deviation from the global meteoric water

line for this water has been attributed to oxygen exchange with carbonate minerals at elevated temperatures (Clayton and others, 1966); deuterium exchange with hydrocarbon, hydrogen sulfide, and hydrated minerals; and mixing with meteoric water (Longstaffe, 1983; Bein and Dutton, 1993; Musgrove and Banner, 1993). Of these processes, the mixing of deep-basin formation water and fresh recharge is known to occur in the Carrizo Formation (Kreitler, 1979).

The flow regime prevalent in the deeper Carrizo Formation is characterized by upward gradients and results in the outward expulsion of formation water (Galloway, 1984). Deep faults provide the conduits for their flow updip where they mix with descending, younger meteoric recharge.
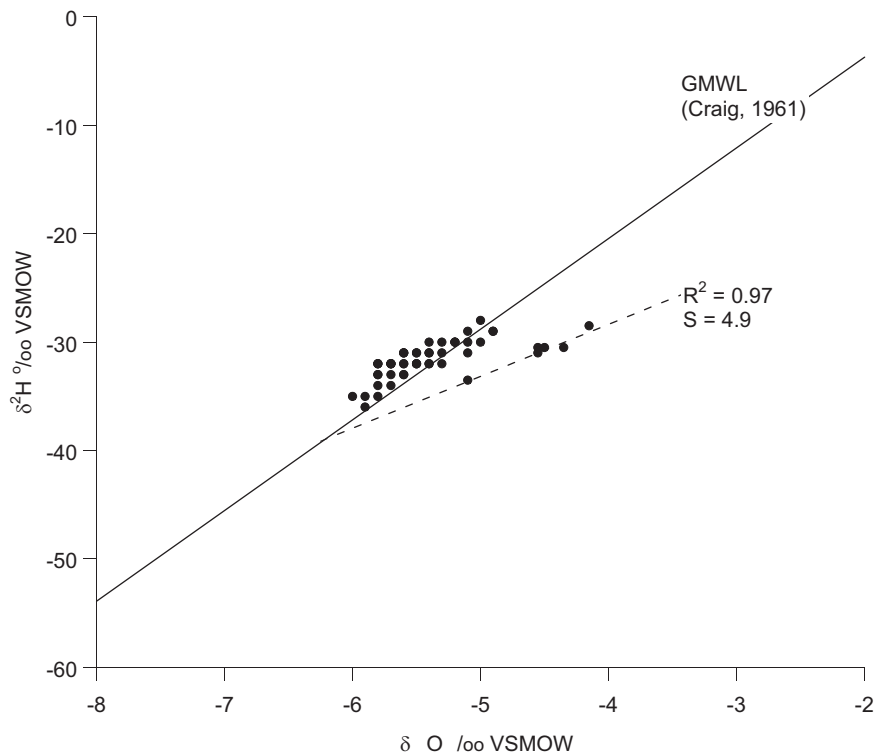
Figure 7-2. Plot of deuterium versus oxygen-18 values for the Carrizo-Wilcox Aquifer.
GMWL=global meteoric water line; VSMOW=Vienna standard mean ocean water; S=slope of the line of best fit; R^2=the coefficient of determination

8 Conclusions

The terrigenous strata composing the Carrizo-Wilcox Aquifer are an abundant source of groundwater for 60 Texas counties. Wells completed in the Carrizo-Wilcox Aquifer yield good quality groundwater with salinities ranging from fresh to slightly saline. As part of its statewide groundwater monitoring program for 2005 and 2006, we analyzed 331 Carrizo-Wilcox groundwater samples for major and minor ions, trace elements, and radionuclides. The chemical composition of most samples complied with primary and secondary drinking standards. Some of the samples, however, exceeded the state-prescribed limits for nitrate, lead, fluoride, chloride, sulfate, iron, manganese, and dissolved solids.

Stable and radiogenic isotope data indicate that groundwater ages in the Carrizo-Wilcox Aquifer increase down-gradient from the recharge area into the confined area and that most of the samples have a meteoric origin, with some deviations possible due to mixing with deep, connate water.

For the most part, salinity showed little change over time in wells from the northern and central sections of the Carrizo-Wilcox Aquifer, although some changes in salinity were noted in wells from the south. The changes were moderate, of no more than 100 milligrams per liter over the period of record, although more drastic fluctuations were observed at locations in Zavala, Dimmit, and Frio counties. Nitrate concentrations have been mostly within the potability limits.

