Chapter 3

Hydrochemical Variability in the Edwards-Trinity Aquifer System, Edwards Plateau, Texas

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Introduction

The Edwards-Trinity aquifer system (Plateau system) (Figure 3-1) of the Edwards Plateau (Plateau) is one of the major aquifer systems in Texas (Ashworth and Hopkins, 1995). Although the Plateau is presently sparsely populated over most of its extent, human and non-human residents depend on its groundwater. In modern times more people have began moving onto the Plateau as urban areas expand and as some of the population have sought residences and established businesses away from cities that are located about the Plateau periphery (for example, San Angelo and Midland). Water-intensive industries like ranching and agriculture constitute a large part of the economic base in the region. Plateau water quality is critically important and a thoroughly analyzed comprehensive hydrochemical database is indispensable to responsible resource management.

This report summarizes basic geologic data that effect groundwater quality, hydrochemical data from the aquifer system, information on the chemical quality of precipitation, and several important aspects of rock/water interactions that can be used not only to evaluate water quality, but also can be used to identify environmentally sensitive major recharge areas. The hydrochemical data is provided by the Texas Water Development Board (TWDB) and is high quality, based on charge-balance calculations. For the Antlers aquifer 67.5 percent of analyses have less than a 1 percent error; 91.9 percent have less than a 2 percent error; 99.4 percent have less than 5 percent error. For the Edwards aquifer 70.9 percent of analyses have less than a 1 percent error; 92.3 percent have less than a 2 percent error; and 98.8 percent have less than a 5 percent error. Although much basic chemical information is available for the Plateau aquifer system, analysis of that data is not highly evolved.

Three different strategies are used to produce groundwater on the Plateau that depend on well location (Figure 3-2). In the south and southeastern one-half of the Plateau, wells are

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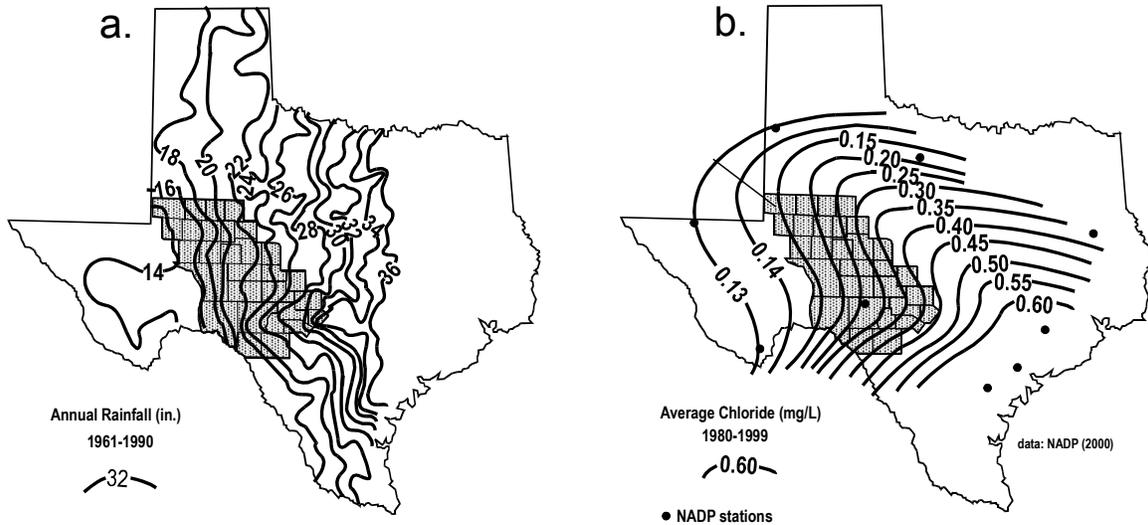
Figure 3-1:   Maps showing statewide distribution of (a) mean annual rainfall (data from Bomar, 1995) and (b) mean wet deposition of chloride (data from NADP, 2003). Stippled area is Plateau aquifer system study area.

completed in the Edwards aquifer. In the north and northwest one-quarter of the area, wells are completed mainly in the Antlers aquifer. In the intervening area, many wells are completed in both aquifers (dual completions). These different completion intervals reflect the water levels relative to the production intervals. Aquifer mineral and hydrochemical composition significantly distinguish the Antlers aquifer from the Edwards aquifer.

Hydrochemical constituents (represented as TDS, pH, cations, and anions) and hydrochemical relationships (represented by ionic ratios and ion concentrations/TDS) show systematic distributions in the Plateau aquifer system, thus demonstrating that groundwater in many wells in a given area has similar histories of reaction with aquifer rocks. Dual-completion wells intermingle Antlers and Edwards groundwater. As maps will show, groundwater constituent compositions in these areas appear to be continuous with those found in the Antlers aquifer. For this reason statistical comparisons of waters from the Antlers and Edwards, respectively, do not include analyses of samples from dual-completion wells.

These data may possibly be used to delineate preferred groundwater flow paths. This paper also presents some potentially significant early findings of hydrochemical data analyses that are part of the author's developing Ph.D. dissertation. Although findings are preliminary, some of the analytical approaches may be useful in delineating recharge zones, estimating recharge rates, and discovering particularly effective flow paths.

Many data in this report are presented on contour maps. Contouring is a common practice in geological analysis and helps focus attention on geographical areas where certain
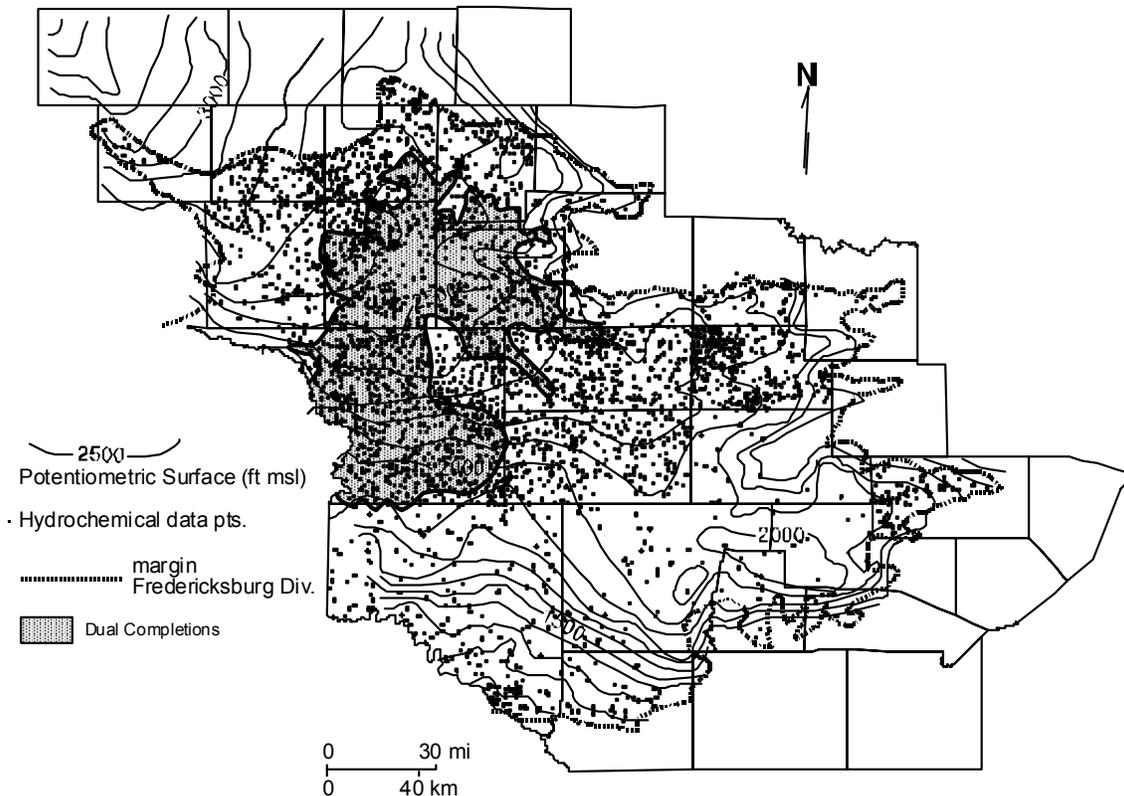
Figure 3- 2:   Map showing distribution of wells with hydrochemical data used in this study, areas that produce from specific aquifer-intervals (data from TWDB, 2003), and potentiometric surface (from Kuniansky, 1990). Stippled area generally produces commingled groundwater from the Edwards and Antlers aquifers. Areas to the north produce mostly from the Antlers aquifer and areas to south produce mostly from the Edwards aquifer.

ranges of parameter values are concentrated. Implicit in its use, however, is an interpretation that areas enveloped by contours are continuums and that additional data collected between data points would still be in the value range specified by contours. Additional data would undoubtedly demonstrate that this assumption is simplistic. This is shown where presently dense distributions of data force the use of complex contouring or where there are many data points that are the sole representatives of the value range specified by a contour interval.

Physiography And Climate

The Edwards Plateau (hereafter called the "Plateau") is a largely flat to rolling extent of the region where Cretaceous-age Trinity Group siliciclastic and carbonate rocks are capped by carbonates of the Fredericksburg and Washita Divisions (stratigraphic

nomenclature recently used by Smith and others, 2000) and is generally referred to as "Edwards and associated limestones", "Fredericksburg Group", and "Edwards" in groundwater reports and in the remainder of this report. The Plateau encompasses approximately 24,000 mi^2 (62,156 km^2) and ranges in elevation from 1,000 ft (305 m) in the southeast to 3,300 ft (1,006 m) in the northwest. Although approximately flat over broad drainage divides, the terrain becomes rolling in areas proximal to streams. A regional topographic drainage divide bisects the Plateau that results in over 70 percent of runoff flowing north and northeast toward the Colorado River and its tributaries (Walker, 1979). The Plateau is within the Low Western Plains physiographic province, characterized as sub-humid to semi-arid from southeast to northwest, respectively. Mean annual rainfall ranges from 34 inches (864 mm) to 12 inches (305 mm) (Figure 3-1). Summertime high temperatures average in the mid-90s (^{o}F) across the Plateau. Average gross annual lake evaporation ranges east to west from 69 inches (1.77 m) to 85 inches (2.18 m), respectively, across the Plateau (Bomar, 1995).

Hydrogeology

Details and summaries of Plateau Cretaceous stratigraphy and hydrogeology are found in Rose (1972), Barker and Ardis (1996a, 1996b), and Smith and others (2000) and will not be described here. In brief, the Plateau system is a mixed siliciclastic-carbonate interval where the lower (Trinity Group) unit is largely siliciclastic in basal intervals and up dip intervals (Antlers and Hensell sandstones) and mostly carbonate (limestone and dolomite) in down-dip intervals (Glen Rose limestone). A cap of Fredericksburg and Washita Division (herein called "Edwards") carbonates extends over the entire study area. Distributions of rock types and permeability fields interact with recharge from rainfall and cross-formational flow (paleo?) to control the present water quality in the system. Minor faulting occurs in the south along the Carta Blanca fault zone in the southern part of the area and the Balcones Fault Zone bounds the southeast part of the area. Mapped fractures near the southeastern margin of the Plateau (Wermund and others, 1979) and caves (Elliot and Veni, 1994; Kastning, 1983) show prominent directionality that parallels fracture-trends in the fault zones. Local solution-controlled subsidence is well documented along the Pecos River and may record sub-surface paleo-drainage along bedding plane cavities toward the Pecos prior to Rio Grande River establishment (Freeman, 1968). Fractures, caves, subsidence depressions, and stratigraphically controlled permeability features may provide particularly effective avenues for recharge and sub-surface flow.

