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Evaluation of Ground-Water Quality in Texas Counties Bordering the Rio Grande

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Evaluation of Ground-Water Quality in Texas Counties Bordering the Rio Grande

by

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ABSTRACT

Even before passage of the North American Free Trade Agreement (NAFTA), several sections in the Texas Water Development Board (TWDB) took stock of their programs along the Texas-Mexico border to assess which presently were in good shape and what additional work needed to be done. This report discusses the results of a recent ground-water sampling study conducted along the Rio Grande by the Hydrologic Monitoring Section of the TWDB to consider the ambient quality of the ground water in the area and what, if any, changes have occurred with time.

To complement the 188 samples taken during routine monitoring of the Edwards-Trinity (Plateau), Carrizo-Wilcox, and Gulf Coast aquifers since 1988, TWDB personnel collected 150 more samples from Zavala, Dimmit, and 11 counties along the border in the spring of 1994. Obviously similar data must be collected from the Mexican side to construct a more integrated picture of ground-water quality along the border.

Certain measurements, including conductivity, pH, alkalinity, and temperature, were taken in the field. Ground-water samples were collected in accordance with methods endorsed by this agency and the EPA. The Texas Department of Health analyzed samples for major anions and cations, radioactivity, selected trace metals, and nutrients. In 1994, samples from Terrell and Val Verde Counties were also screened for organic compounds, and samples from the Gulf Coast aquifer in Cameron and Hidalgo Counties were screened for insecticides and herbicides.

Overall, the best quality water exists in the Edwards-Trinity (Plateau) aquifer in Terrell and Val Verde Counties. Approximately one-third of the samples taken since 1988, however, contained concentrations of dissolved solids, chloride, and sulfate in excess of secondary constituent levels. Sulfate levels exceeded 300 mg/l in parts of the Rio Grande Alluvium, the Laredo, and the Gulf Coast aquifers from Maverick and Cameron, Zapata, and Starr and Hidalgo Counties, respectively. With the exception of Maverick County, chloride levels above 300 mg/l and dissolved solids above 1,000 mg/l were also found in the same areas and in Webb County. Iron and manganese exceeded secondary levels in several samples. Arsenic concentrations in nine wells in Webb County were above primary constituent levels, as were gross alpha in six percent of the sampled wells. No organics were detected in samples from Hidalgo and Cameron Counties; seven of the 3,060 constituents analyzed from Terrell and Val Verde Counties contained measurable quantities of organic compounds, for which most do not have maximum constituent levels set.

TABLE OF CONTENTS

FIGURES

TABLES

TABLE OF CONTENTS (cont'd.)

Page

TABLES (cont'd.)

APPENDIX

(on disk in pocket)

Each directory (COM--comma delimited ascii, or BAR--vertical bar delimited ascii) must first be copied to hard disk and then files within, listed below, decompressed using the ZIPFILE.EXE command:

aquifer.txt
casing.txt
county.txt
infwqual.txt
remarks.txt
storet.txt
weldta.txt
wlevels.txt
wquality.txt

The order of data in each table is listed in the appendix; a complete explanation of all codes can be found in the *TWDB Ground-Water Data System Data Dictionary* (Nordstrom and Quincy, 1993).

