Hydrologic Atlas No. 6

# Water Quality in the Queen City Aquifer



by Eric Brown 1997

Texas Water Development Board

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### by Eric Brown, Environmental Quality Specialist

February 1997

#### **INTRODUCTION**

The Queen City aquifer covers all or parts of 38 counties from Cass County in northeast Texas southwestward to Frio and La Salle counties in south central Texas. The formation is composed of medium to fine sand and interbedded shale deposited during fluctuations of the Tertiary Gulf shoreline. It crops out extensively in northeast Texas, covering several counties; although as it extends southwestward, it decreases in width to roughly 10 miles or less. The map in Figure 1 illustrates the aquifer's outcrop, subsurface downdip portion, and location of sampled wells used in this atlas.



The aquifer dips to the southeast 100 to 150 feet per mile in the south to 15 feet per mile in the north. North of Anderson and Cherokee counties, the aquifer, present only in outcrop, is expressed by hilly terrain and sandy soil. Thickness across the formation ranges from less than 100 feet up to 800 feet, and from 1100 to 1400 feet in Frio and Atascosa counties. Small to moderate amounts of fresh to slightly saline water are available from most of the aquifer, with water becoming more saline farther downdip. High iron levels occur in wells completed in certain sand intervals, especially in the northeast.

Annual rainfall, the primary source of recharge, ranges from 24 inches in McMullen County to 46 inches in Cass County. Other sources of recharge include streams and lakes. Discharge occurs naturally through springs, seeps, evapotranspiration, and, when the formation is full, through streams and lakes. Artificial discharge occurs through wells, the majority being used for domestic use.

The Texas Water Development Board (TWDB) sampled 103 wells completed in the aquifer from 1990 through 1994 (88% in 1993). Of these 103 wells, 101 were entirely completed in the Queen City aquifer and the remaining two wells were dual completed. TWDB maintains an ongoing program to monitor the ambient water quality in major and minor aquifers throughout the state and any changes that may have occurred over time. The author thanks the landowners who permitted their wells to be sampled; the TWDB environmental quality specialists who collected the samples: John Asensio, Merrick Biri, Dennis Jones, Robbie Ozment, Randy Williams, Lennie Winkelman, and Eddie Zapata; and geologist Phil Nordstrom who edited the atlas. TWDB GIS specialist Marc Robichaud created the illustrations using ArcView. Special thanks to Janie Hopkins for editing and technical and creative

#### WATER QUALITY

Most wells completed in the Queen City aquifer are domestic (household use) in nature. This was reflected in the number of wells sampled: 58% were domestic, 17% were public water supply wells, and the remaining 25% were comprised of dewatering, industrial, irrigation, institutional, and stock wells. High yield and high use wells are preferred because they tend to provide a more representative sample, but wells of this type are not common in the study area. Regardless, environmental quality specialists took steps to ensure each well was producing a good sample either by making arrangements to have the well pumping on arrival, or by purging the casing and monitoring certain indicator parameters before drawing a sample. Environmental quality specialists take field measurements and use appropriate sampling techniques as described in the TWDB A Field Manual for Ground Water Sampling (Nordstrom and Beynon, 1991) for dissolved inorganic constituents, nutrients, and, for the first time in this aquifer, radioactivity. Constituent ranges and averages as determined by the Texas Department of Health Laboratory are discussed, and areas in which key constituents are in excess of maximum contaminant levels (MCLs) are illustrated in maps where appropriate. The primary and secondary MCLs, as set by the Texas Natural Resource Conservation Commission (TNRCC), are listed in Table 1.