Plateau Groundwater Hydrochemistry

Water quality in any well is controlled by the chemical composition of infiltrating recharge waters; chemical (organic and inorganic) compositions, textures, and permeability structure of flow units (including soils); sub-surface temperatures; rates at which groundwater moves through flow units; and the composition and relative proportion of admixed groundwater from other flow units.

Rain and Recharge

Rainfall provides the great majority of recharge to the Plateau system. Present distributions of hydraulic gradients appear not to support cross-formational flow into the system from underlying Triassic and Permian formations (Bush and others, 1994). Rain falls through the atmosphere onto the land and infiltrates the soil cover and underlying rock that lies above the water table (unsaturated zone). When accumulating in sufficient quantities that exceed evaporation, soil moisture-retention capacity, and uptake by plants (transpiration), rainwater percolates to a water table (recharge) to become part of the saturated-zone groundwater from which discharges at springs and into wells. Approximating the magnitude of a rain event that sufficiently exceeds evapotranspiration and soil-moisture capacity to contribute recharge is problematic because the occurrence of any of the aforementioned contingencies is influenced by soil-moisture conditions at the time of an event, event intensity (in/hr), and local geologic variations at the surface (for example, soil thickness and fractured sub-soil rock). Also, streams may provide recharge to the aquifer along their routes in portions that are hard to estimate and that also reflect vegetation, soil-moisture conditions, and local geology.

As rain falls through the atmosphere it dissolves CO_2 that is present at a partial pressure of $10^{-3.5}$ atm (approximately 0.03 percent of the atmosphere). The rainwater- CO_2 forms an acidic mixture with an average pH of 5.66. Rain also contains minute quantities of chemical components that are contributed by sea spray and terrestrial particulates. The average abundances and relative proportions of these components are geographically and temporally variable (Figure 3-3), although an average composition that is based on records that span many events is best for understanding rain's contributions to the groundwater composition.

Rates of recharge are often approximated by assuming that discharges by base flow into streams and at springs are in equilibrium with recharge (steady-state conditions) and that a reasonable approximation of aquifer-wide recharge rates is equal to an estimated aquifer-wide discharge rate (for example, Kuniansky, 1989). On this basis Kuniansky (1989) estimated recharge across the Plateau system to be 0.12 to 2.24 in/yr from west to east, respectively. Such estimates are uncertain because aquifer flow paths and rates are generally poorly known, and discharge rates may reflect paleo-recharge under significantly different climatic conditions.

Hydrochemistry may provide the tools with which to estimate aquifer recharge. A chloride mass-balance approach has been used for approximating the proportion of rainfall that contributes to aquifer recharge (for example, Eriksson and Khunakasem, 1969). Chloride is extremely soluble and tends to remain dissolved in groundwater (conservative) whereas other ions (non-conservative) may form compounds with other dissolved ions or aquifer solids or sorb to aquifer solids (especially clay particles). Chloride is concentrated in soil by evaporation of chloride-bearing rain, by deposition of wind-blown chloride-bearing dust, and by aerosols that originate as sea spray. Chloride is delivered to the saturated zone in amounts that record accumulations from numerous rainfall events each of which provided insufficient quantities of water to percolate to the water table. The ratio of rain-deposited chloride to groundwater chloride is related to the
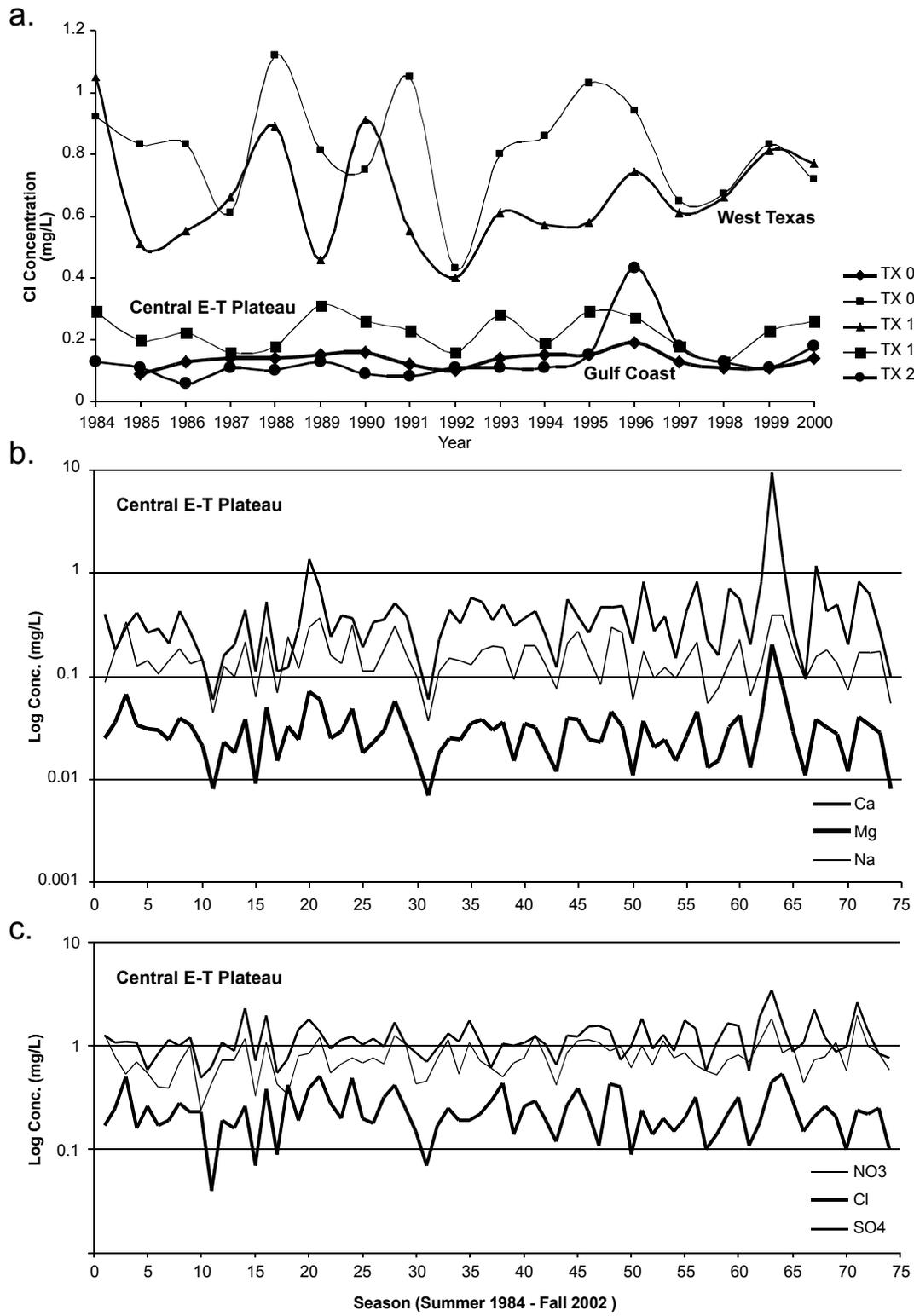
Figure 3-3:   Graphs showing (a) average annual precipitation chloride from several NADP stations in Texas; and average seasonal precipitation (b) cations and (c) anions at the Sonora NADP station (data from NADP, 2003).

rainfall-recharge rate unless significant amounts of chloride is contributed by dissolution of chloride-bearing minerals (for example, NaCl) in the soil or saturated zone, by diffusion of previously deposited chloride from aquifer solids, or by mixing with groundwater with different chloride concentrations. Although knowledge of aquifer mineralogy and geological constraints on flow paths may allow assessment of aquifer-mineralogical factors, knowledge of pre-existing chloride in the aquifer matrix or of mixing dynamics is not certain. Nonetheless, considerations of ideal circumstances whereby chloride concentrations are interpreted to mainly reflect recharge rates provide baselines against which other factors can be evaluated.

Chloride concentrations (designated as [Cl]) in rain average from 0.15-0.45 mg/L on the Plateau, based on 16 years of data from 1985 to 2000 and assumptions of linear gradients between chloride data collected from several stations located in West Texas (Figure 3-1). Assuming that all the chloride in a groundwater sample is derived from precipitation and that recharge moves vertically to the water table (piston flow), $[Cl]_{rain}/[Cl]_{groundwater}$ should reflect the fraction of rain that recharges an aquifer. For example, if rain in a location averages 0.2 mg/L chloride and groundwater chloride averages 20 mg/L (a typical Edwards aquifer value), then 0.2/20 = 0.01; that is, the recharge rate is 1 percent. Given an annual average rain amount of 20 inches, the annual recharge rate would be $R_{annual} = 0.01 \cdot 20 = 0.2$ in/yr. Application of this technique over the basin can provide a first approximation of recharge rates. Maps of recharge rates based on this technique are being prepared and can be used to calculate recharge volumes against which to compare recharge estimates that are based on other techniques.

Mineralogy

The major mineral components of the Edwards-Trinity aquifer system are shown in Table 3-1. The Fredericksburg/Washita and Trinity division carbonate-dominated sections consist mainly of limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Fredericksburg division gypsum ($CaSO_4$) is locally present in amounts sufficient to be an economic resource, although it was deposited in much greater thickness than is preserved. Some thin siliciclastic interbeds and admixed siliciclastic components also occur with carbonates. The dominant mineral component in the Trinity Group sandstones is quartz (average 98 percent). Present in minor amounts are feldspars, clay minerals, limestone and dolomite and heavy minerals including zircon, staurolite, magnetite, and ilmenite (Table 3-1). However, heavy minerals average only 0.025 percent in abundance (Fisher and Rodda, 1967).

Total Dissolved Solids and Ionic Constituents

Total dissolved solids concentrations are the sum of all dissolved mineral components and would be what remains when water is completely evaporated. Total dissolved solids are more concentrated in groundwater from most Antlers wells than water from most Edwards wells (Table 3-2; Figures 3-4 and 3-5). This probably reflects longer residence times of Antlers groundwater caused by generally lower permeability of flow units and

Table 3-1:   Pure mineral constituents that compose the Plateau aquifer system.