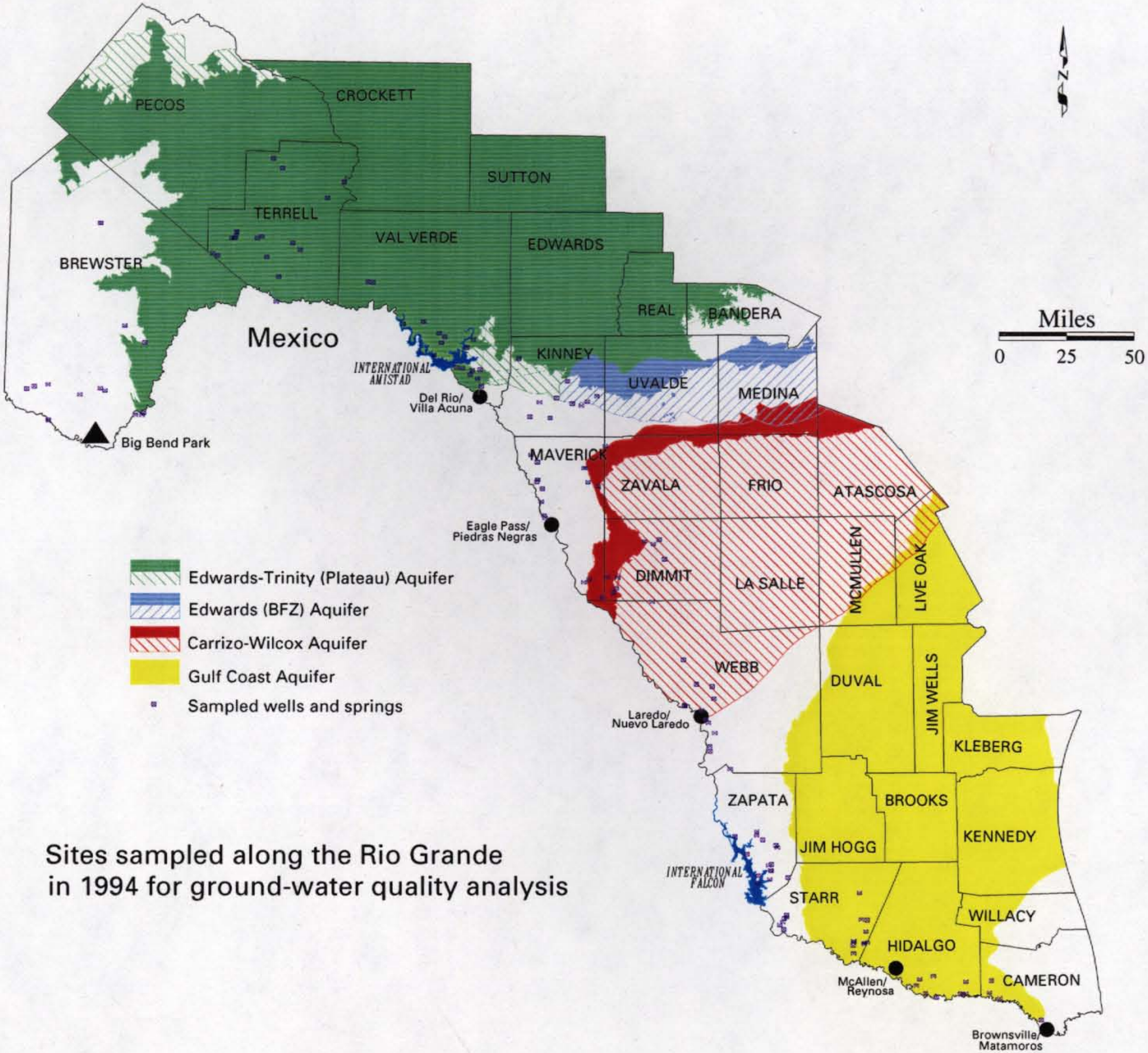
INTRODUCTION

In the spring of 1994, the Hydrologic Monitoring Section altered its ground-water quality monitoring schedule to sample an area covered by several major and smaller "miscellaneous" aquifers (designated neither as major or minor), rather than an area defined by coverage of only one aquifer. Field personnel sampled wells (and springs) in Zavala, Dimmit, and counties immediately adjacent to the Rio Grande, as indicated on the map in Figure 1. Sites shown on the map in the area of a major aquifer generally provided water samples from that aquifer, but not always. For example, several sites visited in Brewster County that appear within the boundaries of the Edwards-Trinity (Plateau) are wells completed in other aquifers such as the Santa Elena or the Rio Grande Alluvium. The amount of samples collected in each county ranged from four in Cameron up to 18 in Terrell for a total of 150; six field personnel collected these in approximately two months using methods endorsed by the EPA; and the Texas Department of Health (TDH) analyzed the samples within the prescribed holding time.

Acknowledgements

The TWDB appreciates the cooperation of the property owners for supplying information about their wells and allowing access to their property to sample water quality. TWDB Environmental Quality Specialists Dennis Jones, Ron Mohr, John Asensio, Robbie Ozment, Lennie Winkleman, Merrick Biri, and Cindy Lee collected water samples. Geologist Phillip Nordstrom of the TWDB edited the report; GIS staff members Mark Hayes and Melanie Miles created report graphics.

Figure 1



Sites sampled along the Rio Grande in 1994 for ground-water quality analysis

WATER QUALITY

Sampling Procedures

Field personnel selected irrigation, municipal, and industrial wells where possible to ensure that water samples were physically representative of a large area of the aquifer. They also followed procedures described in the TWDB Field Manual for Ground Water Sampling (Nordstrom and Beynon, 1991) to obtain water samples that were hydrochemically representative of the aquifer. Sufficient volumes of ground water were first purged from the well before sample collection. Samples were collected near wellheads before the water had gone through pressure tanks, water softeners, or other treatment. Upon arrival at the wellsite, temperature, specific conductance (using a VWR conductivity meter), and pH (using a Beckman pH meter) were monitored at five-minute intervals until the readings stabilized. Field measurements of total alkalinity and Eh (using a pH meter with an Eh diode) were also taken. All samples except those collected for pesticides (organics) were filtered through a 0.45 ìm nonmetallic filter into a one-liter polyethylene bottle and placed on ice. Those collected for determination of dissolved anion and cation/metal content were delivered to the TDH laboratory, and analyses were completed within 28 days; others collected for nutrients, radioactivity, and pesticides were analyzed within the prescribed holding times.

Field Measurements

Tables 1 and 2 list averages and ranges of field measurements for the three major aquifers and for three miscellaneous aquifers calculated from all data collected since 1988. Counties are specified for each aquifer. A few somewhat acidic pH values do not meet the secondary standard, although average pH values exceed 7.0. Temperatures

Table 1. Comparison of field measurement (and lab-calculated dissolved solids) averages and ranges in major aquifers sampled along the Rio Grande since 1988.

Measurement	Edwards-Trinity (Plateau) (Brewster, Terrell, Val Verde)	Carrizo-Wilcox (Zavala, Dimmit, Webb, La Salle)	Gulf Coast (Jim Hogg, Star, Hidalgo, Cameron, Willacy)
pH	7.3	7.6	7.3
	6.7 – 8.7	6.6 – 8.6	6.7 – 8.5
Temperature	25°	28.6°	28°
(° C)	22° – 30°	14° – 35°	25° – 38°
Eh	+85	-45	+73
(mV)	-696 – +658	-304 – +544	-254 – +275
Total	203	321	269
Alkalinity	109 – 315	114 – 1,195	55 – 507
Sp. Conductance	631	1,457	2,932
(μmhos)	240 – 1,780	382 – 7,840	580 – 12,800
Dissolved Solids	398	1,047	2,373
(mg/l)	147 – 1,183	296 – 5,477	751 – 10,953

* One measurement only

are somewhat higher in samples from all aquifers south of Val Verde County. Negative Eh averages indicate reducing conditions in a few wells. Higher total alkalinities correspond to higher values of specific conductance (and dissolved solids), with the highest averages among the major aquifers found in the Gulf Coast, and highest among the miscellaneous found in the Laredo aquifer.

Table 2. Comparison of field measurement (and lab-calculated dissolved solids) averages and ranges in miscellaneous aquifers sampled along the Rio Grande since 1988.