Primary Constituent Levels				
Constituent	Symbol	MCL		
Arsenic	As	50 μg/l		
Barium	Ba	2,000 µg/l		
Cadmium	Cd	5 μg/l		
Chromium	Cr	100 µg/l		
Fluoride	F	4.0 mg/l		
Lead (EPA Lead Rule)	Pb	5 μg/l		
Mercury	Hg	2 µg/l		
Nitrate (as N)	NO <sub>3</sub> (N)	10.0 mg/l		
Selenium	Se	50 µg/l		
Gross Alpha	α	15 pCi/l		
Gross Beta	β	50 pCi/l		
Radium	$Ra^{226} + Ra^{228}$	5 pCi/l		
-	Secondary Constituent Levels			
Chloride	Cl	300 mg/l		
Copper	Cu	1000 µg/l		
Dissolved-Solids	TDS	1000 mg/l		
Fluoride	F	2.0 mg/l		
Iron	Fe	300 µg/l		
Manganese	Mn	50 µg/l		
pH	pH	≥ 7.0		
Silver	Ag	100 µg/l		
Sulfate	SO <sub>4</sub>	300 mg/l		
Zinc	Zn	5,000 μg/l		

#### **Field Measurement**

The ground water temperature of the Queen City samples ranged from 19° to 38°C and averaged 25°C. The average pH of all Queen City analyses was 7.3, the range was from 3.7 to 9.7, with 63% of the samples above 7.0. Secondary drinking water standards indicate that the pH should be greater than 7.0 because acidic water (less than 7.0) will act as a solvent to release metal ions to the water. The specific conductance ranged from 28 to 7,100 micromhos and averaged 708 micromhos. The average total alkalinity as determined in the field was 207 mg/l, with a range of 3 to 1,210 mg/l as CaCO<sub>3</sub>; average bicarbonate ion concentration, calculated from mean total alkalinity, was 251 mg/l; and average phenol alkalinity was 12.5 mg/l. The positive Eh average of 2.0 mV (range: -311 to +305 mV) indicates that the formation tends to have oxidizing conditions.

#### Dissolved Inorganic Constituents

The dissolved-solids content is the main factor limiting or determining the use of ground water. These solids primarily consist of mineral constituents dissolved from the host rock, although other natural sources such as adjacent aquifers or human-affected sources such as oil-field brines can also contribute certain dissolved constituents. Table 2 describes four classes of ground water classified according to dissolved-solids content, as defined by the Texas Ground Water Protection Committee.

Class	Quality *	Examples of Use
Fresh	0 - 1,000	Drinking and all other uses
Slightly Saline	>1,000 - 3,000	Drinking if fresh unavailable; for livestock, irrigation,
Moderately Saline	>3,000 - 10,000	and industrial use Industrial, mineral extraction, oil and gas production; potential/future drinking and limited livestock watering and irrigation if fresh or slightly saline water is unavailable
Very Saline to Brin	e >10,000	Mineral extraction, oil and gas production

\* Concentration range of dissolved-solids in milligrams/liter Table 2. Ground-water classification system.

Table 3 lists average concentrations and ranges of dissolved-solids and other inorganic constituents from the Queen City aquifer. The average for each constituent represents values above detection limits and does not include values below detection levels (flagged with "<").

Constituent	Average*	Range*	# Above MCL	% Below detection level
Bicarbonate	251	0.61 - 1,452	0	0%
Calcium	30	< 0.1 - 170	0	1%
Chloride	131	2.0 - 4,457	7**	0%
Diss. Solids	567	35 - 7,948	12**	0%
Fluoride	0.44	<.0.01 - 3.31	3**	16%
Hardness	110	0 - 705	0	0%
Magnesium	9.0	< 0.1 - 68	0	4%
Potassium	6.5	0.2 - 62	0	0%
Silica	23	10 - 92	0	0%
Sodium	163	1.3 - 2,960	0	0%
Strontium	0.75	< 0.01 - 5.35	0	7%
Sulfate	72	1.0 - 500	3**	0%

\* Expressed in milligrams/liter \*\* Secondary MCL Table 3. Major anions and cations in Queen City aquifer ground water.