Aquifer Minerals	Mineral (pure) Formulas
calcite (aragonite)	$CaCO_3$
dolomite	$CaMg(CO_3)_2$
gypsum	$CaSO_4$
quartz	SiO_2
magnetite	Fe_3O_4
ilmenite	$FeTiO_3$
zircon	$ZrSiO_4$
staurolite.	$Fe_2Al_9O_6(SiO_4)_4(O,OH)_2$
pyrite	FeS_2
celestite	$SrSO_4$
feldspars	$K(AlSi_3O_8)$, $Na(AlSi_3O_8)$, $Ca(Al_2Si_2O_8)$
clays (e.g., montmorillonite)	$(Al,Mg)_8(Si_4O_{10})_3\text{-}(OH)_{10} \cdot 12H_2O$

recharge through a generally greater thickness of overlying rock. Bush and others (1994) reported a TDS median value of 379 mg/L in Edwards-Trinity groundwater and recognized that wells completed in the Trinity (mainly Antlers sandstone) in the northwestern part of the Plateau showed overall higher TDS values than did wells toward the east that were completed in Fredericksburg and Washita strata, based on 2,296 wells. However, they did not separate Antlers from Edwards groundwater in their hydrochemical statistical summaries of the Plateau system. In the present report TDS statistics are based on 1,157 analyses from Antlers wells and 1,985 analyses from Edwards wells (total 3,142 wells) whereby the Antlers aquifer is distinguished from the Edwards aquifer by a significantly higher average concentration of dissolved solids, as well as higher minimum TDS values (Figure 3-4). Based on these analyses the average TDS for the Edwards-Trinity is 682 mg/L and the median is 263 mg/L, a lower value compared to Bush and others. Notably, 13 percent of samples from the Edwards and 62 percent from the Antlers exceed the U. S. Environmental Protection Agency's secondary drinking water standards (500 mg/L) for TDS (USEPA, 2000).

Geographic distribution of TDS values from the Plateau wells is shown in Figure 3-5. The spatially abrupt transition from higher to significantly lower values corresponds to juxtaposition of areas that produce from the Antlers and Edwards aquifers, respectively. Further, each aquifer is characterized by systematic intra-aquifer variations of TDS concentrations. Higher values (greater than 800 mg/L) in Antlers groundwater are concentrated in the central and south-central part of the area defined by Antlers wells, whereas the lowest values (less than 400 mg/L) occur in the east and northeast part of the area. Intermediate concentrations (400 to 800 mg/L) are concentrated in the north and northwest. Notably, higher TDS concentrations correspond to areas of historical major petroleum production. It remains to be demonstrated whether elevated groundwater

Table 3-2:   Statistical summary of major ion composition of Plateau groundwater (data from TWDB, 2003).

Cation	Si (mg/L)	Si (mmol)	Si (%cat)	Ca (mg/L)	Ca (mmol)	Ca (%cat)	Mg (mg/L)	Mg (mmol)	Mg (%cat)	Na (mg/L)	Na (mmol)	Na (%cat)
Edwards Aquifer												
n	1,884	1,884	1,884	1,884	1,884	1,884	1,884	1,884	1,884	1,884	1,884	1,884
Avg	15.14	0.54	13.22	76	1.88	41.03	27	1.11	23.61	46	2	22.14
min	1	0.04	0.07	4	0.1	2.35	1	0.05	1.13	1	0.04	2.33
max	64	2.28	33.67	694	16.96	87.79	263	10.82	75.98	2,670	116.09	92.99
standev	4.63	0.16	4.48	60	1.4	12.7	20	0.82	7.98	132	5.82	15.54
Antlers Aquifer												
n	999	999	999	999	999	999	999	999	999	999	999	999
Avg	18	0.63	8.57	141.69	3.53	34.21	12.87	1.93	16.86	155.98	6.78	40.36
min	1	0.04	0.07	28	0.7	2.07	2.66	0.04	0.79	5	0.22	4.99
max	130	2.78	31.1	1060	26.43	84.92	193.56	20.04	39.66	4,230	183.91	96.05
standev	10.82	0.36	6.3	107.06	2.67	11.89	16.47	1.84	7.89	317.97	13.83	16.42

Cation	HCO₃ (mg/L)	HCO₃ (mmol)	HCO₃ (% an)	SO₄ (mg/L)	SO₄ (mmol)	SO₄ (%an)	Cl (mg/L)	Cl (mmol)	Cl (%an)
Edwards Aquifer									
n	2,036	2,036	2,036	2,036	2,036	2,036	2,030	2,030	2,030
Avg	275	4.51	77	71	0.88	7	64	1.81	16
min	49	0.8	11	0	0	0	2	0.06	3
max	706	11.57	85	4,250	53.13	92	4,900	138	97
standev	54	0.89	19	222	2.78	11	204	5.74	13
Antlers Aquifer									
n	1,175	1,175	1,175	1,162	1,162	1,162	1,162	1,162	1,162
Avg	260	4.26	43	365	3.8	36	207.5	5.8	21
min	5	0.08	1	2	0.02	1	2	0.06	1
max	620	10.16	94	3,360	35	92	16,330	460	97
standev	60.2	0.99	26	444.3	4.6	24	832	23.4	16

n = number
Avg = average
min = minimum
max = maximum
standev = standard deviation

mmol = millimols
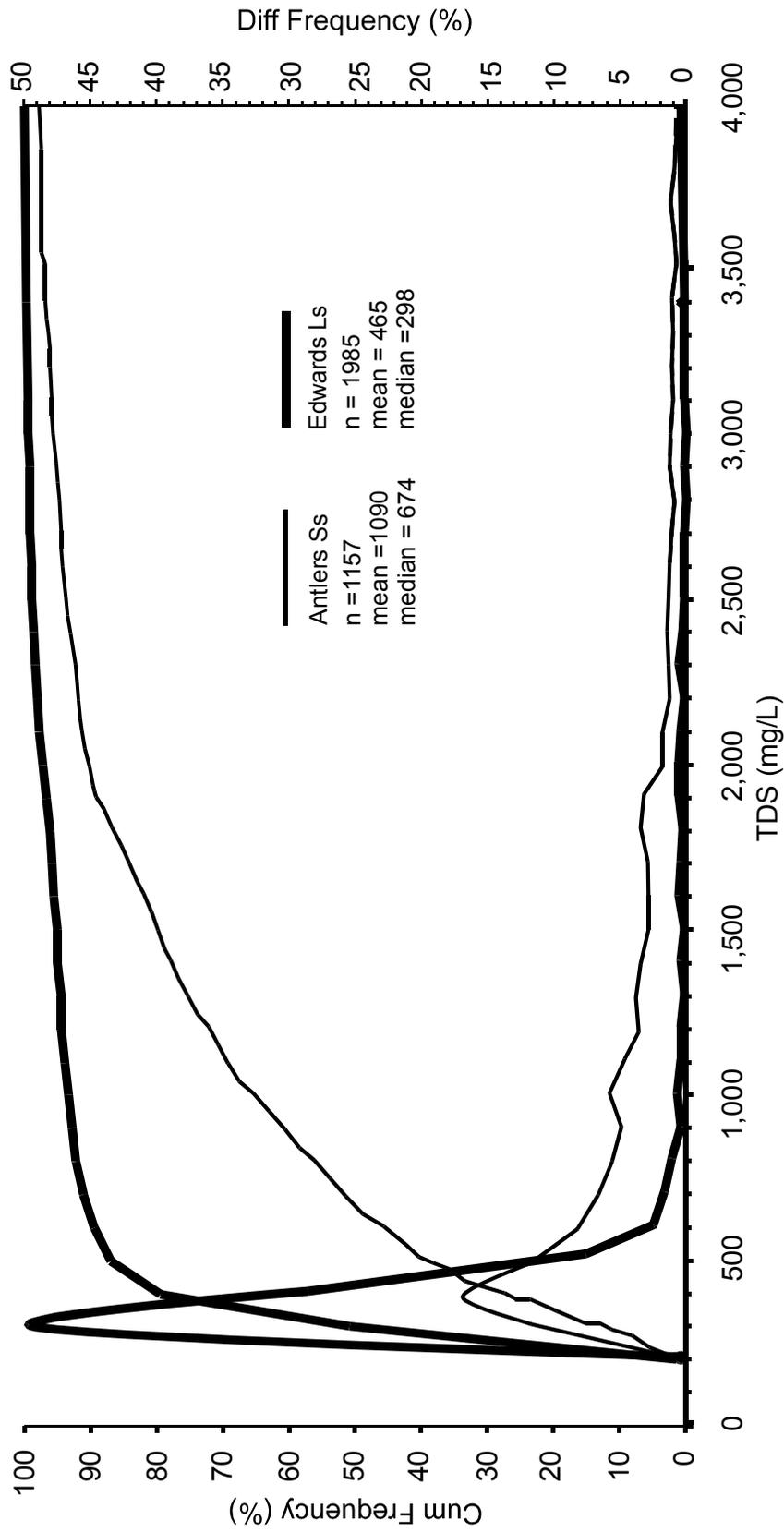mg/l = milligrams per liter
an = anion
cat = cation

Figure 3-4:   Statistical distributions of TDS for the Antlers and Edwards aquifers in the Plateau aquifer system (data from TWDB, 2003). See Figure 3-2 for data points.
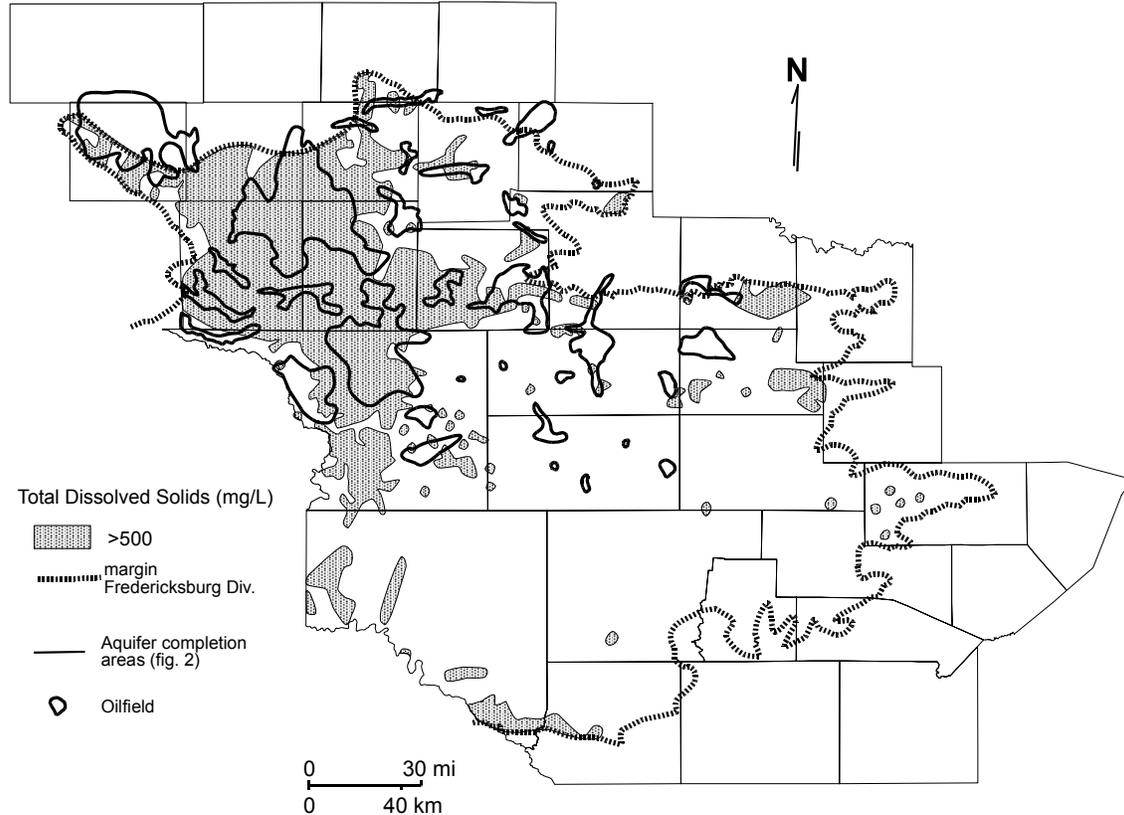
Figure 3-5:   Map showing distribution of total dissolved solids greater than 500 mg/L (data from TWDB, 2003) and major petroleum producing areas (after Walker, 1979).

salinity preceded or resulted from petroleum-related activities in the region. Higher values (greater than 400 mg/L) in Edwards groundwater are concentrated largely in Plateau-margin areas, whereas lower concentrations occur in more interior areas. Margin areas are where the water table in the Edwards is closest to the top of the Antlers Formation. Elevated salinity in these areas suggests that groundwater mixing occurs that is caused by cross-formational flow from the Antlers into the Edwards.