9 Acknowledgments

10 References

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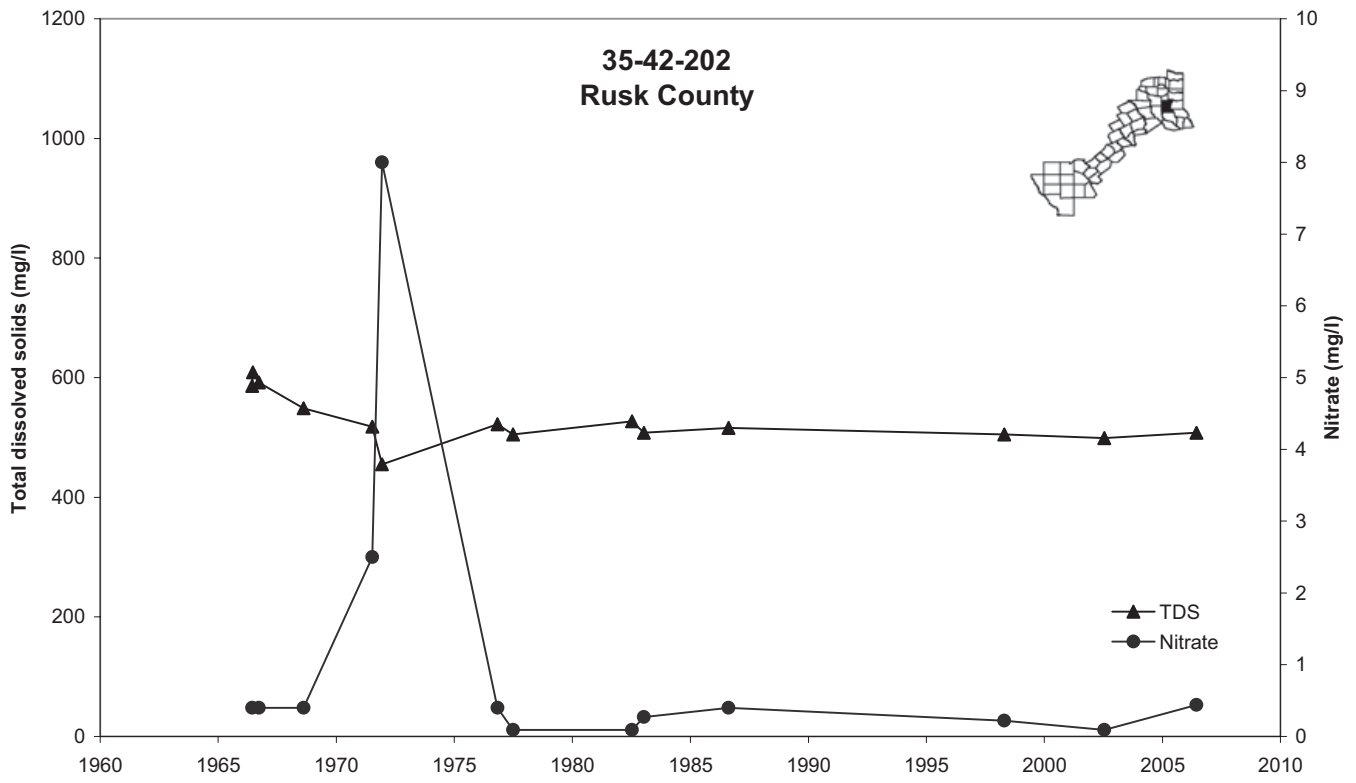
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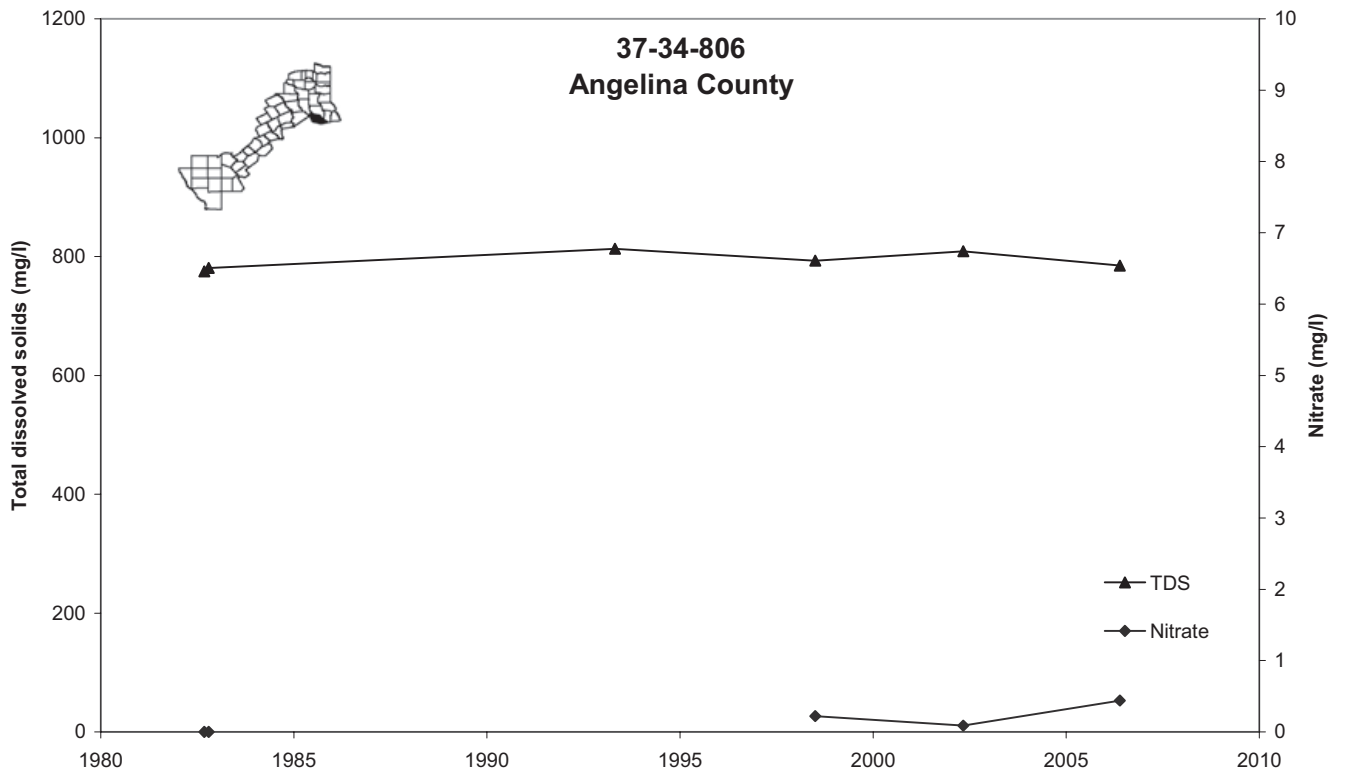