Measurement	Rio Grande Alluvium (Maverick)	Laredo (Zapata, Webb, Starr)	Rio Grande Alluvium (Cameron)
pH	7.4	8.0	7.9
	6.8 – 23.0	6.9 – 8.9	7.0 – 8.1
Temperature	23°	28.5°	27.3°
(° C)	20° – 25°	26° – 31°	27.2° – 27.4°
Eh	+82	-83	-28.8
(mV)	+56 – +115	-134 – +122	
Total	251	349	339
Alkalinity	155 – 366	164 – 742	104 – 476
Sp. Conductance	1,704	4,172	2,814
(μmhos)	903 - 2,912	1,948 - 9,400	1,550 - 6,675
Dissolved Solids	1,286	2,991	1,773
(mg/l)	486 - 2,441	1,348 - 7,152	877 - 7,685

In the discussions that follow, averages and ranges of constituents were calculated for all wells sampled since 1988 in Brewster and nine additional counties to the east and south bordered by the Rio Grande, and Zavala, Dimmit, and Willacy Counties. Samples from each of the 385 sites visited during that period were analyzed for major cations and anions, but fewer were analyzed for trace metals, radioactivity, or have complete data for field measurements. By contrast, maps of dissolved-solids, chloride, and sulfate content reflect all available historical information in the area from additional counties within 100 kilometers of the river. Data from the recent sampling event were the major determinants of contour positions, particularly from wells with multiple sampling events in which recent data could more accurately delineate an increase or decrease in the amount of dissolved solids or other constituents. Historical data were more influential in those areas where 1994 data were not available.

Dissolved Inorganic Constituents, Radioactivity, and Organics

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 man-affected sources such as oil-field brines can also contribute certain dissolved constituents. Table 3 describes four classes of ground water classified according to dissolved-solids content as defined by the Texas Groundwater Protection Committee.

Contours on the map in Figure 2 indicate areas in which the predominant range of dissolved solids is greater than 1,000 mg/l, as well as specific sites with greater than 3,000 mg/l. Table 4 lists average concentrations and ranges of dissolved solids and other inorganic constituents. The average dissolved-solids content of 1,250 mg/l reflects the influence of saline waters in the southern two-thirds of the study area;

Table 3. Ground-water classification system.

Class	Quality (mg/l)	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, and industrial use
Moderately Saline	>3,000 - 10,000	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	>10,000	Mineral extraction, oil and gas production

although the Edwards-Trinity (Plateau) aquifer contains poorer quality water to the north in Crockett and Pecos Counties, these areas are not discussed in this report. Despite incomplete well coverage, it is apparent that the large majority of wells in the Gulf Coast aquifer in Jim Hogg, Starr, Hidalgo, Cameron, and Willacy Counties contain dissolved solids in excess of 1,000 mg/l. Well coverage is greater in the Carrizo-Wilcox in Zavala, Dimmit, and La Salle Counties, and fewer dense clusters of wells with MCLs above 1,000 mg/l could be contoured. With the exception of a small area south of the Amistad Reservoir north of Del Rio, the Edwards-Trinity (Plateau) aquifer in Brewster, Terrell, and Val Verde contains the best quality ground water.

Table 4. Major anions and cations of ground-water from sites sampled since 1988 along the Rio Grande.

Constituent (mg/l)	Range	Average	Percent > MCL*
Silica	10 - 106	25	
Calcium	1 - 710	100	
Magnesium	0.18 - 365	26	
Potassium	BDL** - 47	7	
Sodium	3.5 - 2,330	308	
Strontium	0.1 - 18	2	
Bicarbonate	67 - 1,458	321	
Nitrate	BDL - 376	3	< 0.3
Fluoride	BDL - 5.5	0.9	9
Sulfate	2 - 3,397	327	34
Chloride	5 - 3,139	299	30
Dissolved solids	147 - 7,685	1,266	44
Hardness***	2 - 3,084	355	

*Secondary MCL , **BDL = Below Detection Limit , ***Expressed as $CaCO_3$

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 imparts a salty taste to drinking water and can increase its corrosiveness. The map in Figure 3 indicates areas where the chloride content is greater than the secondary MCL of 300 mg/l. These areas in the Laredo, the Gulf Coast, and the Rio Grande (Cameron County) Alluvium aquifers are of smaller extent, but still appear to be encompassed