The abundances of major ions show a general direct relationship to TDS values (Figure 3-6). A very good correlation (all points fall near a line called a "mixing line") is expected if only two distinctly different groundwaters are mixing in various proportions to produce the water that is delivered to any given well. The point scatter in Figure 3-6 suggests that more than two waters may be mixing or that additional processes are further modifying mixtures. A fairly sharp linear boundary is defined by the data points along the upper left side on each of the plots. Other linear alignments of data points are also evident in the data. These suggest that there could be some simple two-water mixtures among the analyses, but that other data may reflect more complex conditions of mixing;
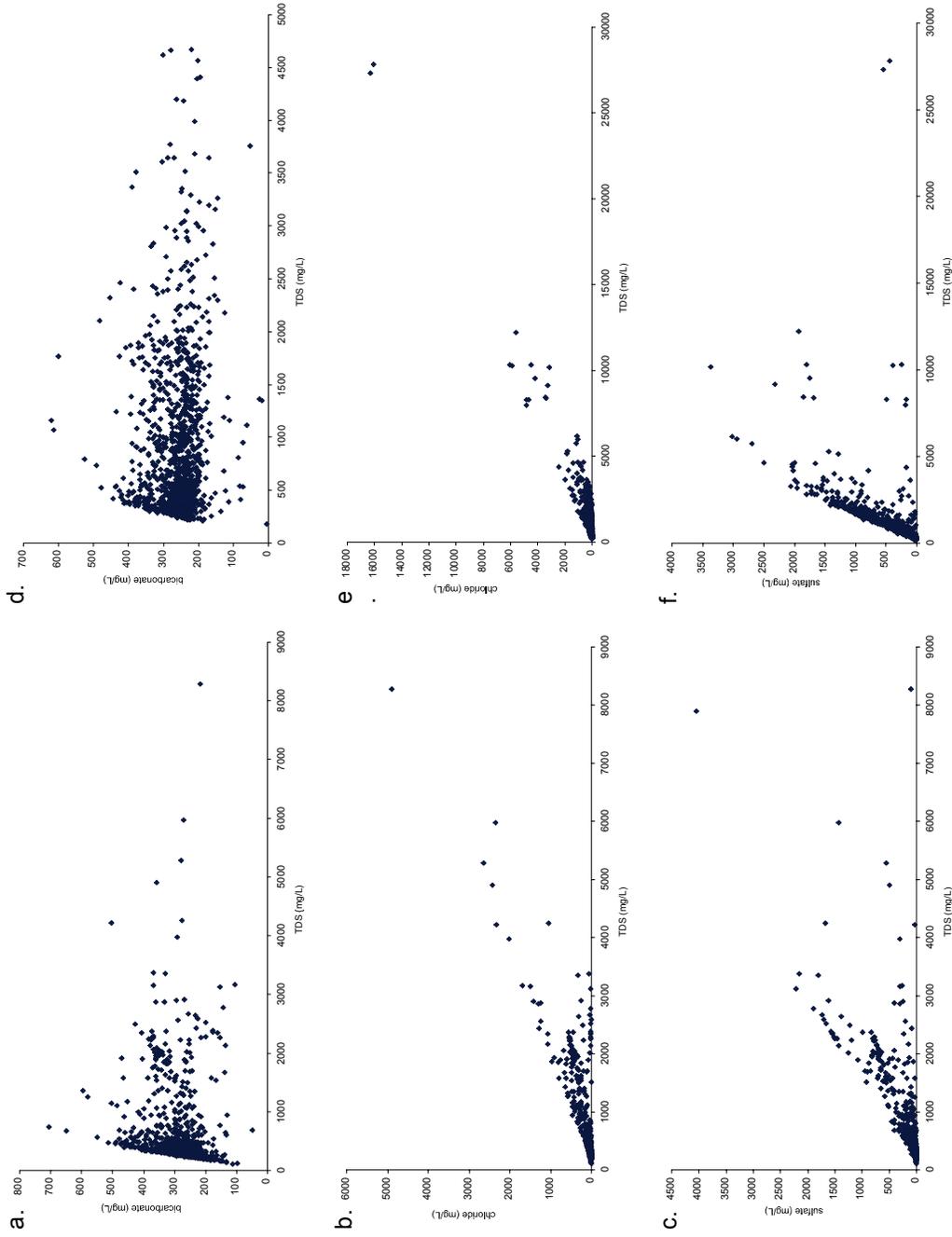
Figure 3-6 :   Graphs showing cross plots of TDS and (a) bicarbonate, (b) chloride, and (c) sulfate from the Edwards aquifer and (d) bicarbonate, (e) chloride, and (f) sulfate from the Antlers aquifer (data from TWDB, 2003).

or water-rock interaction. Further analysis is required to determine if identical wells produce the groundwater that defines specific linear trends on the Edwards or Antlers ion/TDS cross plots.

Major Cations

Cations are the positively charged ions dissolved in groundwater. The most abundant and most commonly analyzed in Plateau groundwater is calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^+). All the major ions occur in rainwater (Figure 3-3) and are concentrated in soils by evaporation. However, their concentrations in groundwater largely involve groundwater-rock interactions (Table 3-1). In the Plateau system Ca^{2+} is produced by carbonate (limestone and dolostone) and gypsum ($Ca\ SO_4$) dissolutionMg^{2+} is produced by Mg-calcite and dolomite dissolution as well as by de-dolomitization of dolomite to calcite by diagenesis in high Ca/Mg groundwater (DeGroot, 1967; Moore and others, 1968). Na^+ is a component in feldspars (for example, albite), and halite (NaCl); and also remains in aquifer rocks from times when more saline conditions prevailed.

On average, Ca^{2+} and Mg^+ compose a higher percentage of the cation composition in Edwards than in Antlers groundwater (Table 3-2), thus reflecting the dominance of limestone and dolomite in the Edwards. However, average Na concentration is higher in the Antlers, perhaps reflecting the presence of sodium feldspars and their clay-mineral weathering products in the aquifer matrix. Another potential source for Na^+ is cross-formational flowing groundwater from underlying Triassic and evaporate-bearing Permian rocks.

Trace Cations

Trace-cation analyses may be useful in distinguishing groundwater that is produced from sandstone from those that are produced from limestones, based on the small set of data from the survey of nine Plateau aquifer system wells. Three samples were collected from Antlers wells, five were collected from Edwards wells, and one was collected from a Dockum well. Groundwater from Edwards aquifer limestone is distinguished somewhat from those produced from Antlers and Dockum sandstones by relative abundances of trace cations. Edwards groundwater tends to be relatively enriched in barium, copper, vanadium, aluminum, nickel, cobalt, chromium, and manganese. Antlers and Dockum sandstones tend to be enriched in boron, zinc, lithium, hodium, yettrium, silver, molybedinum, uranium, and rubidium. Exceptional among sandstone-aquifer groundwater, the Dockum sample was notably depleted in zinc, but very enriched in manganese; the latter occurring in highest concentration among all the water samples.
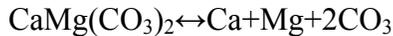
Anions

Anions are the negatively charged ions dissolved in groundwater. The most commonly analyzed are bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), and fluoride (F^-). In the Plateau system, HCO_3 (along with CO_3^{2-}) is produced by carbonate

dissolution, whereas HCO_3^- is also produced by silicate dissolution and dissociation of water molecules (see pH section) Three simplified common water-mineral reactions are the following:

calcite dissolution,

$$Ca\ CO_3 \leftrightarrow Ca + CO_3$$
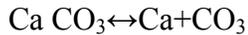
dolomite dissolution, and

$$CaMg(CO_3)_2 \leftrightarrow Ca + Mg + 2CO_3$$

feldspar dissolution (for example, Na-feldspar $\leftrightarrow$ kaolinite)

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$$

Chloride is produced by (a) evaporation of rainwater prior to recharge, (b) diffusion of chloride that remains from times when the aquifer rock was more saline, or (c) halite dissolution

$$NaCl \leftrightarrow Na^+ + Cl^-$$
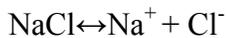
Sulfate is a product of gypsum ($Ca\ SO_4$) dissolution:

$$Ca\ SO_4 \leftrightarrow Ca + SO_4$$
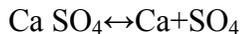
F^- is present in trace amounts in many soils and rocks and is also added to municipal water supplies for its well-known dental effects (Walker, 1979). Fluoride exceeds USEPA secondary standards in 9 percent of samples from the Edwards and 34 percent from the Antlers. NO_3^- is produced by decay of organic materials, dissolution of fertilizers, and other causes.

Edwards HCO_3^- average values are higher than those for the Antlers (Table 3-2), probably owing to the almost entirely carbonate composition of the Edwards. However, Antlers HCO_3^- is also high, probably reflecting the abundance of carbonate cements, presence of carbonate interbeds, and recharge of the Antlers by waters that have percolated through the Edwards. Edwards Cl^- and SO_4^{2-} values are significantly less than Antlers values, probably reflecting Edwards direct recharge by rainwater whereas Antlers recharge is by groundwater that has percolated through greater thickness of rock (including the Edwards) and has therefore chemically interacted with more rock over a longer time. Chloride levels in 6 percent of samples from the Edwards and 13 percent from the Antlers exceed U. S. Environmental Protection Agency secondary aesthetic limits (250 mg/L) for chloride in drinking water. Although Fredericksburg division gypsum was more widespread in the past (most notably, the Kirschburg evaporite of the Ft. Terrett Formation) sulfate produced by its dissolution probably washed down into the Antlers or have been otherwise swept from the Edwards and discharged from springs. Sulfate levels in 7 percent of samples from the Edwards and 43 percent from the Antlers

exceed U. S. Environmental Protection Agency secondary aesthetic limits (250 mg/L) for sulfate in drinking water.