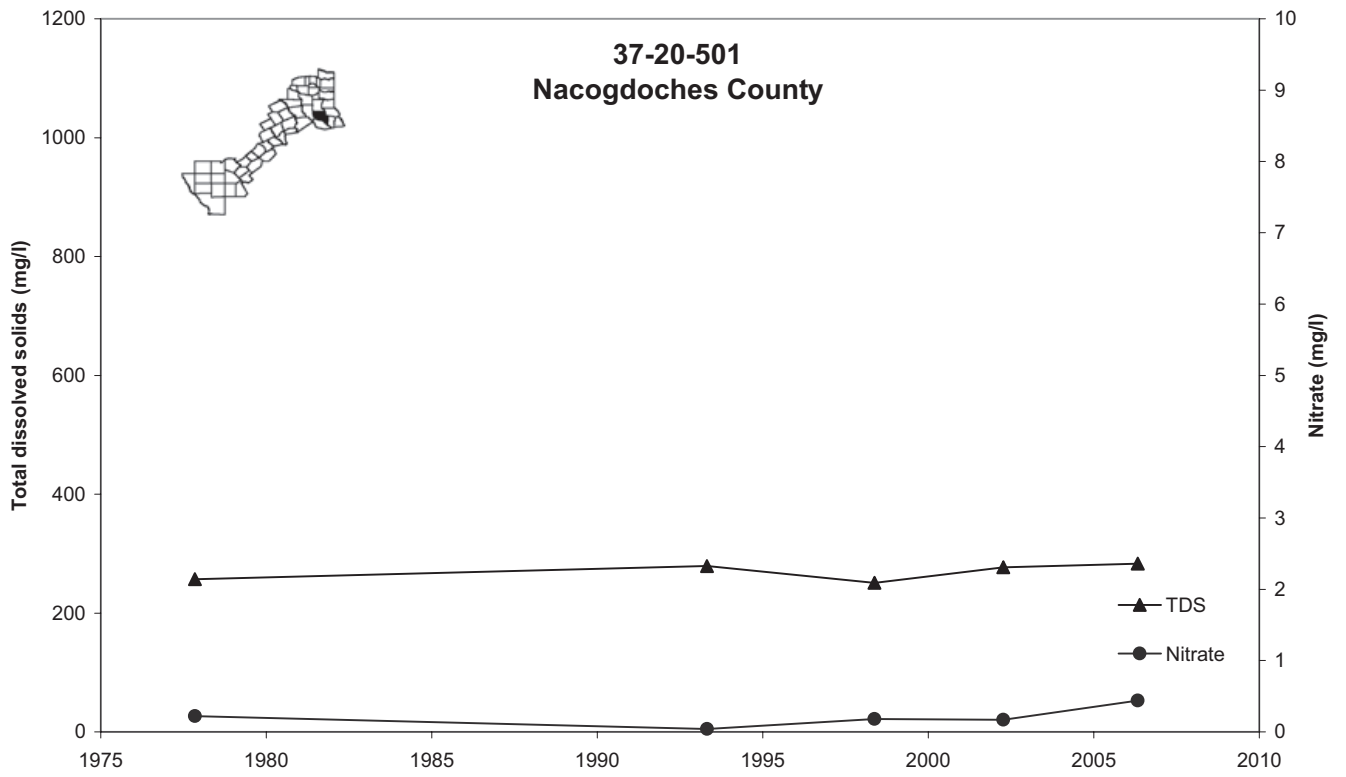
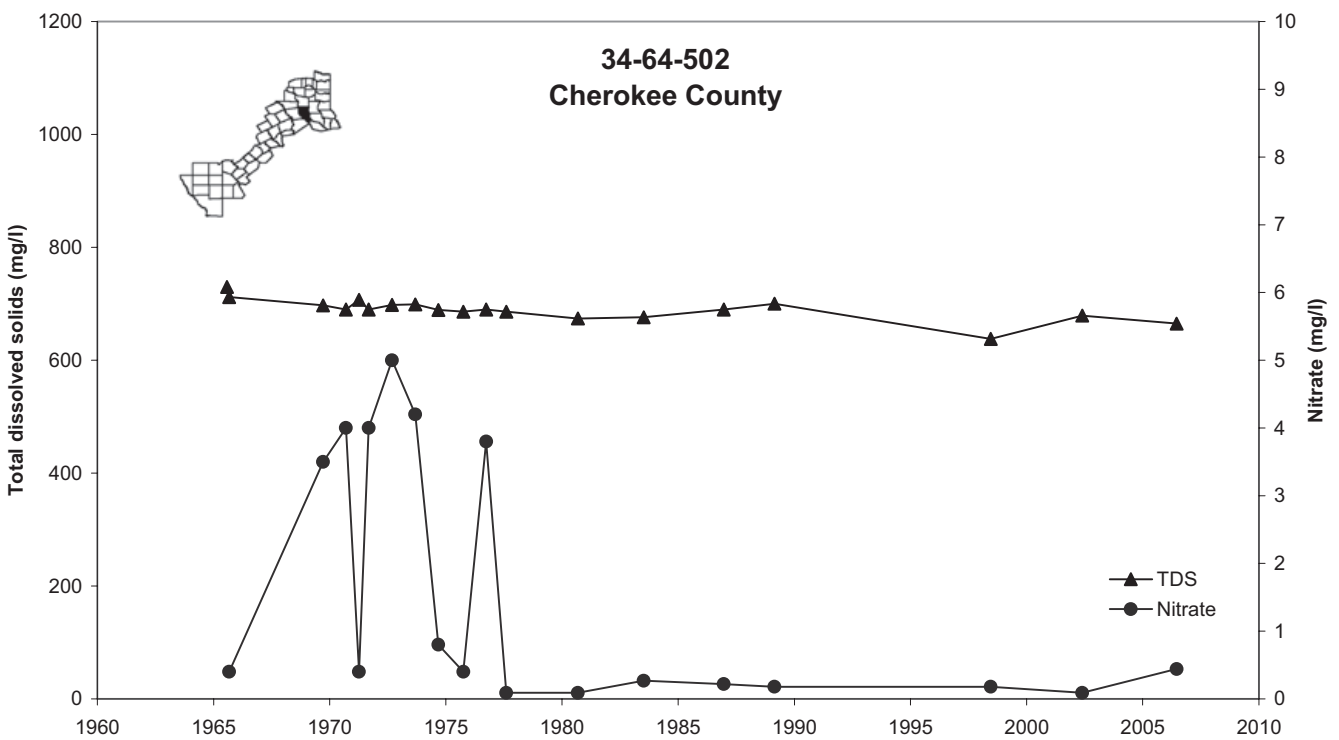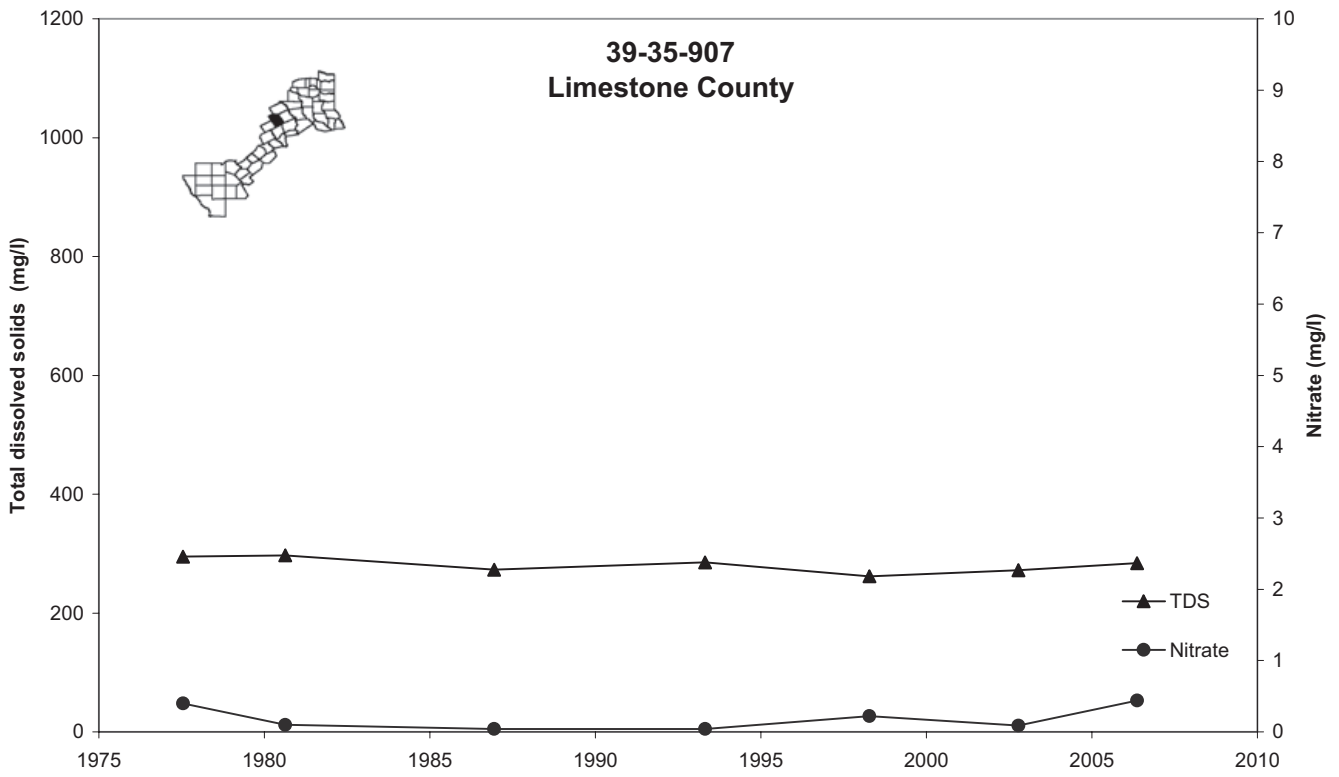TWDB Water Use Survey, http://www.twdb.state.tx.us/wushistorical/DesktopDefault.aspx?PageID=2.