The average dissolved-solids content of 567 mg/l reflects the normally fresh character of Queen City water. Of the 103 wells recently sampled, 12 wells had dissolved-solids levels above the secondary MCL of 1,000 mg/l. Ten of these wells were located in the southern portion of the aquifer (Fig. 2), but were not restricted to the downdip portion. Although three wells with the highest readings are far into downdip with depths exceeding 1,500 feet, the other wells are scattered both in the downdip and in the outcrop with depths ranging from 102 - 905 feet. The high dissolved-solids concentrations of the two wells located outside of this southernmost portion could be explained by well construction. The well in Robertson County is 860 feet deep and dual completed in the downdip portions of both the Queen City and the Carrizo-Wilcox aquifer. The well in Lee County is 1,330 feet deep, completed in the Queen City downdip, and screened from 1,277 to 1,329 feet.

Chloride, naturally dissolved from rocks and soils, can also be introduced into ground water by human activities, as it is present in sewage, oil-field brines, industrial brines, and seawater (a possible contaminant of fresh-water aquifers in areas of heavy pumpage). In large amounts in combination with sodium, chloride gives a salty taste to drinking water and can increase the corrosiveness of the water. Of the 1990 - 1994 samples, seven wells had chloride levels above the MCL of 300 mg/l (Fig. 2). A high chloride level usually coincides with high dissolved-solids content; all seven of these wells had corresponding dissolved-solids readings over 1,000 mg/l. As Figure 2 shows, poorer water quality is confined to the southernmost portion of the aquifer.



Sulfate is formed by the dissolution of sulfur from rocks and soils containing sulfur compounds such as gypsum, anhydrite, and iron sulfide. Sulfate in large amounts in combination with other ions gives drinking water a bitter taste. Three of the wells recently sampled contained sulfate in excess of the secondary MCL of 300 mg/l; all three in the southern portion of the aquifer (Fig. 2) also contained high dissolved-solids and/or chloride levels.

Fluoride is dissolved in small amounts from most rocks and soils. In drinking water it helps to inhibit tooth decay, but high levels can cause mottling of teeth. Fluoride concentrations throughout the entire aquifer were below primary MCLs, and only three wells exceeded secondary standards. These wells, located in the southern section, also contained high levels of dissolved-solids and/or chloride.

Major constituents of dissolved-solids in Queen City ground water are illustrated in Figure 3 with Stiff diagrams plotted for representative sampling of wells in the aquifer. Thin, nearly vertical lines typical in the northeast indicate low dissolved-solids. Larger diagrams with longer axes become more common to the southwest, indicative of increasing amounts of dissolved-solids. Magnesium and/or sodium are the dominant cations throughout, while bicarbonate is the dominant anion. However, a few analyses in which sulfate and chloride predominate occur in Wilson County southward.



Table 4 lists averages and ranges of dissolved trace metal constituents in the Queen City aquifer, for the most part detected in insignificant amounts. A majority of the analyses for several of the constituents were below lab detection levels. Two of these constituents, silver and vanadium, had 100% of the results below detection levels; cadmium, chromium, mercury, and molybdenum had all but one analysis below detection levels; and aluminum, arsenic, lead, and selenium all had 90% or more of their results below detection levels. *Please note*. Each average for the corresponding constituent reflects values above detection limits, that is, values that do not have a "<" sign. For constituents that have 90% or more of their results below detection limits, the actual number of samples averaged is in parentheses.