Some of the constituents in the Antlers may have originated from underlying, generally more saline Permian and Triassic strata. Although modern head distributions in these aquifers do not appear to promote upward cross-formational flow (Bush and others, 1994), hydraulic connection between the Antlers and these units prior to upslope incision by the Pecos River may have compelled upward flow into formations that do not show it presently (Dutton and Simpkins, 1986). Antlers waters show overall greater concentrations of NO_3^- than do Edwards waters. However, correlation of NO_3 with probable agricultural sources on the Plateau was not performed for this report and is more appropriately in the realm of a contaminant investigation.

pH

The measure of "acidity" in groundwater is pH. Technically, pH is defined as the negative logarithm of hydronium-ion activity (designated aH_3O^+) in a solution (Fetter, 1994). For convenience, aH_3O^+ is abbreviated to aH^+. Assuming that aH^+ is approximately equal to concentration $[H^+]$, a reasonable assumption in dilute solutions, groundwater with $[H^+]$ of 10^{-6} moles has a pH value of 6. Activity of OH^- (OH^-), the hydroxyl ion, is always such that pH and pOH sum to 14. Neutral aqueous solutions at 25^oC have pH = pOH = 7. Acidic groundwater has pH values of less than 7, whereas basic groundwater has pH values greater than 7. In pure water, higher temperatures produce lower pH values.

Atmospheric CO_2 and CO_2 produced in soils by organic decay dissolve in rainwater to produce a dilute form of carbonic acid (H_2CO_3). Rain has an initial pH of approximately 5.7 (Drever, 1997), whereas pH of infiltrated rainwater (soil water) may be lower because the $[CO_2]$ in soils (commonly 10^{-2} atm) is generally higher than atmospheric concentrations (average $10^{-3.5}$ atm). Reaction of soil and rock minerals with acidic rain- and soil water is the major cause of chemical weathering. Chemical weathering transfers much of the carbon in CO_2 to bicarbonate (HCO_3^-), a process which raises pH to values greater than 7.0 under normal conditions of shallow aquifers.

The range of pH in Antlers groundwater is significantly broader than that in Edwards groundwater (Figure 3-7), although average pH and median pH are similar. This difference may reflect the mineralogical differences between the two aquifers: The Edwards is mainly composed of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), whereas the Antlers is dominated by quartz and minor amounts of other silicates with calcite cement. Additionally, residence times for Antlers groundwater may generally be greater than for Edwards ground waters, thus allowing closer approach to chemical equilibration between groundwater and aquifer rock.
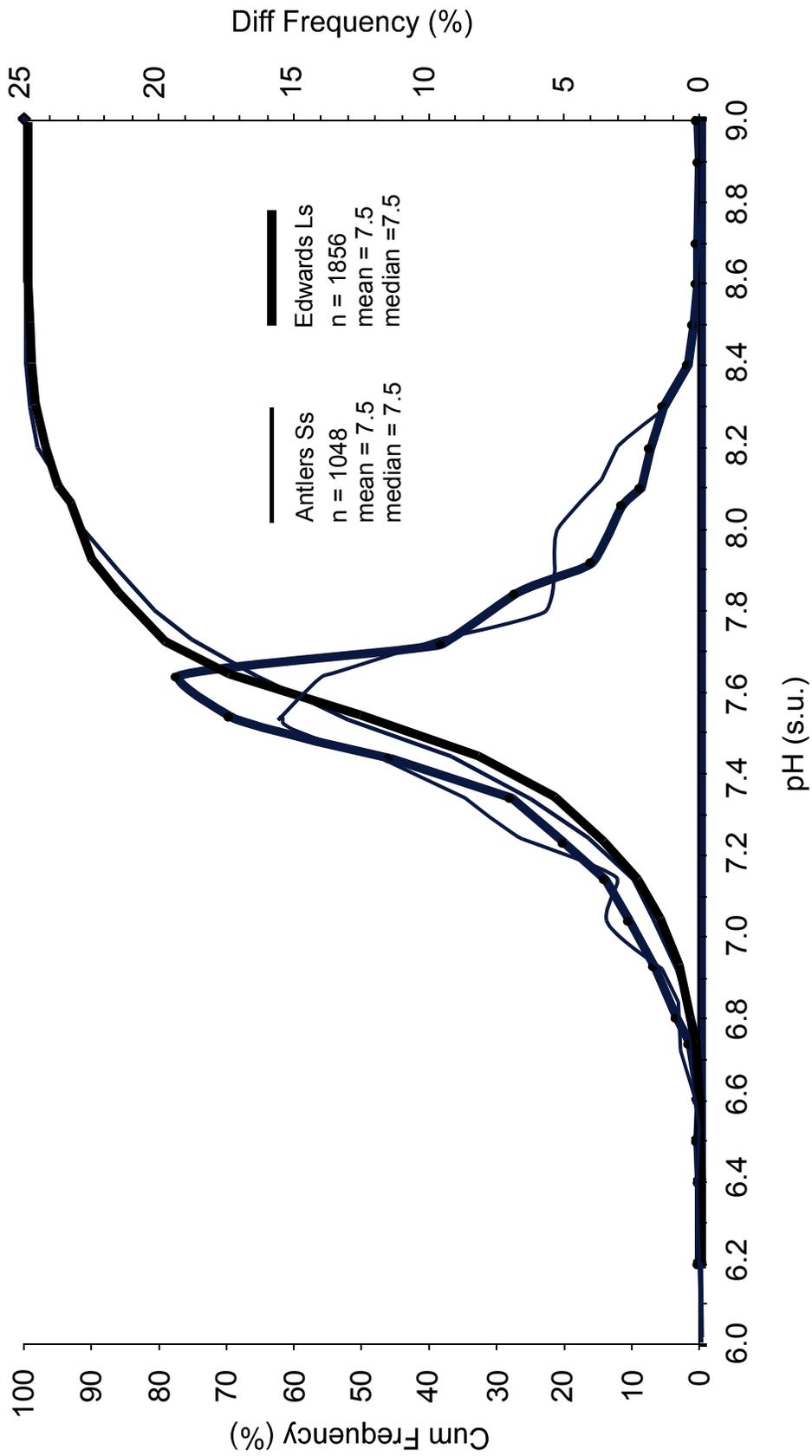
Figure 3-7: Statistical distributions of pH for the Antlers and Edwards aquifers in the Plateau aquifer system (data from TWDB, 2003).

Hydrochemical Facies

Groundwater is commonly classified into hydrochemical facies that are groups of samples whose assigned names indicate the most concentrated cations and anions in the sample. Abundance values are based on "equivalents" or "milliequivalents (meq)" rather than on mg/L or molar concentrations. Equivalents are calculated as molar concentration of an ion times its electrical charge (z). For example, in a sample with 5 millimoles (mmol) of Ca^{2+}

$$[Ca^{2+}] \cdot z = (5mmol) \cdot 2 = 10 \text{ meq}$$

Facies compositions reflect interactions between recharge water and aquifer lithology (Back, 1960). The compositional ranges that are specified by facies-names can be adjusted to most effectively map hydrochemical zones in a given aquifer (Freeze and Cherry, 1979). For example, in one scheme groundwater whose cation abundance is 90 percent Ca^{2+} and whose anion abundance is 75 percent Cl^- may be classified as a Ca-Cl-type. As another example of the same scheme, water with cation abundances of 55 percent Ca^{2+} and 45 percent Mg^{2+}, and with anion abundances of 55 percent HCO_3^- and 45 percent SO_4^{2-} may be classified as a Ca-Mg-HCO$_3$-SO$_4$-type. Groundwater with sub-equal proportions of cations or anions are called mixed-cation or mixed-anion, as in a case where the cation composition is 45 percent Ca^{2+}, 30 percent Mg^{2+}, 25 percent Na^+ and the anion composition is 45 percent HCO_3^-, 30 percent Cl^-, 25 percent SO_4^{2-}. Compositional-facies complexity can reflect lithologic heterogeneity along separate flow paths and/or mixing of groundwater at convergences of multiple paths from lithologically dissimilar areas.

Bush and others (1994) classified Edwards-Trinity groundwater into facies that were mapped on 6-mile centers whereby compositional analyses from all wells within each 36-mi^2 area were averaged. The map produced from their analysis reflected a classification scheme where the cation and anion designation in the facies name represented the dominant cation or anion in a sample based on abundances greater than 50 percent. For example, water with a cation concentration that is 90 percent Ca^{2+} and water with 40 percent Ca^{2+}, 30 percent Mg^{2+}, and 30 percent Na^+ were both named a Ca-type water. The same quantitative criteria were applied to the anion designations. Based on this classification scheme, they observed that bicarbonate facies dominated the southern, eastern, and northeastern parts of the Plateau system, whereas chloride and sulfate facies dominated the western and northwestern parts of the area. Ca-type facies dominated in most of the sample wells, although Mg^{2+} and Na^+ were locally prominent in sulfate-dominated areas.

Although useful to describe average quality of groundwater that is being produced in an area, the practice of averaging analyses from several wells may obscure hydrochemical details that could be helpful in identifying anomalies, considerations of which might illuminate locally significant processes of recharge or groundwater mixing. An approach that uses similar hydrochemical-facies criteria to address identification of dominant processes and significant deviations from them is shown in Figures 3-8, 3-9, and 3-10.
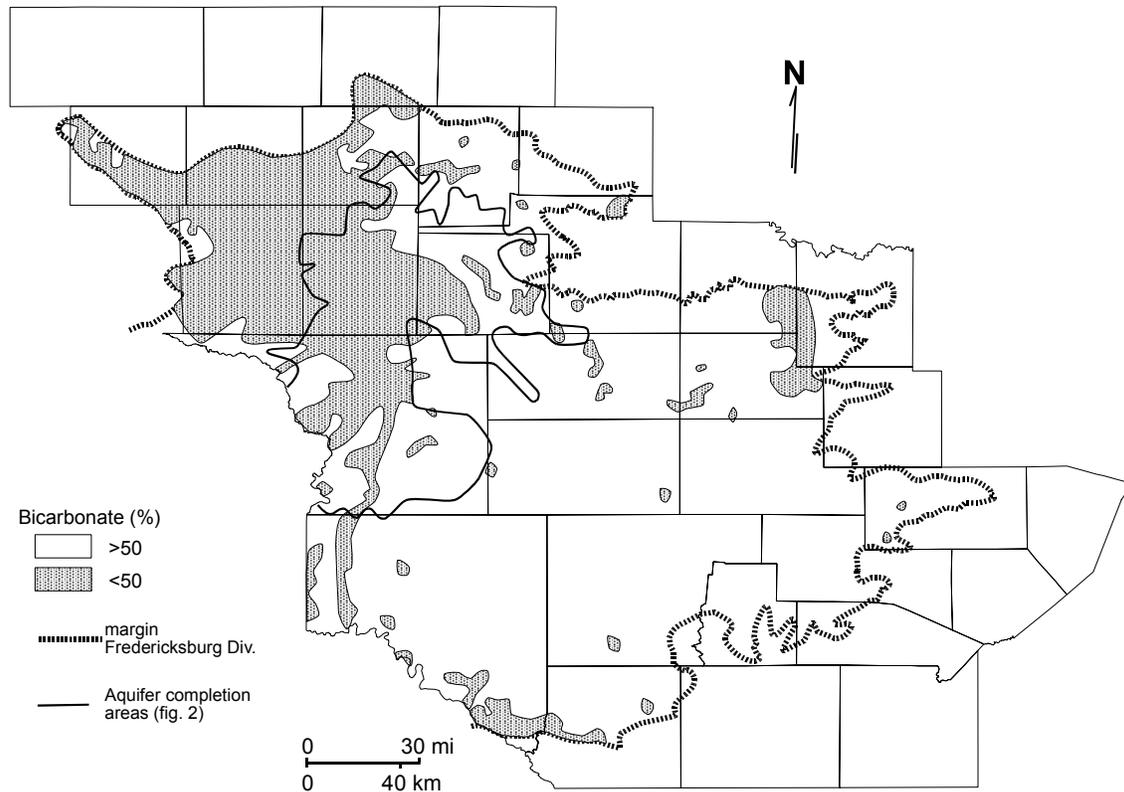
Figure 3-8:   Map showing distribution of wells with bicarbonate concentrations of less than 50 percent of cationic constituents (data from TWDB, 2003). See Figure 3-2 for data points.