APPENDIX

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16-54-403
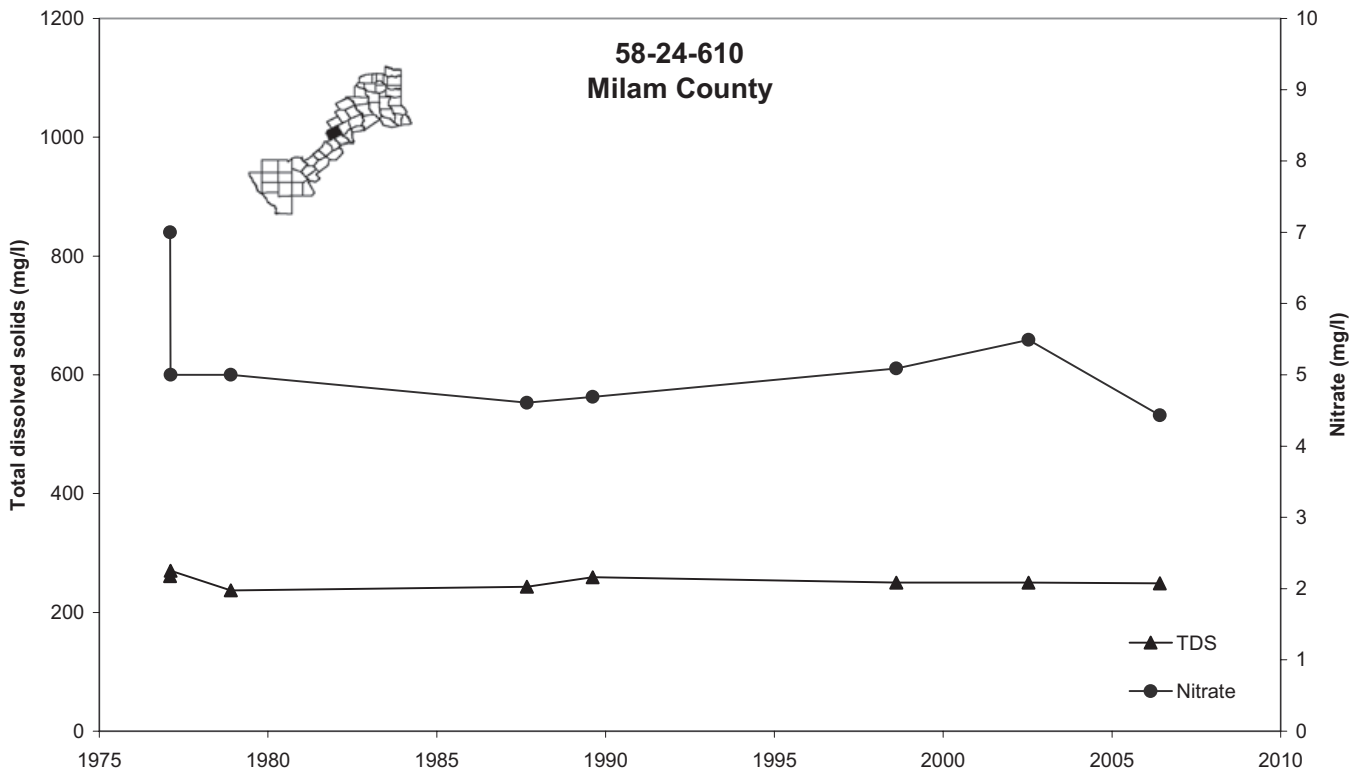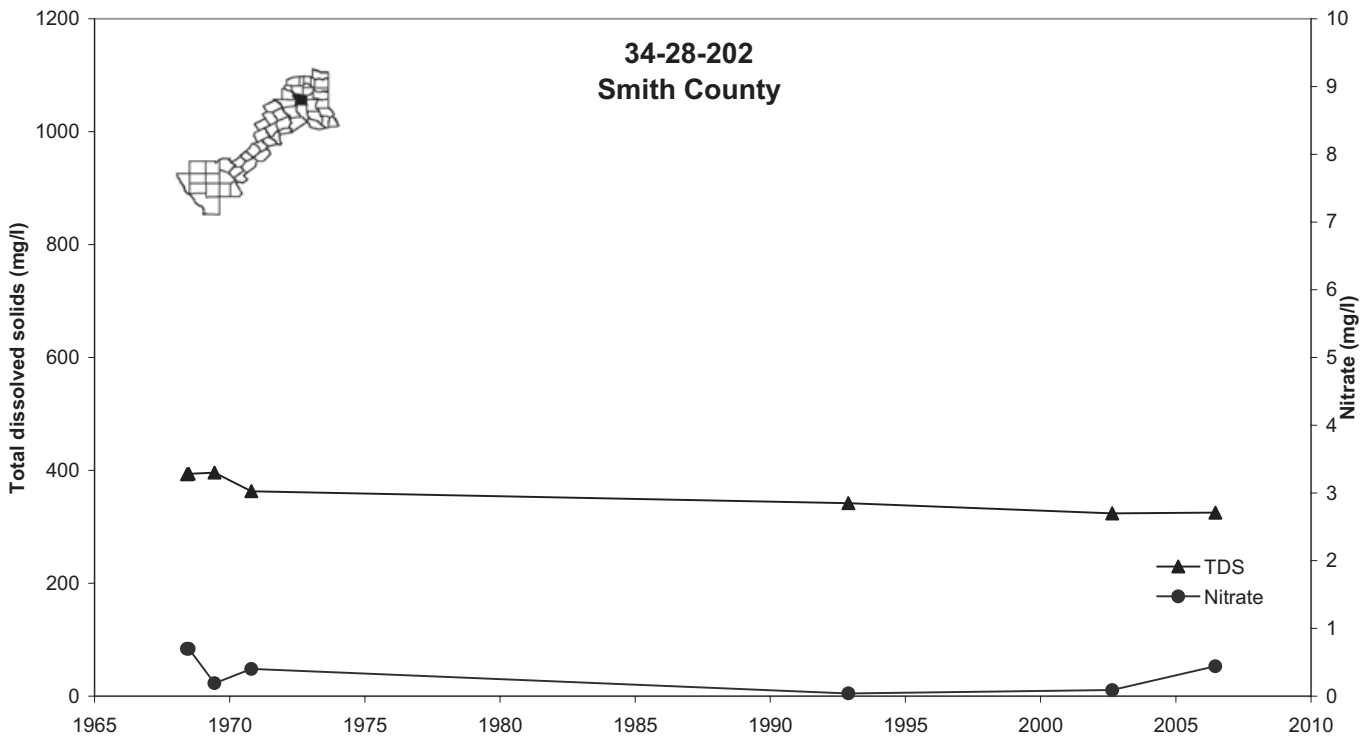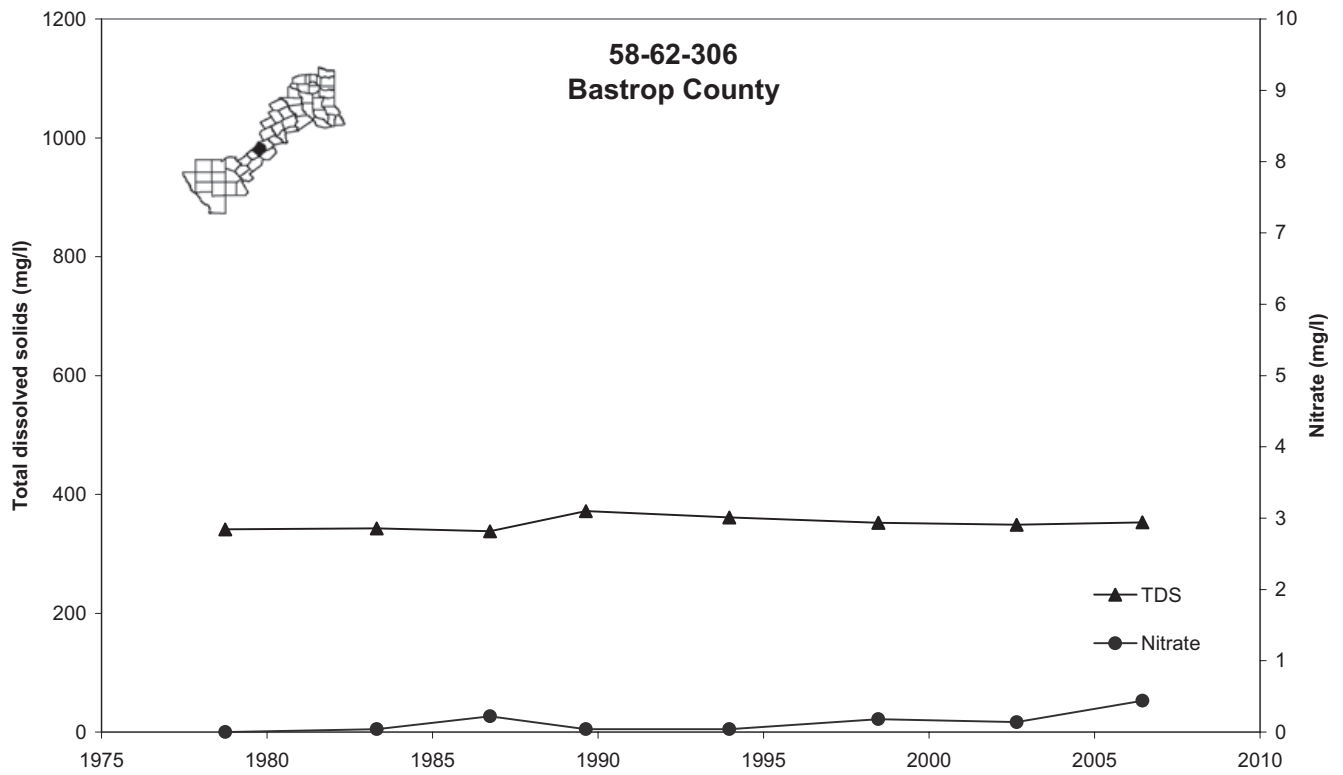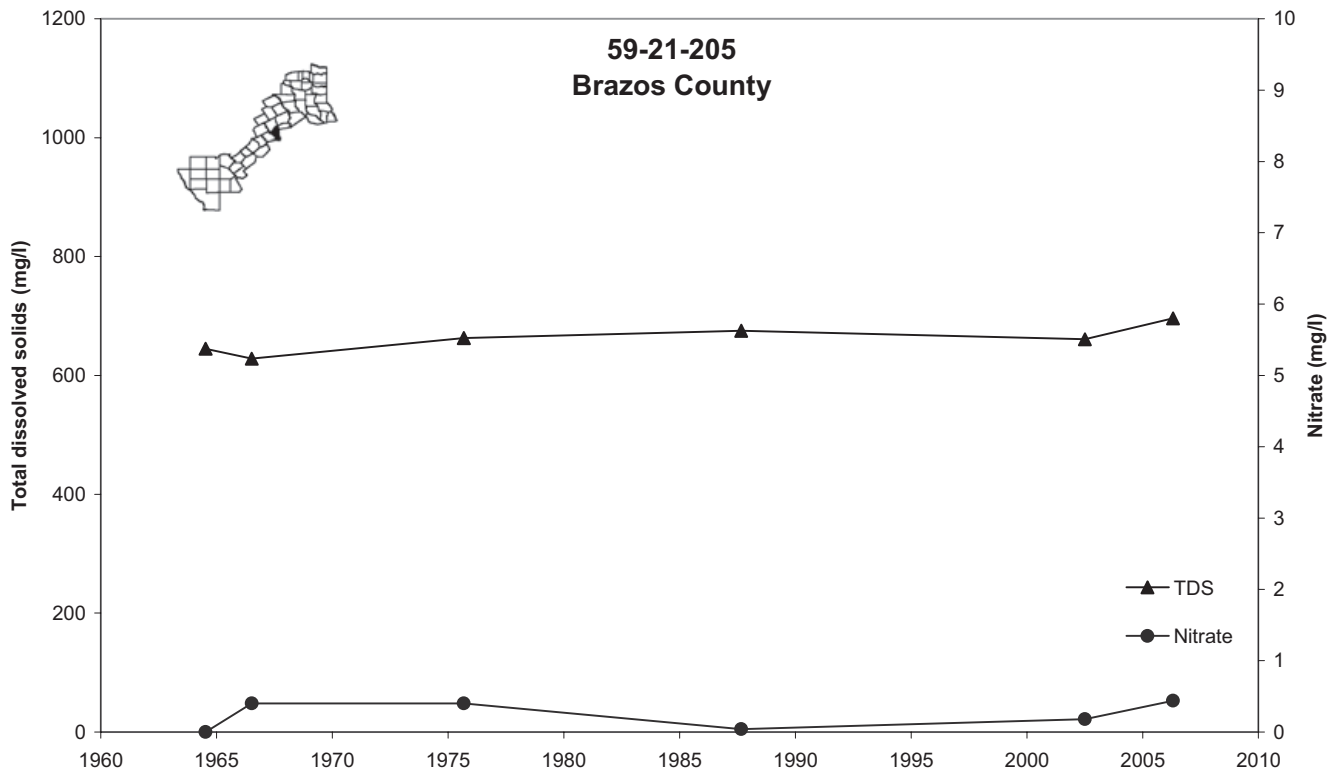## Cass County