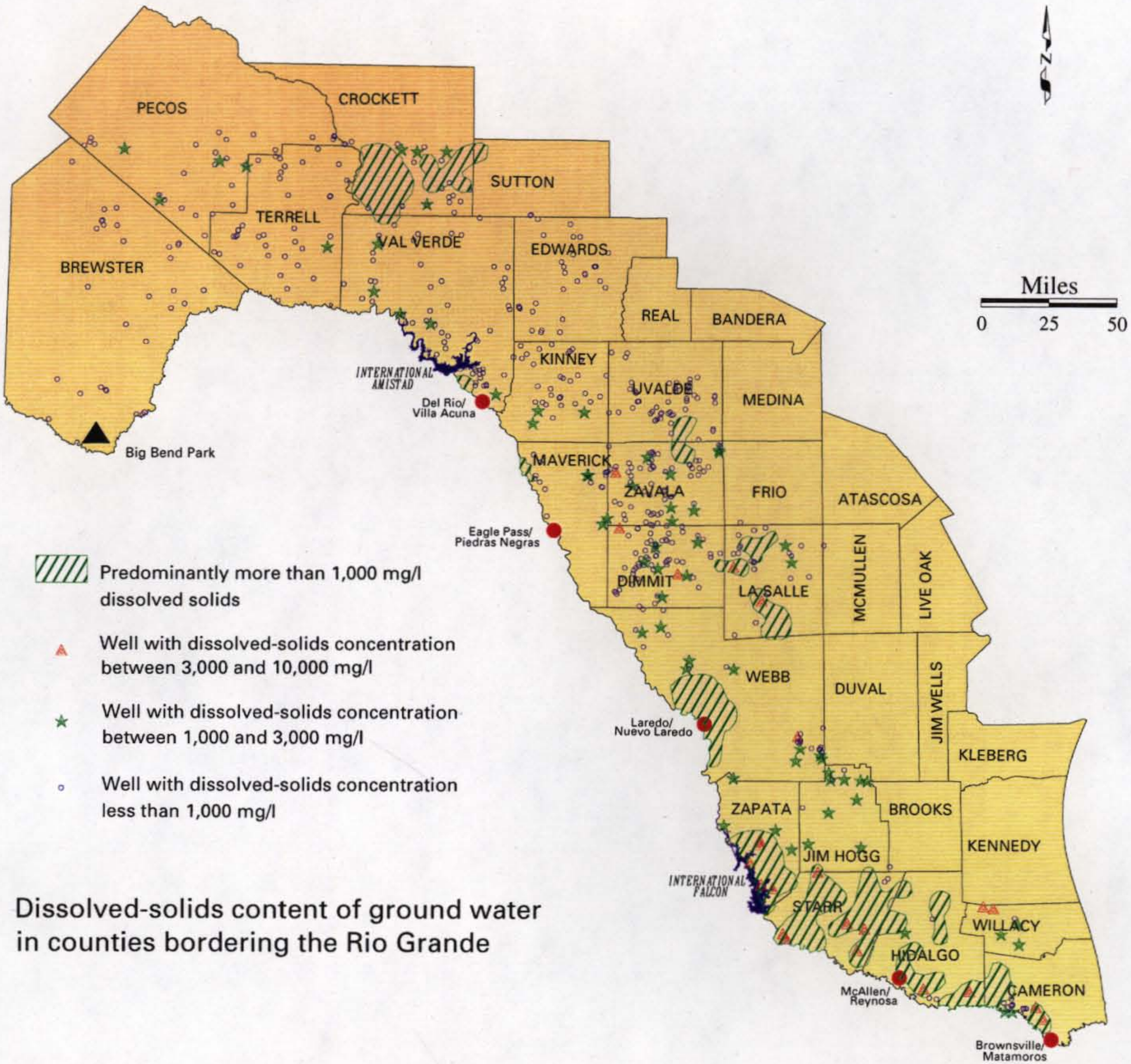


Figure 2

Dissolved-solids content of ground water in counties bordering the Rio Grande

Chloride content of ground water
in counties bordering the Rio Grande

Figure 3

within the larger areas defined by the contours on the dissolved-solids map, corresponding to the smaller percentage of samples containing chloride in excess of the secondary MCL (30 percent) compared to that percentage containing excess dissolved solids (44 percent). As in the map of dissolved solids, isolated occurrences of wellwater with chloride values greater than 300 mg/l exist outside of these contours, particularly in the Carrizo-Wilcox and Rio Grande (Maverick County) Alluvium aquifers.

Sulfate is formed by the dissolution of sulfur from rocks and soils containing sulfur compounds such as gypsum, anhydrite, and iron sulfide. In large amounts, sulfate in combination with other ions gives a bitter taste and rotten-egg odor to drinking water. As shown in the map in Figure 4, sites where sulfate content exceeds the secondary MCL of 300 mg/l are generally in the vicinity of greater dissolved solids; 34 percent of all samples collected since 1988 contained sulfate in excess of the secondary MCL.

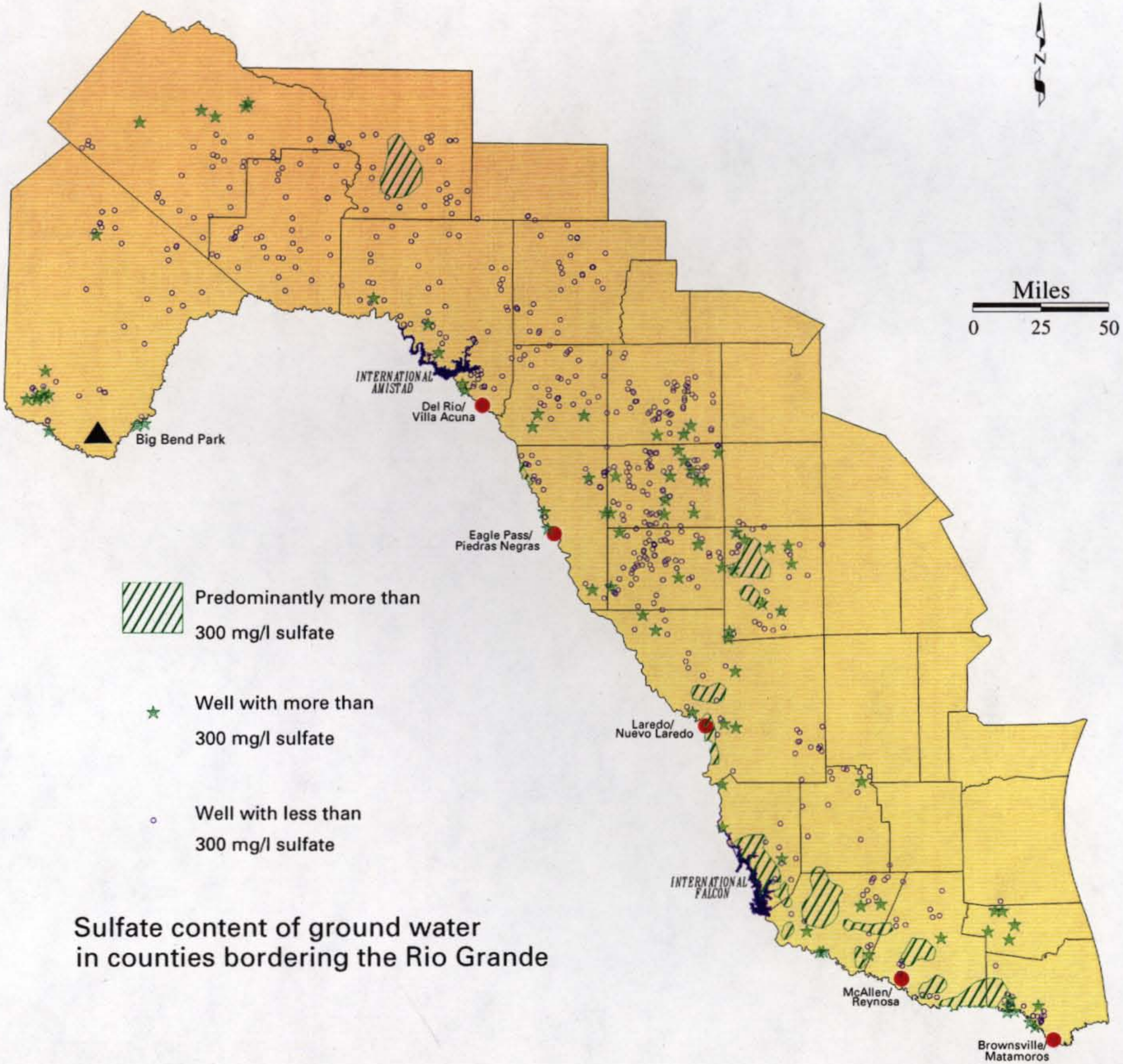
Using data from the analyses of the same six aquifers in Tables 1 and 2, trilinear diagrams in Figures 5 and 6 illustrate the ground-water chemistries characteristic of each aquifer. Calcium and bicarbonate are the dominant ions in the Edwards-Trinity (Plateau) samples; larger chloride components are apparent in the Carrizo-Wilcox and Gulf Coast samples. Of the "miscellaneous" aquifers, the Rio Grande Alluvium in Maverick County contains proportionately less sodium and chloride than in Cameron County; the Laredo aquifer, also characterized by a large percentage of sodium, contains more chloride and sulfate.