Figure 3-8 shows areas characterized by <50 percent bicarbonate. This depiction is useful because it focuses on areas where groundwater deviates from the more commonly occurring bicarbonate facies that record weathering of carbonates and silicates. Bicarbonate-deficient zones probably indicate areas where most of the waters have been involved in evaporate dissolution somewhere along its flow paths.

Bicarbonate deficiency in the Edwards occurs along the northwestern margin of the Edwards production area and in some cases reflects well completion in both aquifers (dual completion) that results in the intermingling of Antlers and Edwards groundwater. Where dual completion is not evident, bicarbonate deficiency may signify cross-formational flow of chloride- and sulfate-rich groundwater from the Antlers in response to pumping from the Edwards in areas where the water table is near the top of the Trinity aquifer. Bicarbonate-deficiency near the southwestern and northeastern margins of the Edwards productive area may also reflect pumping near the top of the Trinity. The

Antlers groundwater productive area is generally bicarbonate-depleted except near the north and northeast margin. Bicarbonate-deficiency probably signifies inclusion of dissolved constituents delivered by flow originating in underlying Permian and Triassic strata. The characteristic siliciclastic composition of the Antlers is probably not relevant
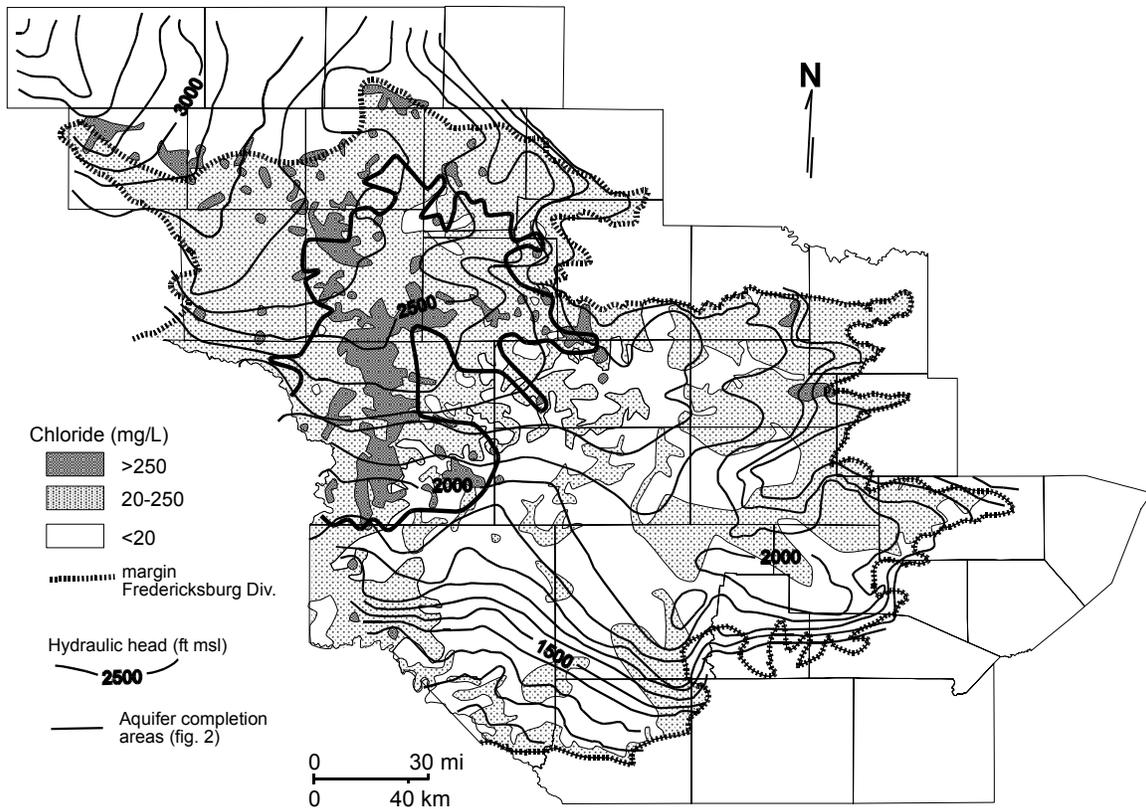
Figure 3-9:   Map showing distribution of groundwater chloride (data from TWDB, 2003) and the distribution of hydraulic head. 250 mg/L is USEPA-recommended maximum level of chloride in drinking water. See Figure 3-2 for data points.

to its bicarbonate deficiency because weathering of silicates also produces bicarbonate. The stark difference in overall bicarbonate content between the Edwards and Antlers aquifers supports the contention that the two units are hydraulically poorly connected. Figure 3-9 is a map that shows chloride and hydraulic head distribution in the Plateau aquifer system. The chloride mapping thresholds focus on areas where the water is particularly fresh (chloride less than 20 mg/L) and on areas where chloride exceeds the USEPA secondary standards (greater than 250 mg/L) for chloride in drinking water (USEPA, 2000). Similar to TDS distributions, the highest chloride concentrations correspond to areas of historical hydrocarbon production in the Midland Basin (Figure 3-5). The freshest groundwater is concentrated in the interior of the Edwards groundwater productive zone and is especially evident in the potentiometric trough in the southwestern part of the area and on the top and southern flank of the potentiometric mound that is defined by the 2,000-ft contour in the southeast part of the area. Both these areas are characterized by well-developed surface drainage systems that serve as groundwater discharge zones.
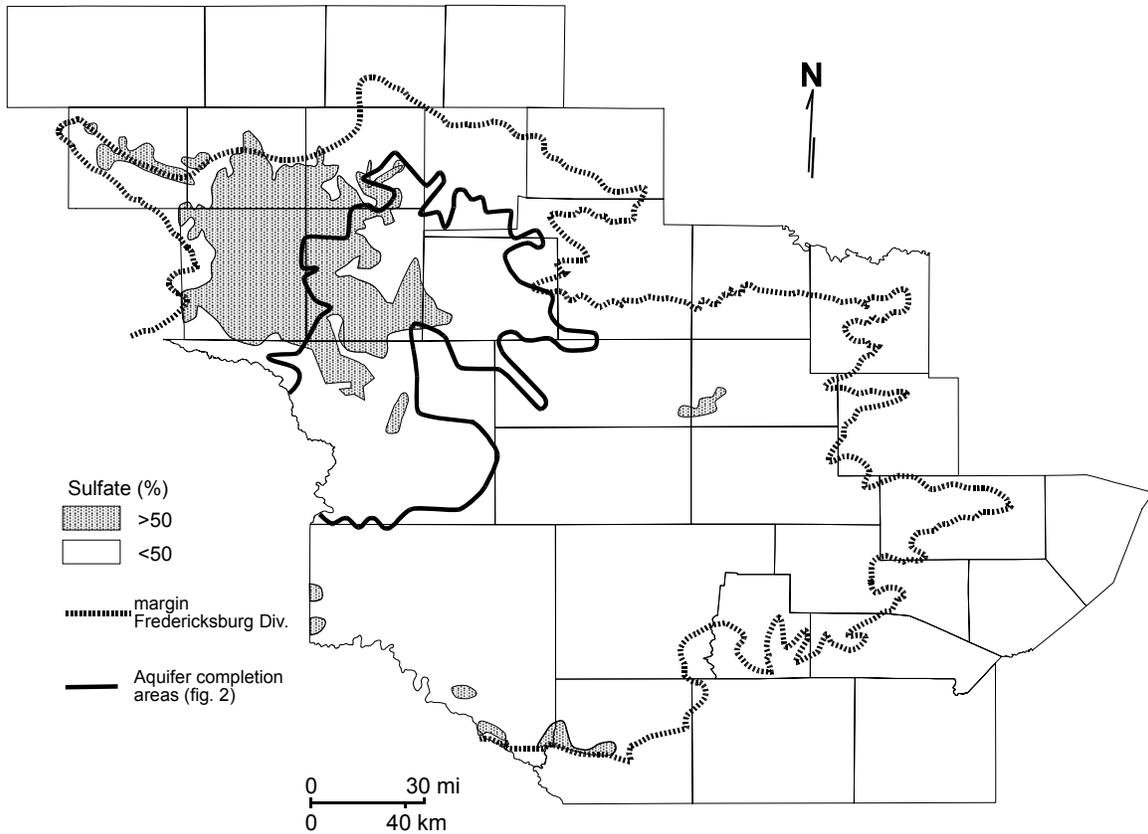
Figure 3-10:   Map showing distribution of wells with groundwater sulfate concentrations of greater than 50 percent of anion constituents (data from TWDB, 2003). See Figure 3-2 for data points.

Figure 3-10 is a map of areas with greater than 50 percent sulfate. Similar to chloride distributions (Figure 3-9), higher sulfate concentrations are evident near major petroleum producing areas (Figure 3-5). Occurrences of sulfate-enriched groundwater may reflect cross-formational flow into the Antlers from underlying Triassic and evaporitic Permian intervals and into the Edwards from the Antlers. Evaporites are not reported from the Antlers. However, gypsum in the Edwards could have provided sulfate to the Antlers in the past. As stated above, some of the bicarbonate-deficient areas near the northern margin of the Edwards productive area are marked by dual well completions. Similar to the other hydrochemical maps, the significant difference in sulfate concentration between Antlers and Edwards groundwater suggests that the two aquifers are not well connected hydraulically.

Equilibrium (Solubility Indices)

Concentrations in groundwater of the kinds of ions that compose aquifer mineral solids will achieve maximum levels (equilibrium) given sufficient groundwater residence time for chemical reactions to proceed to their fullest possible extent under any given set of

conditions (Kehew, 2001). In reality, flow through compositionally heterogeneous aquifers and mixing of waters at flow path convergences generally prevents the attainment of fully equilibrated conditions. For example, it is possible to produce a solution that is under saturated with respect to a given mineral by mixing two distinctly different waters, each of which is saturated with respect to the mineral. The two waters may have different ionic strengths or pH. In the Plateau system, groundwater quality is controlled largely by dissolution/precipitation reactions involving calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4$), and silicates (quartz, feldspars, and clay minerals) and by ion exchange reactions mainly involving clay minerals. The carbonate and sulfate reactions probably dominate currently because they proceed at faster rates than do silicate reactions and carbonate minerals are very abundant in the Plateau system.