17-56-417
Titus County
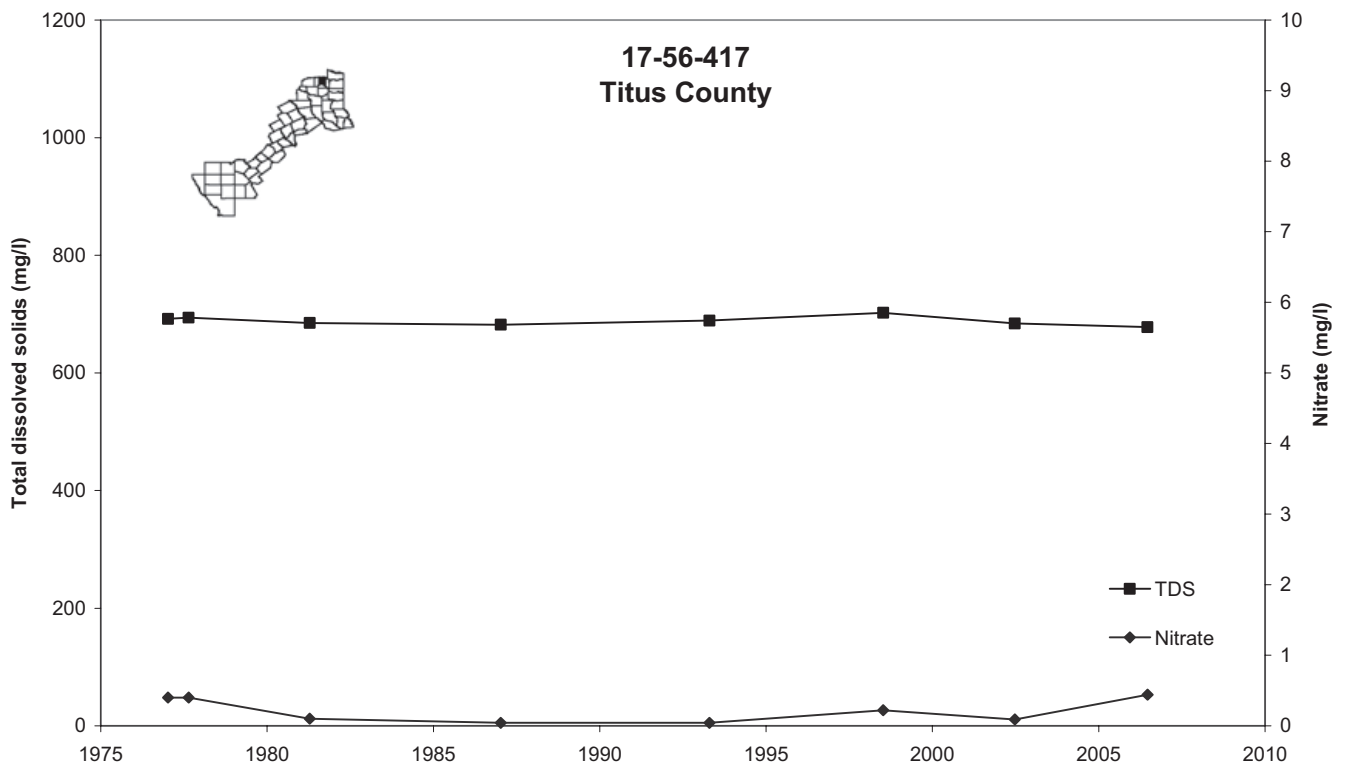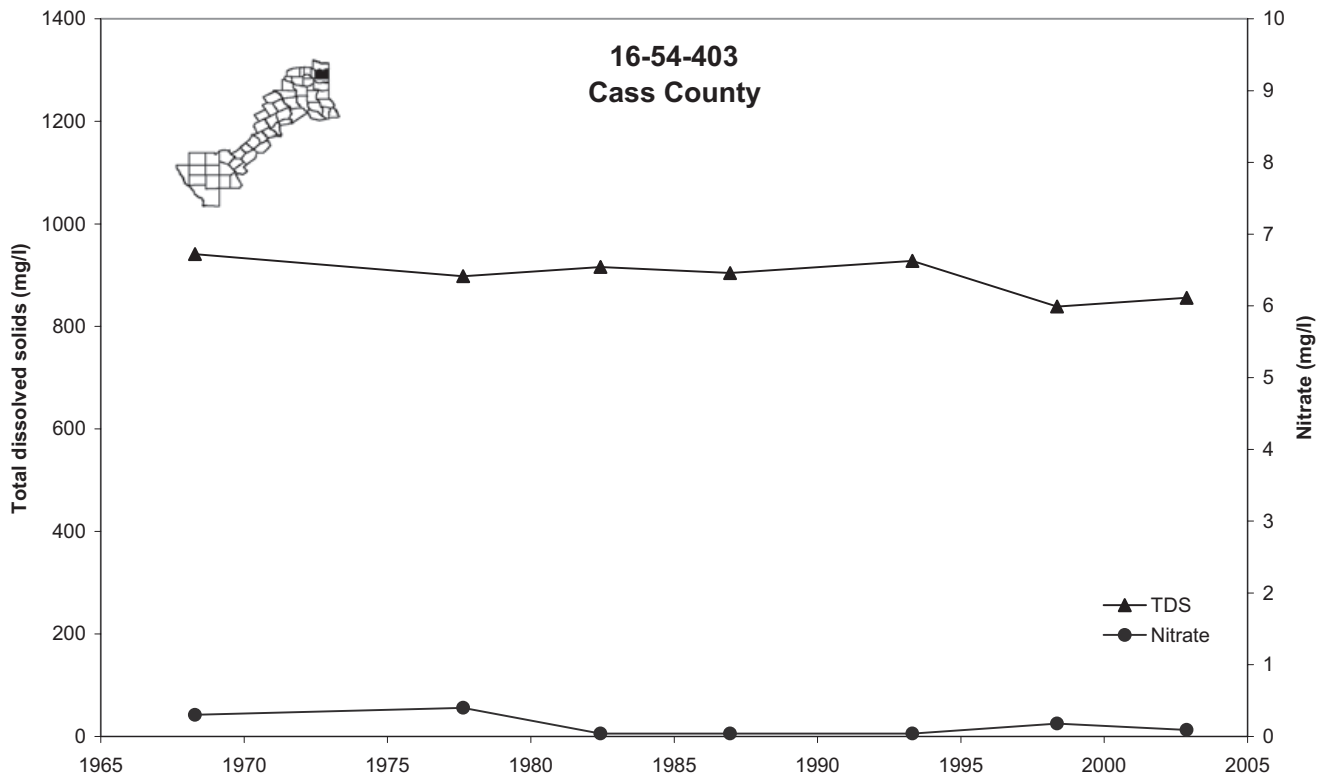
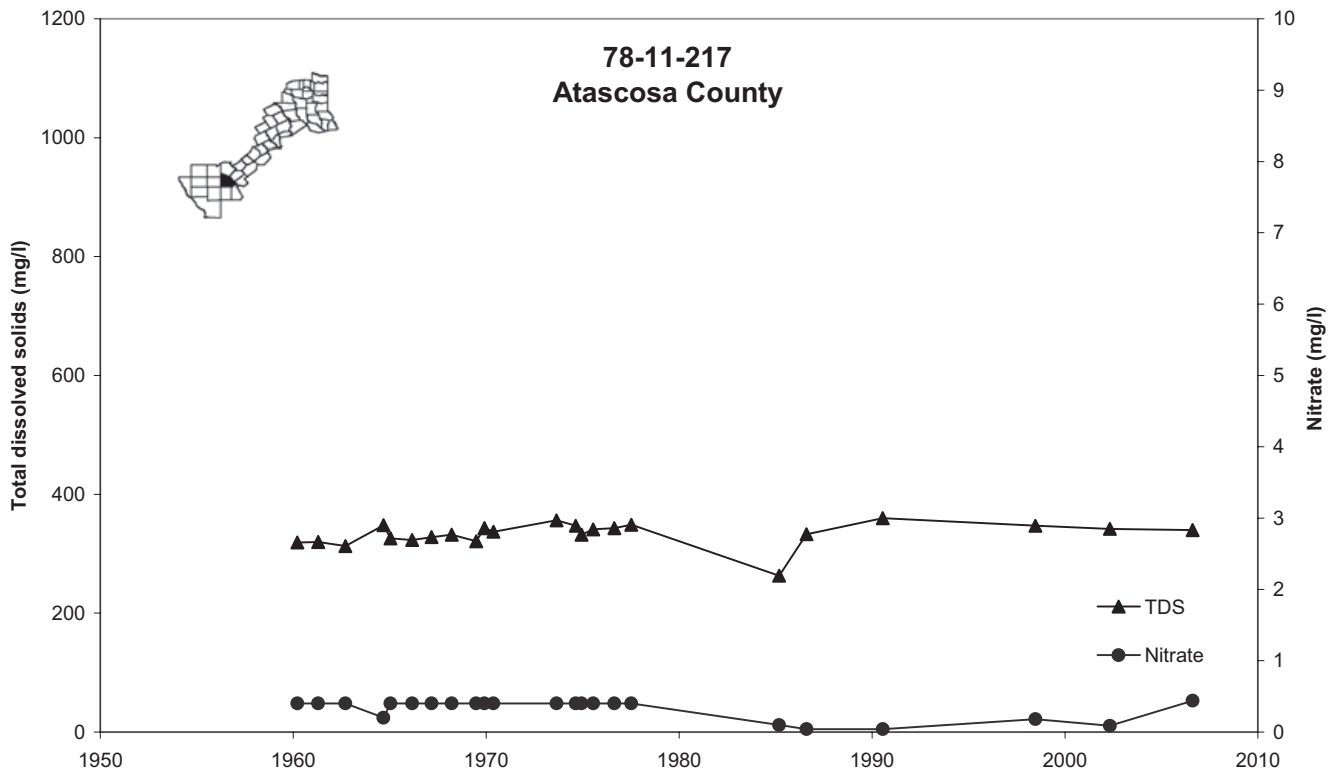