Constituent	Average*	Range*	# Above MCL	% Below detection level
Aluminum (3)	291	< 20 - 640	0	90%
Arsenic (12)	2.3	< 1 -10	0	90%
Barium	71	2.3 - 331	0	0%
Boron	690	< 0.2 - 3,490	0	14%
Cadmium (1)	8.0	< 2 - 10	1	98%
Chromium (1)	4.6	< 4 - 20	0	98%
Copper	14.5	< 2 - 119	0	64%
Iron	722	< 4 - 13,700	23**	2%
Lead (3)	24	< 5 - 50	3	97%
Manganese	36	< 0.5 - 270	20**	18%
Mercury (1)	0.14	< 0.13 - 0.2	0	98%
Molybdenum(1)	24	< 20 - 50	0	97%
Selenium (3)	21	< 2 - 43	0	94%
Silver	NA	NA	0	100%
Vanadium	NA	NA	0	100%
Zinc	102	< 5 - 1,670	0	24%
* Expressed in mic	rograms/liter	(uø/l)		

Expressed in micrograms/liter (µg/1) \*\* Secondary MCL

Table 4. Dissolved trace metal constituents in Queen City ground water.

Boron is a minor constituent in most natural waters. Although it has no drinking water standard, its concentration in ground water is important because it determines the suitability of the water for irrigation. Concentrations as high as 1,000  $\mu$ g/l are permissible for irrigation of boron-sensitive crops such as deciduous fruit and nut trees; as high as 2,000 µg/l for irrigation of semi-tolerant crops such as most grains, cotton, and potatoes; and as much as 3,000 µg/l for tolerant crops such as alfalfa and most root vegetables. Only six wells, widely scattered across the entire aquifer, contained boron in excess of 1,000

Cadmium is a rare mineral that occurs naturally at low levels in rocks, coal, and oil. It can enter ground water from these sources but also from industrial and mining operations and landfills. Cadmium was found in excess of the primary MCL of 5  $\mu$ g/l in only one 42-foot deep well in Henderson County.

Iron, dissolved from rocks and soils, occurs naturally at low levels in ground water. Higher levels can often be traced to iron casing and other equipment used in well construction, or attributed to natural causes depending on the geology of the water-bearing formations. Several previous studies have found that iron can be a problem in certain sand intervals, mainly in wells completed between depths of 50 to 200 feet in the northeastern part of the aquifer (outcrop region). Manganese, found naturally in ground water, and typically at low levels, can also occur naturally at high levels, often in conjunction with high iron levels. Figure 4 illustrates well locations where iron and manganese exceeded their secondary contaminant levels of 300 µg/l and 50 µg/l, respectively. Some wells exceeded only the iron secondary MCL and some only the manganese secondary MCL; these wells are marked with different symbols in Figure 4. The locations of wells with high levels are widespread, but tend to be confined to either the northernmost or southernmost portion of the aquifer.



Lead is a rare element and is widely dispersed in sedimentary rocks and metallic ores. High levels can usually be traced to lead plumbing or industrial wastes. Elevated lead levels have also been traced to new submersible pumps with brass components. Three wells had concentrations over the primary MCL (for source water) of 5  $\mu$ g/l. Well records do not specifically indicate the use of lead pipe in the construction of these wells, but all three are similar in certain aspects: depths are less than 90 feet and casings are brick or concrete tile. The well with the highest reading (40  $\mu$ g/l) was drilled in 1910 to a depth of 16 feet.

Of the five nutrients analyzed in each well, only nitrate and nitrite have drinking water standards. Nitrate, an end product of the aerobic stabilization of nitrogen, particularly organic nitrogen, is a potential pollutant in any agricultural area. It is to be expected at high concentrations where fertilizers are used and in decayed animal and vegetable matter. Ground water concentrations are also commonly higher in leachates from sludge and refuse disposal and in industrial discharges. Nitrite, formed by the action of bacteria upon ammonia and organic nitrogen, when detected in potable water in considerable amounts, is an indication of sewage/bacterial contamination and inadequate disinfection (De Zuane, 1990). In such reducing environments, nitrite is not oxidized to nitrate. However, in the oxidizing environments common in most aquifers, nitrites are converted into nitrates, and their values are lower. In this study, one well was found to contain nitrate (as N) in excess of the MCL of 10 mg/l, with a reading of 21.84 mg/l. Nitrate problems are usually associated with shallow wells easily contaminated by seepage from stock pens or irrigation runoff. This particular well is shallow (66'), concrete cased, and located next to a barn. It is primarily used for house water but also for stock.