For the most part, ground water sampled along the Rio Grande contained insignificant amounts of dissolved trace metal constituents (Table 5). Only iron and manganese exceeded secondary constituent levels of 300 µg/l and 50 µg/l, respectively, in slightly higher percentages. These occur naturally as iron-rich carbonates are dissolved and are generally indicative of localized reducing conditions in the aquifer. High iron and

Table 5. Major anions and cations of ground-water from sites sampled since 1988 along the Rio Grande.

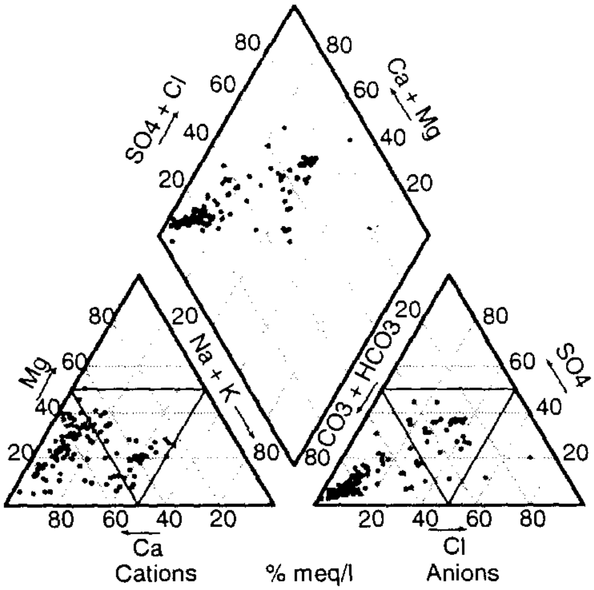
Constituent (µg/l)	% Above Detection	Average	Range	# > MCL
Arsenic	29	18	1 - 160	9*
Barium	92	81	0.03 - 1,760	
Boron	79	1,526	0.5 - 21,790	
Cadmium	0			
Chromium	0			
Copper	1			
Iron	59	429	1 - 4,240	52** (14%)
Lead	0			
Manganese	58	85	0.6 - 1,410	62** (17%)
Molybdenum	9	67	21 - 400	
Silver	0			
Vanadium	11	43	10 - 189	
Zinc	63	218	7 - 4,030	1
Aluminum	10	74	21 - 410	
Selenium	16	13	2 - 43	1
Mercury	5	0.4	0.13 - 1.12	
Alpha (pCi/l)	67	15	2 - 1,120	34 (12%)
Beta (pCi/l)	5	14	4 -590	2

* In Webb County

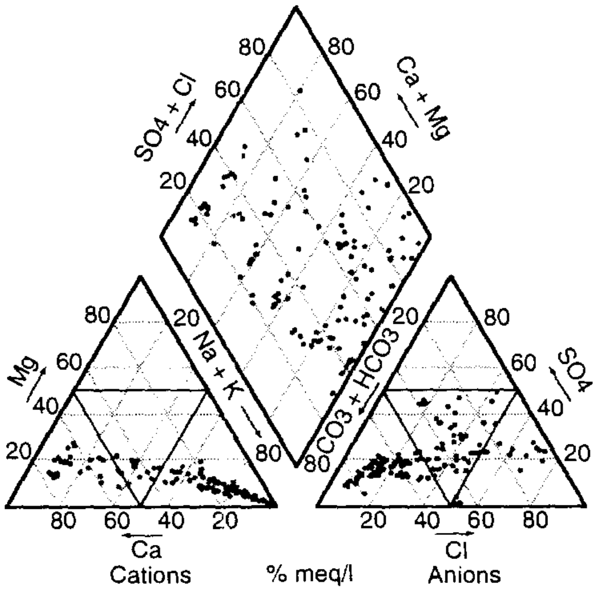


Sulfate content of ground water
in counties bordering the Rio Grande

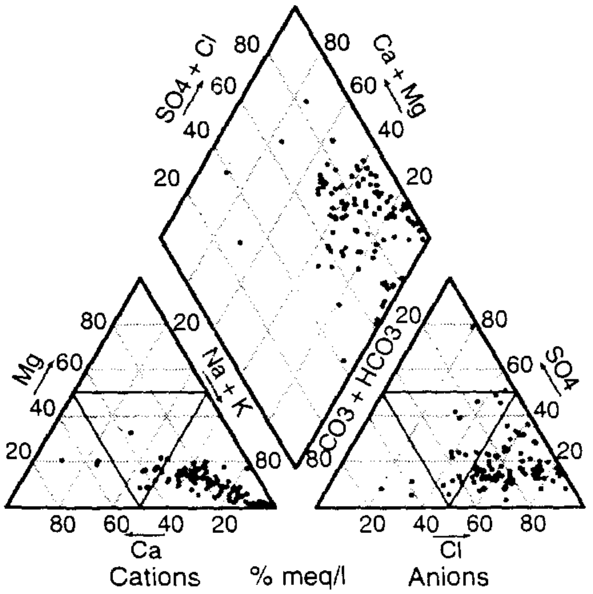
Figure 4



a.) The Edwards-Trinity (Plateau) aquifer in Brewster, Terrell, and Val Verde Counties contains primarily Ca-HCO_3 water.