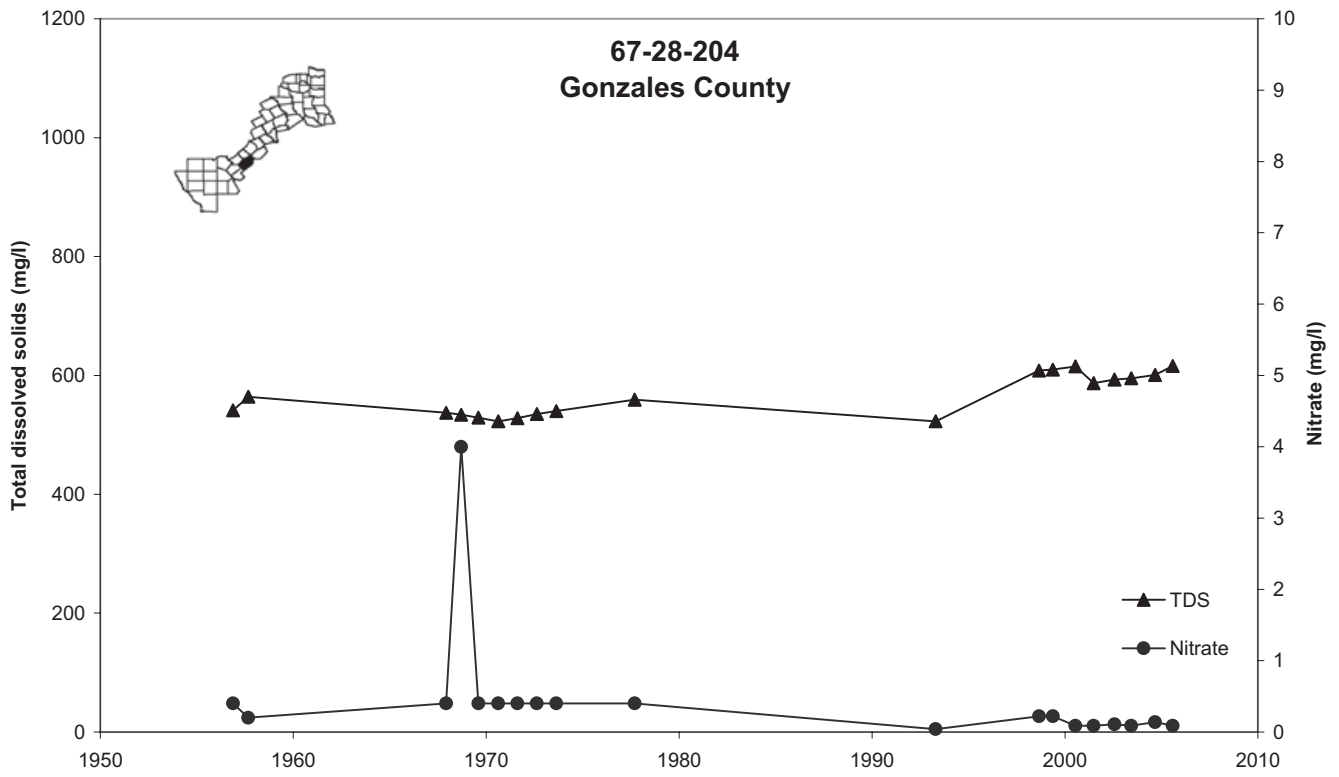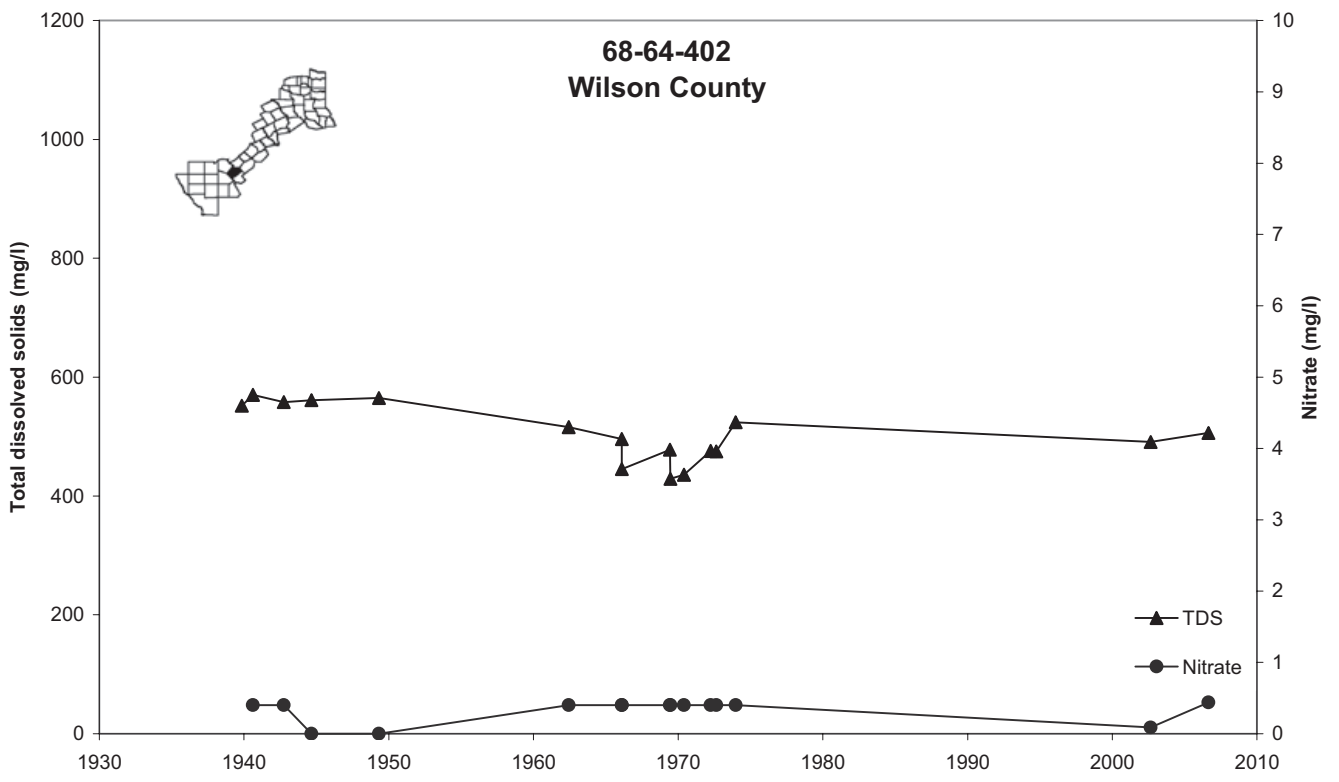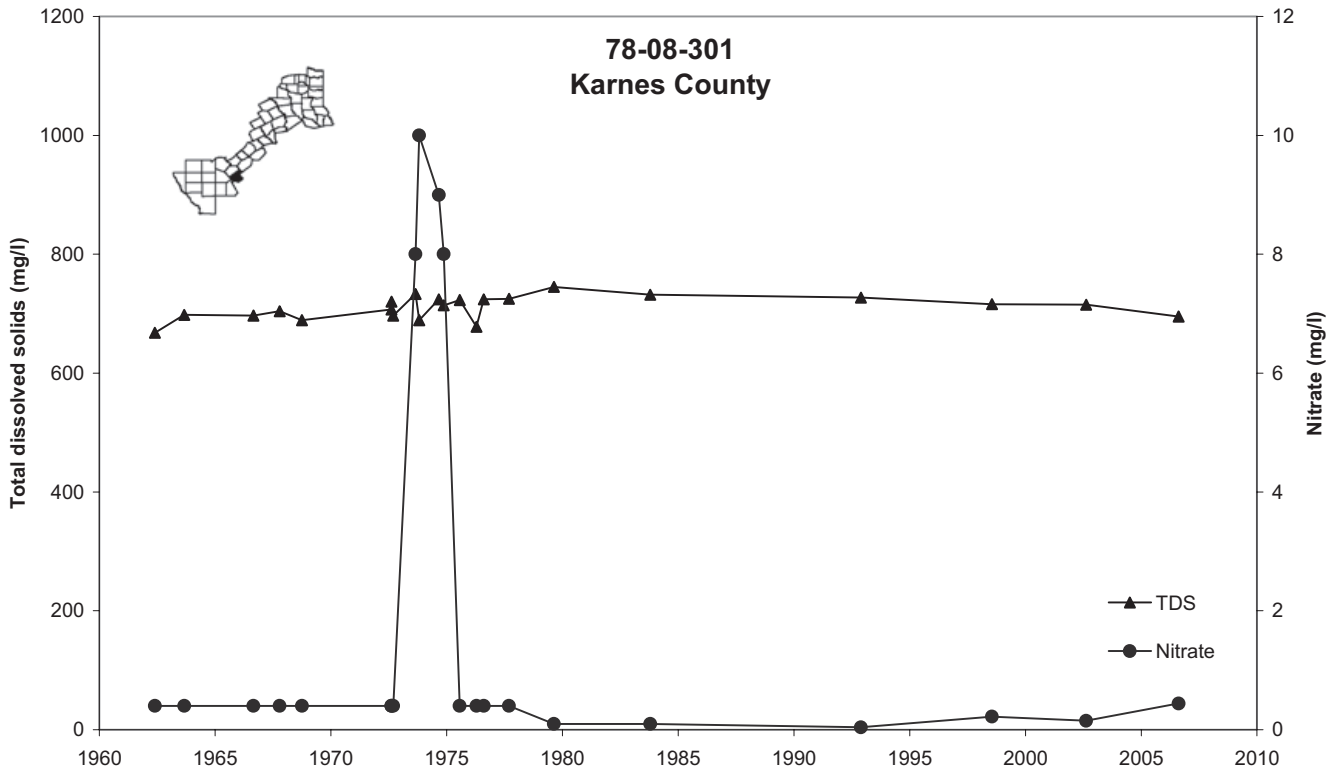