Constituent	Average *	Range *	# Above MCL	% Below detection level
Ammonia	0.45	< 0.02 - 3.0	0	16%
Nitrite	0.02	< 0.01 - 0.03	0	92%
Nitrate (as N)	1.03	< 0.01 - 21.84	1	20%
Kjeldahl	0.65	< 0.01 - 4.0	0	11%
Orthophosphate	0.07	< 0.01 - 0.18	0	28%

\* Expressed in milligrams/liter Table 5. Dissolved nutrients in Queen City ground water.

#### Radioactivity

Gross alpha ( $\alpha$ ) is the total radioactivity, measured in units of picocuries per liter (pCi/l), due to alpha particle emission. Alpha-emitting isotopes in natural waters are primarily isotopes of radium-226 and radium-228 and usually occur in deep aquifers or in areas affected by uranium or phosphate mining. Gross beta ( $\alpha$ ) radiation is the total radioactivity due to beta particle emission. Natural  $\alpha$ -emitting isotopes occur in the uranium and thorium disintegration series, among other natural sources. Radium is derived from igneous rocks such as granites, uranium ores, certain shales and sandstones, and volcanic rocks. The dominant radium isotopes found and detected in natural waters are radium-226 and radium-228. In these analyses, none of the samples exceeded primary MCLs for gross alpha and gross beta. Only four samples were tested for radium, two below detection limits and two with actual levels, 1.20 pCi/l and 1.70 pCi/l.

Constituent	Average *	Range *	# Above MCL	% Below detection level
Gross alpha	4.21	< 2.0 - 10	0	80%
Gross beta	8.56	< 3 - 20	0	64%
Radium (2)	1.45	1.2 - < 2.0	0	50%

Expressed in picocuries/liter Table 6. Radioactivity in Queen City ground water.

#### **COMPARISON TO PREVIOUS WORK**

A brief review of past studies show findings similar to those in this report. In the northeastern portion of the aquifer, water-quality problems were not widespread, with the exception of high iron levels, depending on the depths the wells were screened. Broom (1971) reported that all Tertiary sediments in Northeast Texas typically have high iron contents in an intermediate depth zone of 50-200 feet. In Cass and Marion counties, high iron levels were found in wells from 50 to 200 feet deep, and in Gregg and Upshur counties in wells between 100 and 200 feet deep (Broom, 1969). Preston and Moore (1991) reported high iron levels within some sand intervals in Angelina, Cherokee, Gregg, Nacogdoches, Rusk, and Smith counties.

Guyton and Associates (1972) found water from the Queen City aquifer to be relatively low in dissolved solids in Anderson, Cherokee, Freestone, and Henderson counties. Preston and Moore (1991) reported that water at depths greater than 600 feet and in the downdip portion of the aquifer is rarely fresh (less than 1,000 mg/l dissolved solids). In Cass and Marion counties, high nitrate levels were localized in nature and restricted to shallow wells (Broom, 1971).

Farther southwest, the only widespread water-quality problem was high chloride and dissolved- solids, although Anders (1957) states that high iron is a problem in the Queen City aquifer in Wilson County. Here, water available in and near the outcrop was fresh, but increased in dissolved-solids content farther downdip because of decreased permeability (Anders, 1957). In 1965, 83% of water samples in Gonzales County met standards for drinking water, although the author noted that at depths below 500 feet, water becomes more saline and unsuitable for drinking and eventually for irrigation (Shafer, 1965). In Atascosa and Frio counties, Alexander and White (1966) found better water quality in the lower part of the Queen City where sands are thicker (well depths 485 to 2185 feet). In the upper sands, dissolvedsolids ranged from 662 mg/l to 1891 mg/l, and the water was classified as very hard. McCoy (1991) reported that most of the water from the Queen City in McMullen and La Salle counties exceeded drinking water standards for several constituents.