Evaluation of the potential of groundwater to dissolve or precipitate minerals involves consideration of the solubility indices (SI) of minerals under measured conditions of ionic concentrations, pH, and temperature. SI is a ratio whereby the ion activity product (IAP) of a given dissolution/precipitation reaction calculated under aquifer conditions is divided by the equilibrium constant (K) of the reaction under conditions where the mineral of interest is the only species in solution. K varies systematically with and is adjusted for temperature. IAP values for solubility in water of calcite, dolomite, and gypsum are:

$$IAP_{cal} = a[Ca^{2+}] \bullet a[CO_3^{2-}]$$

$$IAP_{dolo} = a[Ca^{2+}] \bullet a[Mg^{2+}] \bullet a^2[CO_3^{2-}]$$

$$IAP_{gyp} = a[Ca^{2+}] \bullet a[SO_4^{2-}]$$

Activity (a) of a given ion is controlled by its concentration and the solution ionic strength (combined concentrations of all the diverse ions in the water). When only one mineral species is dissolved in the water, $a = 1$.

When $SI = IAP/K_{cal} = 1$, the groundwater is in equilibrium with the mineral and the mineral is expected to neither dissolve nor precipitate. Dissolution is expected when $IAP/K_{mineral} < 1$, and precipitation is expected when $IAP/K_{mineral} > 1$. Some writers use Log(SI) to describe solubility conditions in which case Log(SI) = 0 denotes equilibrium with negative or positive values denoting conditions favoring dissolution or precipitation, respectively.

Most Plateau groundwater is supersaturated with respect to calcite. Only 9 percent of Edwards analyses indicate under saturation, whereas approximately 5 percent of Antlers analyses indicate calcite under saturation (Figure 3-11). Over 99 percent of Edwards waters and 97 percent of Antlers groundwater is under saturated with respect to gypsum. Thus, conditions appear to be generally favorable toward precipitation of calcite and
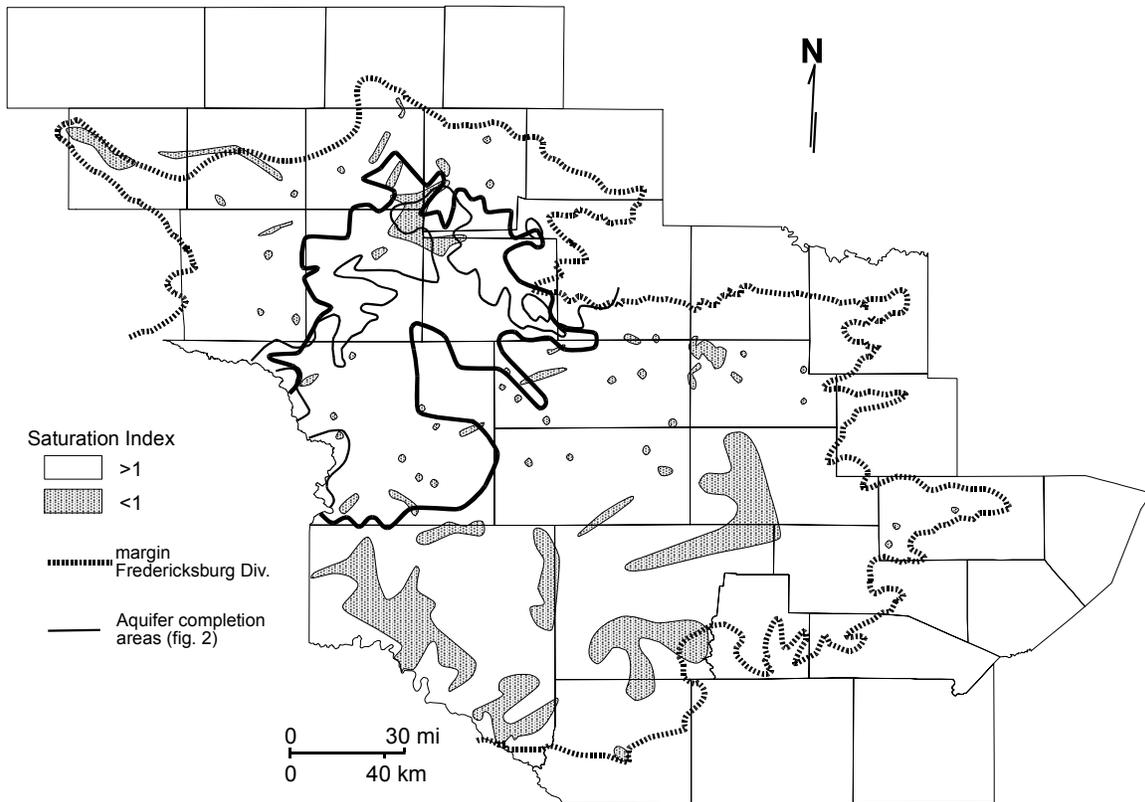
Figure 3-11:   Map showing distribution of saturation indices for calcite (constituent
                analyses from TWDB, 2003). See Figure 3-2 for data points.

dissolution of gypsum. Perhaps the low values of SI $_{gyp}$ reflect general scarcity of gypsum
in the system after millions of years of leaching by gypsum under-saturated groundwater.
With respect to dolomite, from 12 to 43 percent of Edwards waters and 12 to 35 percent
of Antlers waters are under saturated, depending on the choice between two K $_{dolo}$ values
provided by Drever (1997). Although some of the samples suggest conditions that are
favorable for dolomite precipitation, dolomite is very difficult to precipitate and is
thought to form mostly from alteration of calcite or aragonite (Drever, 1997). However,
Drever (1997) states that this conversion is difficult under conditions of near-surface
temperatures unless aMg/aCa values are considerably higher than 1. However, values of
aMg/aCa barely exceed 1 in Plateau groundwater analyses. Only 9 percent of Edwards
analyses (average = 0.67) and 2 percent of Antlers analyses (average = 1.04) have
aMg/aCa values greater than 1.1. When considering the implications of saturation
calculations, it should be known that errors in field or laboratory measurements corrupt
SI calculations. Errors as small as 0.1 pH standard units can mean the difference between
supersaturated and under saturated conditions as determined from SI calculations.
Temperature errors, however, produce much smaller SI variations.

Mg/Ca and Cation Exchange

Relative abundances of various cations change with groundwater residence times at rates and to extents that depend on aquifer conditions, including rock type, recharge rates, and mixing of waters that originate in separate parts of the system. Two parameters considered here are Mg/Ca and [Na]/[Ca + Mg] values. Two processes that cause these changes are (1) dissolution of calcite and dolomite and (2) cation exchange of Ca^{2+} and Mg^{2+} with Na^+. Calcite dissolves more readily than dolomite (Kehew, 2001). As dolomite dissolves, Ca^+ and Mg^+ are released. Ca^+ is added to that produced by calcite dissolution, thus promoting calcite precipitation. Even if the groundwater is supersaturated with respect to calcite and calcite precipitates, (Ca^+ is removed from solution) dolomite will continue to dissolve until Mg^+ is equilibrated. Therefore Mg/Ca will tend to rise in groundwater with increasing residence time (Freeze and Cherry, 1979).

Cation exchange occurs when Ca^{2+} and Mg^{2+} substitute for Na^+ on mineral surfaces; clay minerals are common substrates on which exchanges occur. The process delivers 2 Na^+ ions to solution for every Ca^{2+} or Mg^{2+} that sorbs to mineral surface. This process increases the $[Na^+]/[Ca^{2+} + Mg^{2+}]$ with groundwater residence time as long as $[Na^+]$ is not so high as to overwhelm the process. Mapping of an operational parameter that represents this cation exchange

$$Log(Ca^{2+} + Mg^{2+})/(Na^+)^2$$

has been used to interpret groundwater flow directions. For example, Henderson (1984) demonstrated correlations between flow directions inferred from potentiometric maps and trends of decreasing values of the parameter in two sandstone aquifer systems the northern Great Plains.

The operational parameter was calculated and mapped for the Plateau system (Figure 3-12). The map shows the lowest values (implying greatest extent of cation exchange reactions) toward the margins of both the Edwards and Antlers groundwater production areas. The higher values (implying the least extent of cation exchange) may be related to higher rates of recharge perhaps coupled with lower concentrations of clay minerals. Preliminary analysis does not reveal an obvious correspondence between cation exchange alone and potential flow directions that are interpreted from the potentiometric map (Figure 3-13). Conspicuous broad zones with low values appear to occur in areas where wells are completed within the Edwards close to the top of the Antlers, where many wells are completed in both aquifers, and in the area on the north margin of the Antlers productive zone where bicarbonate proportions are high (Figure 3-8) and sulfate proportions are low (Figure 3-10). Further investigation is required to ascertain the interrelationships of these correspondences.

Given that residence time generally increases [Cl] and Mg/Ca, and decreases $Log(Ca^{2+} + Mg^{2+})/(Na^+)^2$, one might expect the three parameters to vary simultaneously in water samples. Although a general correspondence can be observed (not presented here), the
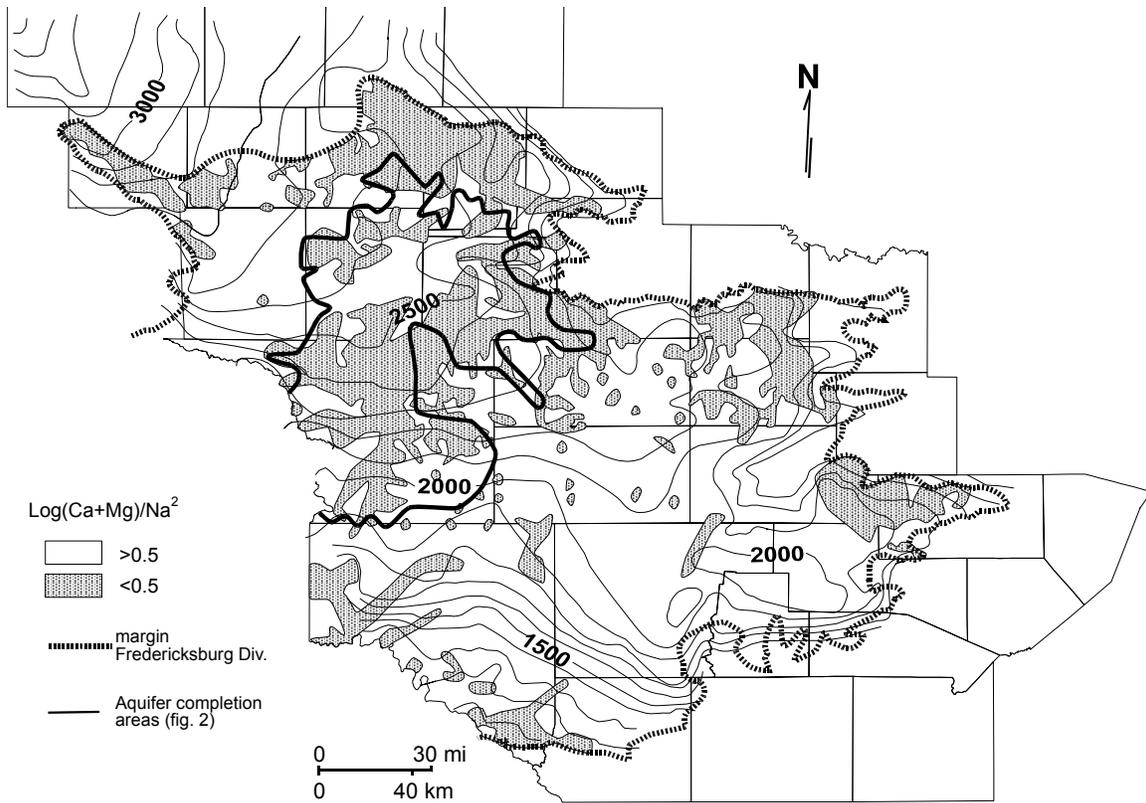
Figure 3-12: Map showing distribution of operational-parameter values that are may represent relative extents of Ca-Mg/Na cation exchange reactions (see text for explanation). Lower values interpreted to reflect greater extent of reaction. See Figure 3-2 for data points.

correlations are not well defined. Mixing of groundwater and variations in aquifer rock composition may explain deviations from an ideal distribution.