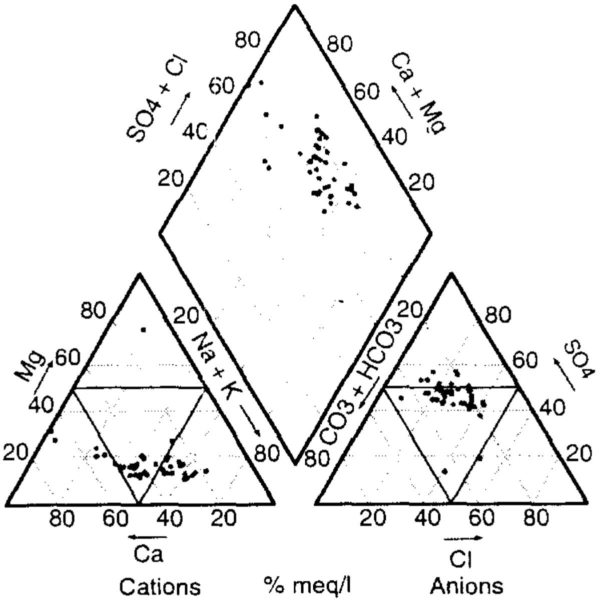


b.) The Carrizo-Wilcox aquifer in Zavala, Dimmit, Webb, and La Salle Counties contains Ca-HCO_3 to Na-mixed-anion water.

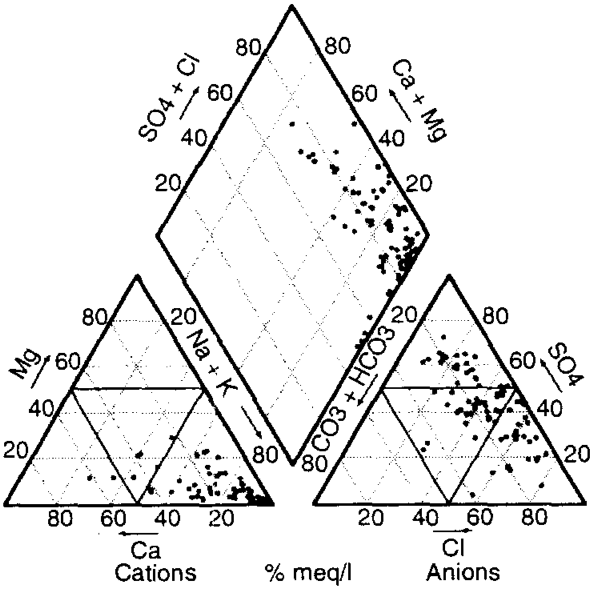


c.) The Gulf Coast aquifer in Jim Hogg, Starr, Hidalgo, Cameron, and Webb Counties contains primarily Na-Cl to Na-mixed-anion water.

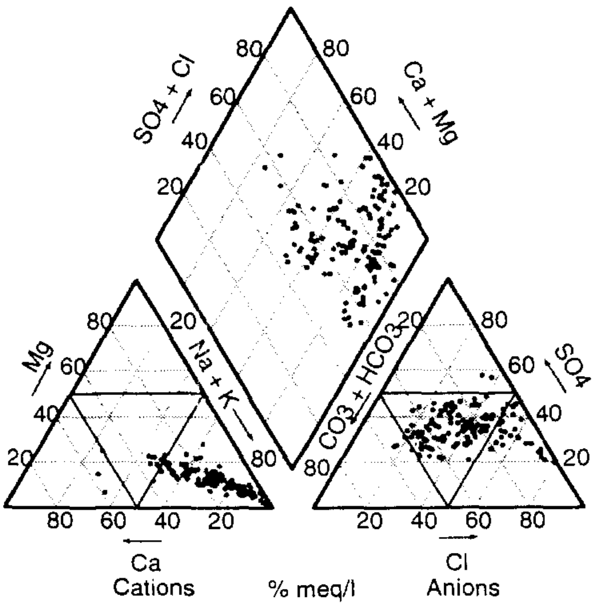
Figure 5. Piper diagrams of ground water in three major aquifers sampled along the Rio Grande.



a.) The Rio Grande Alluvium in Maverick County contains Ca-Na-mixed-anion water.