Historical data taken from balanced analyses in the TWDB ground-water database were examined to assess water-quality changes over time. Query language was used to calculate averages of chloride, dissolved-solids, fluoride, hardness, nitrate, and sulfate during the last five decades and the present partial decade (Table 7). Because of variations in the natural water quality of the Queen City aquifer, the coverage area was divided into three regions: northern (Cass County to Madison County), middle (Robertson County to Gonzales County), and southern (Wilson County south). Averages do not reflect the same sample population for each time period; although the same wells were often sampled more than one decade, few were sampled in more than two. Furthermore, the choice of decades as the time period most appropriate for the calculation of averages is arbitrary, as sampling events were not timed to correspond with any certain time period.

Constituent	1950 - 1959	1960 - 1969	1970 - 1979	1980 - 1989	1990 - 1994
		North	ern		
Chloride	19	26	23	24	23
Dissolved-Solids	183	236	205	208	224
Fluoride	0.12	0.25	0.16	0.18	0.18
Hardness	92	73	77	61	60
Nitrate	0.01	0.79	1.59	1.46	1.5
Sulfate	34	46	27	25	29
		Midd	lle		
Chloride	115	85	103	66	70
Dissolved-Solids	654	584	626	576	322
Fluoride	0.16	0.29	0.35	0.33	0.3
Hardness	227	176	198	150	137
Nitrate	0.05	0.17	0.25	0.14	0.03
Sulfate	214	137	148	138	98
		South	ern		
Chloride	395	149	459	401	486
Dissolved-Solids	1,352	745	1,481	1,559	1,481
Fluoride	0.5	0.6	0.8	1.31	1.00
Hardness	104	79	322	139	212
Nitrate	0.04	0.02	0.06	0.05	0.06
Sulfate	120	63	229	204	161

Table 7. Comparison of averages of dissolved constituents in the Queen City aquifer



Of these six parameters, none show any clear increasing trends in any of the three regions. Some, however, appear to be improving over time. These trends could possibly be explained by collection, sampling, transportation, and testing methods. Before 1989, wells were sampled without specific guidelines, therefore, reliability of collection and transportation methods are questionable in some cases. In addition, sampling and testing techniques have improved over the decades, and the purpose of the TWDB monitoring program has broadened in scope to include a representative sampling of wells throughout the entire aquifer.

Figures 5, 6, and 7 illustrate historical regional differences in water quality. Query language was used to select wells that have exceeded standards for dissolved-solids, chloride, and sulfate since samples were first taken in 1936. All three maps, especially dissolved-solids and chloride, confirm that water quality tends to be worse in the middle and southern sections of the aquifer.

Another way of assessing change in water quality over time is by examining analyses from wells sampled more than once. Wells sampled four or more times, from each region, were examined and trends found were similar to ones presented in Table 7. Constituent values remained constant, with some wells improving consistently over time. Again, this is most likely explained by improved sampling methods.

### CONCLUSIONS

The overall water quality of the Queen City aquifer is good. No constituents with primary standards exceeded MCLs in a widespread manner. Only five wells exceeded a particular primary standard: one well was over the cadmium MCL, three wells were over the lead standard, and one well was over the nitrate MCL. These excess values are more likely the result of well placement, construction, completion, depth, point source pollution, and/or unknown causes (old landfills) rather than a reflection of overall ambient water quality of the Queen City. For example, all five of these wells are shallow, less than 100 feet deep.

Problems with the water quality in the Queen City aquifer relate to secondary standards. Iron and manganese are found in excess of their secondary standards over the entire extent of the aquifer. Dissolved-solids and chloride appear to be a regional problem in the southernmost portion of the aquifer. All together, the southern portion of the aquifer has the worst water quality. Wells in this area not only contain high dissolved-solids, chloride, iron, and manganese, but several also contain high levels of sulfate and fluoride.



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