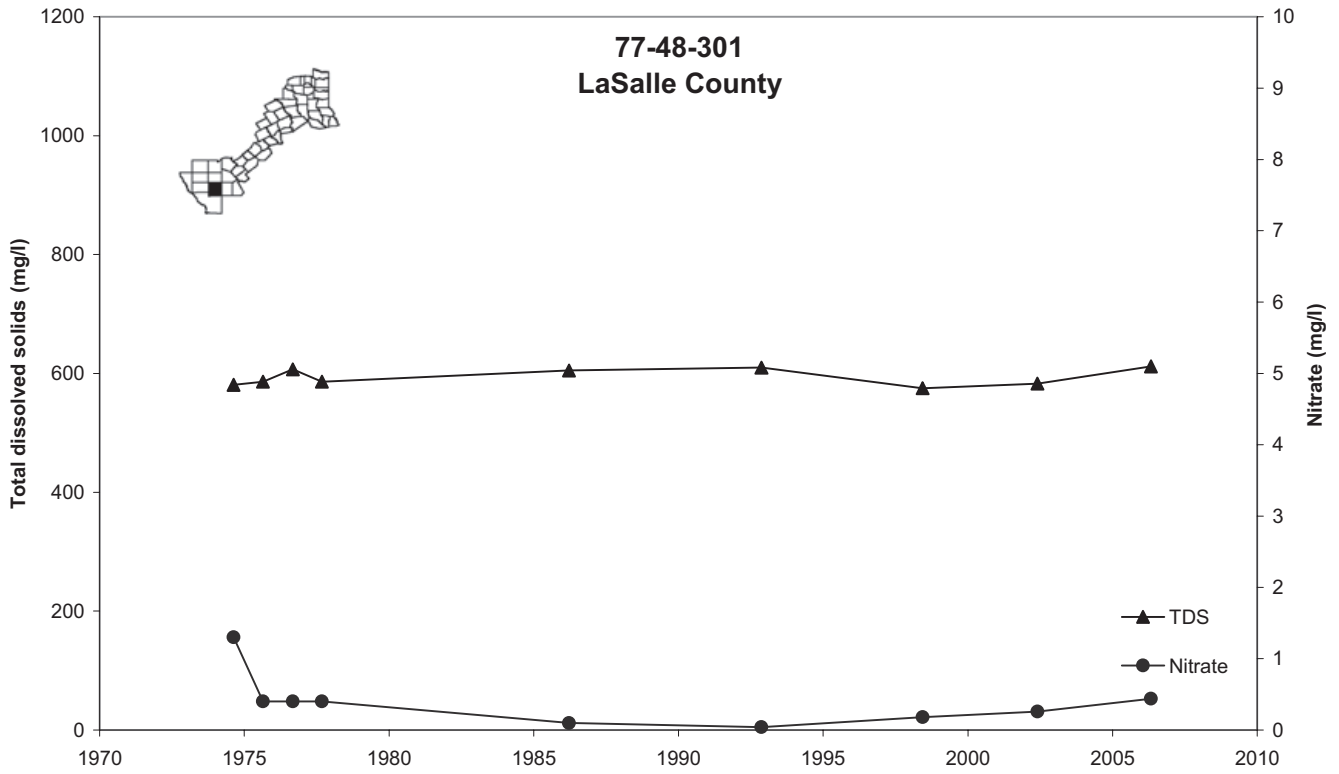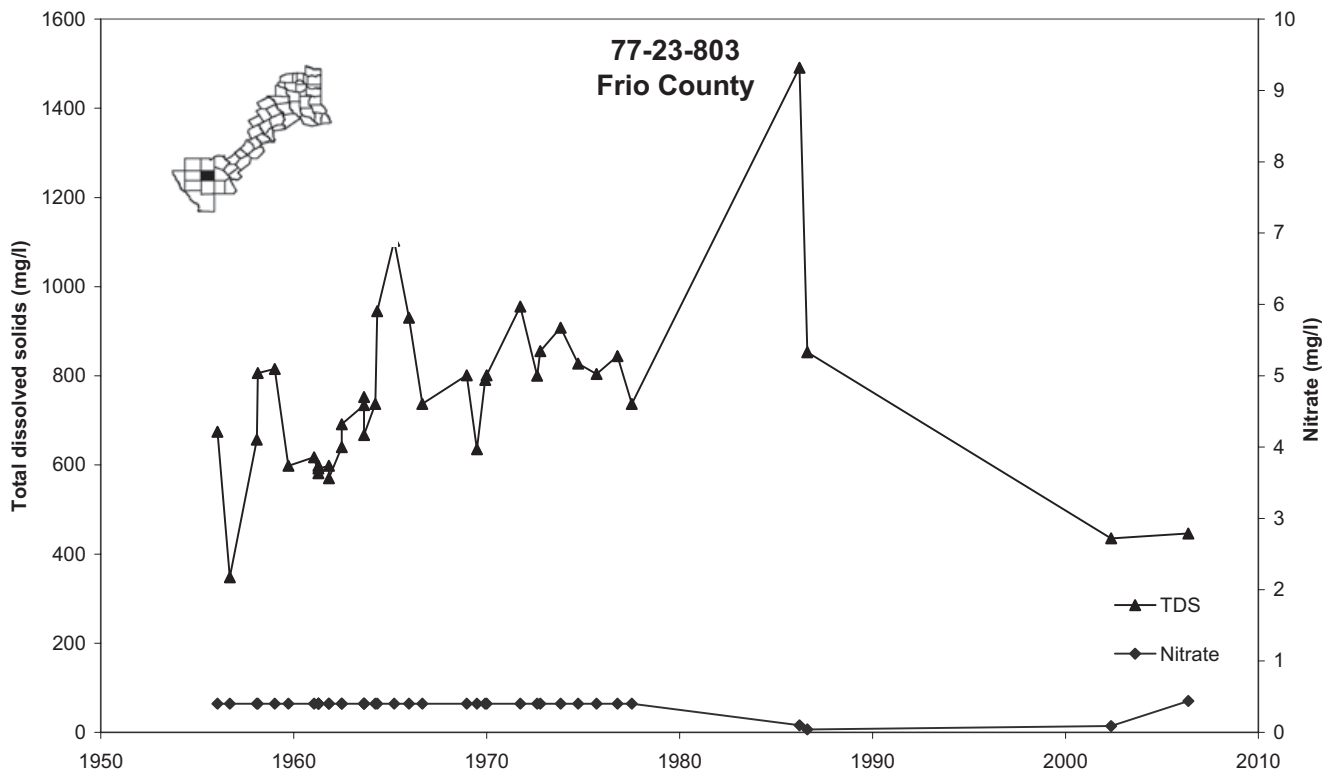Explanation: TDS=total dissolved solids; mg/l=milligrams per liter.