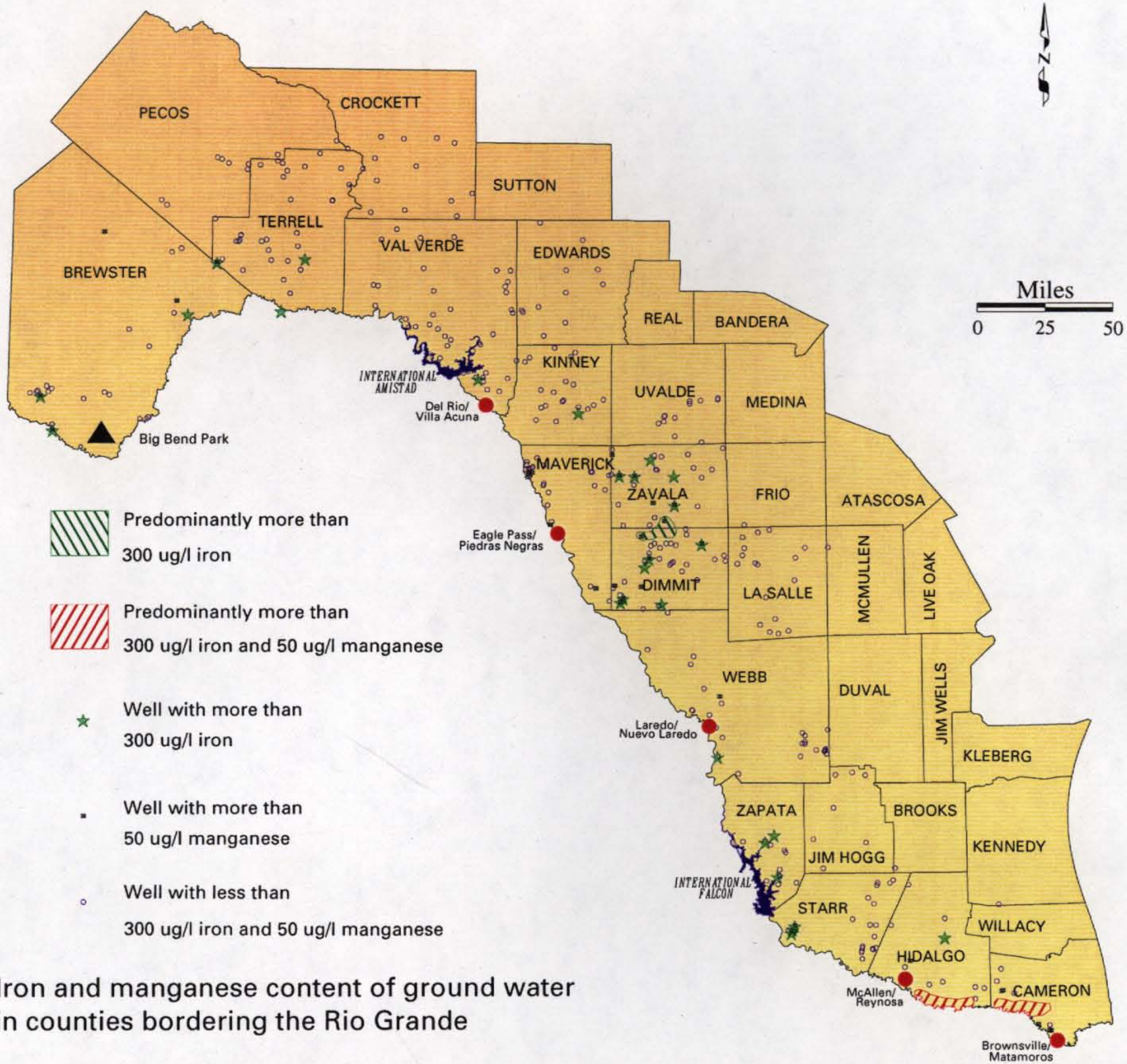
b.) The Laredo aquifer in Webb, Zapata, and Starr Counties contains primarily Na-Cl-SO_4 water.



c.) The Rio Grande Alluvium in Cameron County contains Na-mixed-anion water.

Figure 6. Piper diagrams of ground water in miscellaneous aquifers sampled along the Rio Grande.

Figure 7



Iron and manganese content of ground water in counties bordering the Rio Grande manganese contents pose less of a health hazard and more of a nuisance, due to their staining abilities and undesirable taste and odor. High iron and manganese, although found throughout the study area (Figure 7), are most abundant in the Carrizo-Wilcox in Zavala and Dimmit Counties, and immediately adjacent to the river in the Gulf Coast aquifer in Hidalgo County and in the Rio Grande Alluvium in Cameron County.

The average boron content is below 1.0 mg/l in the three northern aquifers. In the southern aquifers, however, the content is higher and averages 3.0 mg/l in the Laredo aquifer and 2.6 mg/l in the Gulf Coast aquifer due to natural conditions (McCoy, 1991). Although no MCL has been set, boron is toxic to plants at high concentrations, and a maximum permissible range of between 1.0 and 3.0 mg/l has been established for boron in irrigation waters.

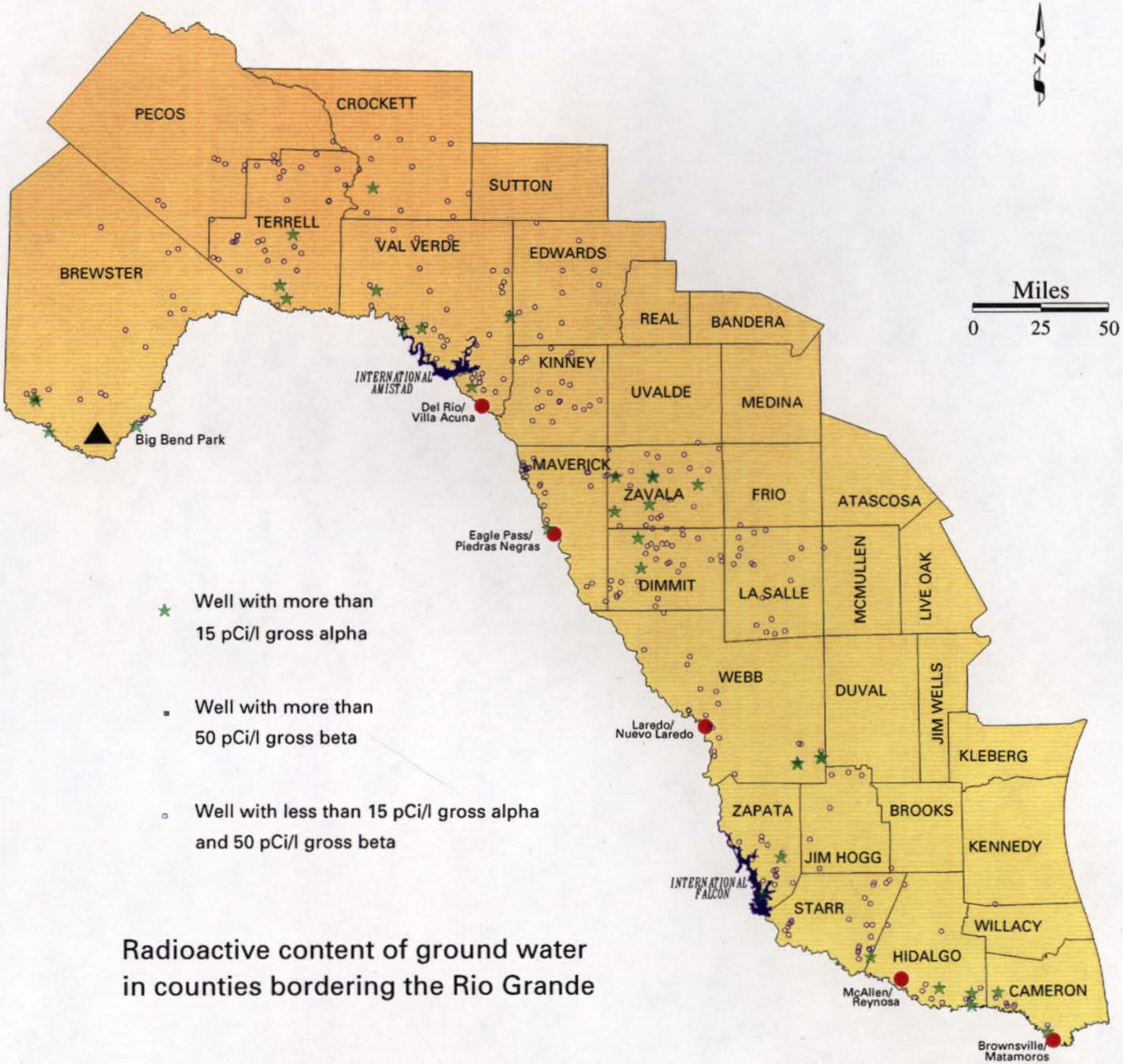
Nine wells in Webb County near Bruni were found to contain arsenic in amounts above the primary MCL, ranging from 58 to 197 µg/l; these same also contained radon gas in excess of the primary MCL of 300 pCi/l, ranging from 336 to 6,030 pCi/l; and four contained gross alpha in excess of the primary MCL of 15 pCi/l, ranging from 19 to 74 pCi/l. Arsenic is associated with the naturally occurring uranium found in this part of the Catahoula and Goliad (Gulf Coast) aquifers in which Bruni municipal water wells are completed (Adidas, 1991).