Conclusions

Over most of its area, the Plateau aquifer system is composed of two mineralogically and hydrochemically distinct aquifer intervals: (1) a lower interval of hydraulically confined Antlers quartz-dominated conglomerate and sandstone with associated limestone thin interbeds and (2) an upper interval of generally unconfined Fredericksburg/Washita Division carbonates composed of limestone, dolomite, and minor gypsum. Rainfall provides most recharge to the system. Hydrochemical constituents (for example, TDS, pH, ions) and hydrochemical relationships (for example, ionic ratios) show systematic distributions in the Plateau aquifer system. Dissolved ionic species originate from meteoric recharge, water-rock interactions in the aquifer system, and cross-formational flow from adjacent formations. Mass-balance approaches using $Cl_{rain}/Cl_{groundwater}$ in conjunction with average annual rainfall amounts may provide reasonable estimates of
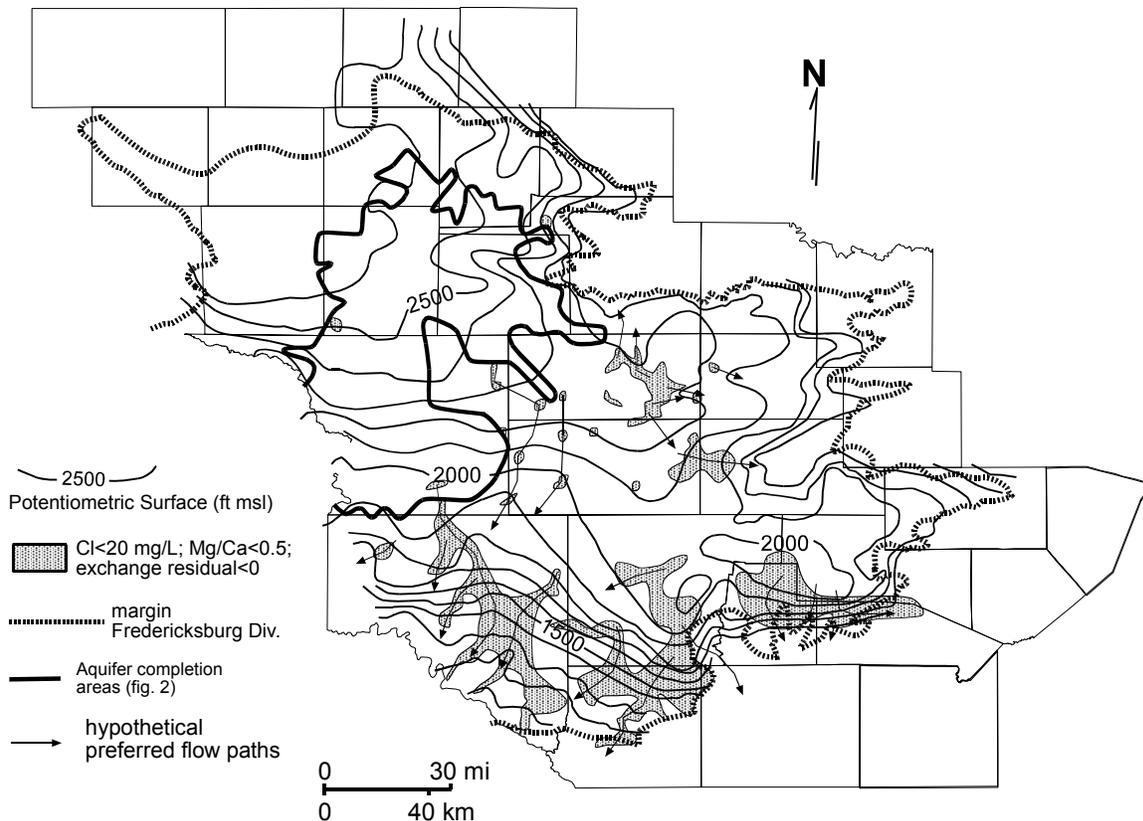
Figure 3-13: Map showing distribution of wells with groundwater chloride less than 20 mg/L, Mg/Ca less than 0.5, and above average values of Log $(Ca+Mg)/(Na)^2$ calculated for specified Mg/Ca ranges (see text) (data from TWDB, 2003).

aquifer recharge rates. Groundwater in both aquifers is largely supersaturated with respect to calcite, close to saturation with respect to dolomite, and under saturated with respect to gypsum. Chloride concentrations, Mg/Ca and cation exchange products tend to increase with groundwater residence times. Use of combinations of hydrochemical screening criteria may allow delineation of more effective recharge areas and groundwater flow paths.

References

Ashworth, J. B., and Hopkins, Janie, 1995, Aquifers of Texas: Texas Water Development Board Report 345, 69 p.

Back, W., 1960, Origin of hydrochemical facies of ground water in the Atlantic coastal plain: International Geological Congress, 21st, Copenhagen, 1960, [Proceedings], pt. 1, p. 87-95.

Barker, R. A., and Ardis, A. F., 1996a, Hydrogeologic framework of the Edwards-Trinity aquifer, West-Central Texas: United States Geological Society Professional Paper 1421-B, 61 p.

Barker, R. A., and Ardis, A. F., 1996b, Configuration of the base of the Edwards-Trinity aquifer system and hydrogeology of the underlying pre-Cretaceous rocks, West-Central Texas: United States Geological Society Professional Paper 91-4071, 25 p.

Bomar, G. W., 1995, Texas Weather: University of Texas Press, 275 p.

Bush, P. W., Ulery, R. L., and Rittmaster, R. L., 1994, Dissolved-solids concentrations and hydrochemical facies in water of the Edwards-Trinity aquifer system, West-Central Texas: United States Geologic Survey, Water Resources Investigations Report 93-4126, 29 p.

Drever, J. I., 1982, The geochemistry of natural waters: Prentice-Hall, New Jersey, 436 p.

Dutton, A. R., and Simpkins, W. W., 1989, Isotopic evidence for paleohydrologic evolution of ground-water flow paths, southern Great Plains, United States: Geology, v. 17, p. 653-656.

Elliot, W. R., and Veni, G., eds., 1994, The caves and karst of Texas: National Speleological Society, Huntsville, Alabama, 342 p.

Eriksson, E., and Khunakasem, V., 1969, Chloride concentration in groundwater, recharge rate and rate of deposition of chloride in the Israel coastal plain: Journal of Hydrology, V. 7, p. 178-197.

Fetter, C. W., 1994, Applied hydrogeology: Prentice-Hall, New Jersey, 691 p.

Freeman, V. L., 1968, Geology of the Comstock-Indian Wells area, Val Verde, Terrell, and Brewster Counties, Texas: United States Geological Survey Professional Paper 594-K, 26 p.

Freeze, R. A., and Cherry, J. A., 1979, Groundwater: Prentice-Hall, Inc., New Jersey, 604 p.

Henderson, T., 1984, Geochemistry of ground-water in two sandstone aquifer systems in the northern Great Plains in parts of Montana, Wyoming, North Dakota, and South Dakota: United States Geological Survey Professional Paper 1402-C, 84 p.

Hurlbut, C. S., 1971, Dana's manual of mineralogy: John Wiley & Sons, Inc., 579 p.

Kastning, E. H., 1983, Relict caves as evidence of landscape and aquifer evolution in a deeply dissected carbonate terrane: Southwest Edwards Plateau, Texas, U.S.A: Journal of Hydrology, 61, p. 89-112.

Kehew, A. E., 2001, Applied chemical hydrogeology: Prentice-Hall, New Jersey, 368 p.

Kuniansky, E. L., 1989, Precipitation, streamflow, and baseflow in west-central Texas, December 1974 through March 1977: United States Geologic Survey Water-Resources Investigations Report 89-4208, 2 sheets.

Kuniansky, E. L., 1990, Potentiometric surface of the Edwards-Trinity aquifer system and contiguous hydraulically-connected units, West-Central Texas, winter 1974-75:

United States Geological Survey Water-Resources Investigations Report 89-4208, 2 sheets.

Kuniansky, E. L., and Holligan, K. Q., 1994, Simulations of flow in the Edwards-Trinity aquifer system and contiguous hydraulically-connected units, west-central Texas: U. S. Geological Survey Water-Resources Investigations Report 93-4039, 40 p., 3 plates.

Rose, P. R., 1972, Edwards Group, surface and subsurface, central Texas: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations 74, 198 p.

TWDB, 1969, Well tests of Texas aquifers: Texas Water Development Board Report 98, 532 p.

TDWB, 2003, On-line well data and groundwater quality databases, Texas Water Development Board, http:///www.twdb.state.tx.us/data/groundwater_toc.htm.

Matthew, M., and Sharp, J. M., Jr, in press, Tracing regional flow paths to major springs in Trans-Pecos Texas using geochemical data and geochemical models: Chemical Geology.

Smith, C. I., Brown, J. B., and Lozo, F. E., 2000, Regional stratigraphic cross sections, Comanche Cretaceous (Fredericksburg-Washita division), Edwards and Stockton Plateaus, West Texas: The University of Texas at Austin, Bureau of Economic Geology, 39 p., 6 plates.

USEPA, 2000, Drinking water standards and health advisories: U. S. Environmental Protection Agency, Washington, EPA 822-B-00-001, http://www.epa.gov/ost/drinking/standards/dwstandards.pdf

Walker, L. E., 1979, Occurrence, availability, and chemical quality of ground water in the Edwards Plateau region of Texas: Texas Department of Water Resources, Report 235, 337 p.

Webster, R. E., 1982, Geology of the Carta Valley fault zone area, Edwards, Kinney, and Val Verde Counties, Texas: The University of Texas at Austin, Bureau of Economic Geology Geologic Quadrangle Map No. 53, 23 p., 1 map.

Wermund, E. G, Cepeda, J. C., and Lutrell, P. E., 1978, Regional distribution of fractures in the southern Edwards Plateau and their relationship to tectonics and caves: The University of Texas at Austin, Bureau of Economic Geology, GC 78-2, 14 p.

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