35-42-202
Rusk County

35-62-703
Panola County

37-20-501
Nacogdoches County

37-34-806
Angelina County

39-35-907
Limestone County

34-64-502
Cherokee County

34-28-202
Smith County

58-24-610
Milam County

59-21-205
Brazos County

58-62-306
Bastrop County

67-28-204
Gonzales County

78-11-217
Atascosa County

78-08-301
Karnes County

68-64-402
Wilson County

77-48-301
LaSalle County

77-02-403
Zavala County

77-35-802
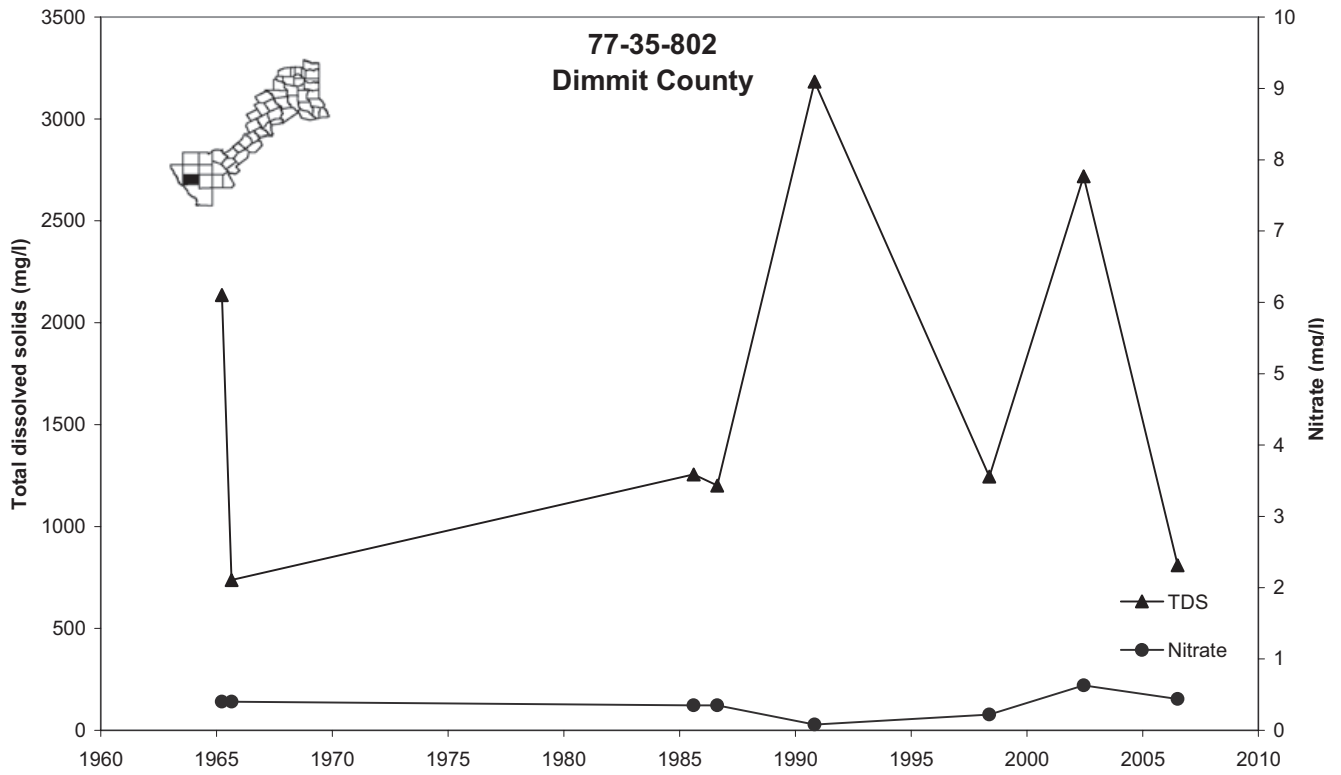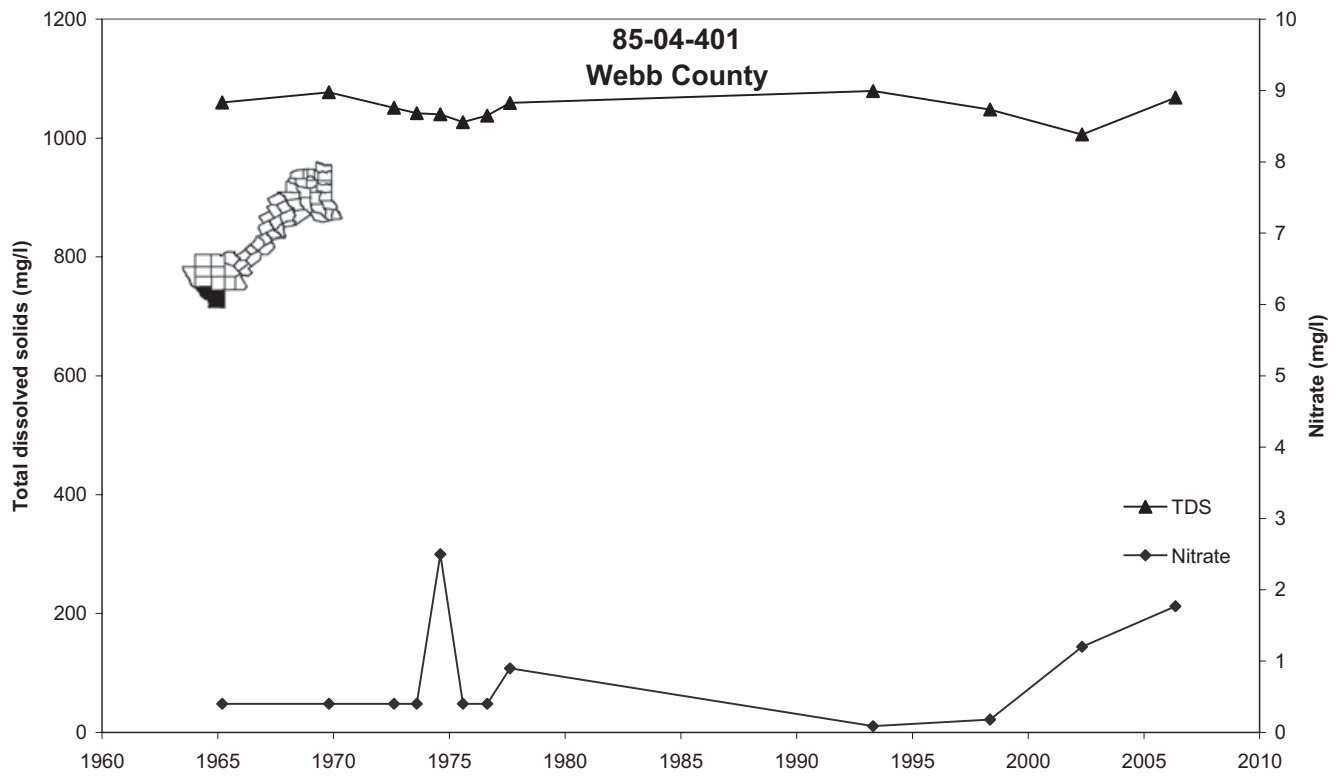Dimmit County

77-23-803
Frio County

85-04-401
Webb County

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