Of the 327 samples collected and analyzed for gross alpha, eight from the Edwards-Trinity in Terrell and Val Verde, nine from the Carrizo-Wilcox in Zavala and Dimmit, and nine from the Gulf Coast in Webb, Starr, Hidalgo, and Cameron Counties contained gross alpha in excess of 15 pCi/l (Table 5 and Figure 8). Eight samples from miscellaneous aquifers in almost every other county in the study area also contained excessive amounts of gross alpha. One sample of wellwater from the Santa Elena aquifer in southwest Brewster County and from the Carrizo in northwest Zavala contained 70 pCi/l and 560 pCi/l gross beta, respectively. All of this radioactivity is believed to be naturally occurring, whether in association with the disintegration of localized uranium-bearing deposits within the aquifer, as Beynon (1991) suggests for the radioactivity in the Carrizo-Wilcox, or in association with such deposits in adjacent aquifers such as the Dockum (Cech and others, 1987; Kier and others, 1977), immediately underlying the Edwards-Trinity in the western part of the Edwards Plateau and the Trans-Pecos.

Organic samples are not normally taken during network sampling, however, samples from seven irrigation wells in Hidalgo and Cameron were analyzed for more than 40 organic compounds commonly used as pesticides, including atrazine, chlordane, endrin, malathion, diazinon, and banvel. None of these, as none of the few samples collected in 1989 for a few particular pesticides, contained any amounts above detection limits. Thirty-four wells in the Edwards-Trinity in Terrell and Val Verde were analyzed for more than 90 pesticides and other organics. One well in Terrell and two in Val Verde contained trace amounts of organics; two samples of bis (2-ethylhexyl) phthalate, at 15 µg/l and 22 µg/l, were in excess of the MCL of 6 µg/l, although no MCLs are set for the remaining tentatively identified organics.

Comparison With Results of Previous Analyses

To compare results from previous sampling events is difficult as no quality assurance or quality control predures existed in either sample collection or laboratory analyses, and lab instruments lacked the analytical precision of modern equipment. However, dissolved solids, chloride, and sulfate can be compared with some confidence. Sulfate and chloride concentrations of ground water are relatively stable and not subject to decomposition if a water sample is detained or misplaced on the way to the lab. Averages listed in Table 6 by aquifer include whatever results were available for each



Radioactive content of ground water
in counties bordering the Rio Grande

time period but not necessarily results from the same wells. A trend toward increased dissolved solids and sulfates with time appears to exist in the Carrizo-Wilcox, Gulf Coast, and Laredo aquifers; greater amounts of chloride are found in recent samples collected from the Gulf Coast and Laredo aquifers.

Table 6. Comparison, in mg/l, of average amounts of dissolved solids, chloride, and sulfate in four aquifers over time.

Time period	Edwards-Trinity (Plateau)	Carrizo-Wilcox	Gulf Coast	Laredo
1950 - 1959	633-152-144	659-231-67	NA	NA
1960 - 1969	545-62-172	586-117-98	1,827-720-227	2,169-498-678
1970 - 1979	500-87-95	901-215-167	1,834-547-465	2,632-674-810
1988 - 1994	398-49-63	1,009-233-178	2,373-776-525	2,991-864-821

CONCLUSIONS

With the exception of the Edwards-Trinity (Plateau) aquifer in Brewster, Terrell, and Val Verde Counties, ground-water quality in the other two major aquifers and several miscellaneous aquifers is poor, with dissolved-solids averages ranging from 1,009 to close to 3,000 mg/l. Comparison of dissolved-solids, chloride, and sulfate values from earlier analyses in the three major aquifers and in the Laredo aquifer reveals that water quality has deteriorated somewhat in all but the Edwards-Trinity (Plateau) in Brewster, Terrell, and Val Verde Counties. Iron and manganese, also detected in excess of secondary MCLs in several wells in the Carrizo-Wilcox and the Gulf Coast, contributed to the dissolved solids and poorer water quality. The averages of boron content in the Laredo, Gulf Coast, and Rio Grande Alluvium (Cameron County) aquifers are higher than maximum permissible levels in irrigation waters.

Several wells throughout the study area contained gross alpha and several near Bruni contained arsenic in excess of the MCLs; these high levels are associated with the disintegration of naturally occurring uranium deposits within or in hydraulic communication with the aquifer. Although not enough evidence from this study can support complete absence of contamination by pesticides, no traces were detected in wells in Cameron and Hidalgo Counties; similarly, while trace amounts of organics were detected in less than 0.5 percent of the 3,000 constituents analyzed from wells in Val Verde and Terrell Counties, widespread contamination by organic compounds cannot be documented.

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